

## EQUILIBRIUM PROCESSES WITH REACTION COMPONENTS OF ISOMERIC COMPOSITION\*

Z. SLANINA

*The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,  
Czechoslovak Academy of Sciences, 121 38 Prague 2*

Received August 6th, 1974

Equilibrium processes are studied which are represented by a single chemical equation and whose reaction components are mixtures of isomers. Relationships have been derived between characteristics of the entire process and  $K_p$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  of partial processes, the latter referring to defined isomers of reaction components. The formulas are of importance for comparisons of theoretical and experimental characteristics of equilibrium processes, in particular in the cases of weak interactions. It is shown that the calculation of  $\Delta H^\circ$  for an entire process with reaction components of isomeric composition requires computation of both enthalpic and entropic changes accompanying partial processes.

The problem of competitive equilibrium processes has been most widely treated in chemical engineering studies<sup>1,2</sup>. The major goal is to estimate the composition of the equilibrium mixture on the basis of the knowledge of equilibrium constants of several competitive reactions of common reactants. The task leads to the numerical solution of sets of equations for unknown concentrations. In this paper a special type of simultaneous equilibria is studied *viz.* processes whose reaction components are of isomeric composition. A need for such a treatment resulted from the theoretical approach to some equilibria. A typical example is the following equilibrium



which was studied<sup>3</sup> by the quantum chemical method MINDO/2. Three  $\text{C}_4$  isomers of symmetries  $D_{2h}$ ,  $D_2$  and  $T_d$  have been found. The quantum chemical treatment accounts primarily for the equilibrium constants and enthalpy and entropy changes for the following partial reactions



\* Part V in the series Calculations of Absolute Values of Equilibrium and Rate Constants; Part IV: This Journal 40, 799 (1975).

However, the experimental values do not correspond to any process of (B)–(D) but to the total equilibrium (A). The experimental characteristics of the total process (A) represent effective values comprising contributions from the three partial processes (B)–(D) of differing weights. Obviously, a direct comparison of the characteristics for the total and the partial processes would be inadequate. It is necessary to derive relationships for the effective thermodynamic quantities of the process (A) with those of the partial processes (B)–(D). Though the processes (B)–(D) constitute a system of simultaneous equilibria, the problem is different from the above-mentioned solution of simultaneous equilibrium reactions in chemical engineering treatments.

Let us note other examples of reactions with the isomerism of reaction components. These are mostly reactions to which a single chemical equation was assigned on the basis of the experimental treatment and where isomerism was revealed with at least one reaction component by a subsequent theoretical analysis. Hence a process which originally appeared to be simple became a series of partial reactions with reaction components in states of particular isomers.

Recent results for the  $(\text{H}_2)_2$  dimer, which has been studied quantum chemically rather extensively<sup>4</sup>, predict four minima on the potential energy hypersurface<sup>5</sup>. The respective molecular geometries differ considerably. Since the calculations (*ab initio* SCF-CI) are highly accurate, it is certainly desirable to make a comparison with the enthalpy inferred from spectroscopic experiments<sup>6</sup>. To do that it is necessary to find a quantity from the characteristics of the four partial processes which would be compatible with the experimental  $\Delta H^0$ . Averaging<sup>7</sup> is not satisfactory because it involves the assumption of equal weights of all structures and yields results that are more likely consistent with the data derived from observed compressibilities<sup>4</sup>.

The presence of isomerism in the formation of charge-transfer complexes was pointed out by Orgel and Mulliken<sup>8</sup>, who established the relation between the observed quantities and characteristics of partial processes. Semiempirical quantum chemical calculations<sup>9</sup> predict a series of potential energy minima in the case of weak intermolecular interactions. Besides molecular complexes there are numerous processes with the standard enthalpy change of several dozens of kcal/mol that have at least one reaction component formed by isomers. Dimerization of the nitrogen difluoride radical  $\text{NF}_2$  to tetrafluorohydrazine  $\text{N}_2\text{F}_4$  is an example. In determining  $\Delta H^0$  and  $\Delta S^0$  from the temperature dependence of the equilibrium constant, the equilibrium has been treated as a single process (*e.g.* ref.<sup>10</sup>), though it is known that  $\text{N}_2\text{F}_4$  is a roughly equimolar mixture of two isomers<sup>11</sup> (*trans* and *gauche*). A theoretical treatment gives of course characteristics for the partial dimerization to *trans*- $\text{N}_2\text{F}_4$  and *gauche*- $\text{N}_2\text{F}_4$ . Another example of that type of reaction is the isomerism of atomic clusters which are of importance in the theory of nucleation. In ref.<sup>12</sup> this isomerism was involved in the configuration partition function. The results of ref.<sup>9</sup> suggest the isomeric reaction components should also be expected with the

equilibria between solvated ions (*e.g.* ref.<sup>13</sup>), where experiment again gives only effective equilibrium characteristics.

All these families of problems are at present, or will be soon, the subject of quantum chemical treatments. The present state of the numerical quantum chemistry requires, however, to compare most of the results with the experimental data. Such a comparison represents a test of the method which may show us how well the physical reality is described by the theoretical approach. In comparisons with experimental data use must be made of proper observables in order to avoid the indefiniteness which is due to the inadequacy of the theoretical counterpart. In the case with the equilibria of isomeric reaction components, the condition is as follows: correct comparison requires to carry out the calculation up to the thermodynamic functions of the total processes because only the latter are quantities determined experimentally. If disagreement is then found, it can be assigned to the imperfection of the used theoretical method provided the experiment is correct.

The above examples indicate two problems encountered in the treatments of equilibria with the isomeric reaction components:

1) The conversion of the characteristics of partial processes to effective  $\Delta H^0$  and  $\Delta S^0$  *i.e.* to convert results of the theoretical treatment to characteristics compatible with the observed quantities.

2) The treatment of the observed quantities in such a way as to arrive at the thermodynamic characteristics of partial processes.

The two tasks are the subject of this paper.

### *Formulation of the Problem*

Consider an equilibrium process in the ideal gaseous phase between  $n$  reaction components  $A_k$  with the stoichiometric coefficients  $\nu_k$

$$\sum_{k=1}^n \nu_k A_k = 0. \quad (1)$$

The principal thermodynamic characteristics of the process (1) are the equilibrium constant  $K$ , standard enthalpy change  $\Delta H^0$  and standard entropy change  $\Delta S^0$ . These are given by the following relationships

$$K = \prod_{k=1}^n p_k^{\nu_k}, \quad (2)$$

$$\Delta H^0 = RT^2 \frac{d \ln K}{dT}, \quad (3)$$

$$\Delta S^0 = R \ln K + \Delta H^0/T, \quad (4)$$

where  $p_k$  is a partial pressure of the reaction component  $A_k$  in the equilibrium mixture. Let the reaction component  $A_k$  be a mixture of  $j_k$  isomers  $A_k^{(1)}, A_k^{(2)}, \dots, A_k^{(j_k)}$ , where the  $A_k^{(1)}$  isomer is the lowest in energy. Process (1) becomes then a superposition of

$\prod_{k=1}^n j_k$  partial processes:

$$\sum_{k=1}^n v_k A_k^{(i_k)} = 0 \quad (i_k = 1, 2, \dots, j_k). \quad (5)$$

For the principal thermodynamic characteristics of processes (5) it holds analogously to Eqs (2)–(4):

$$K_{i_1, i_2, \dots, i_n} = \prod_{k=1}^n p_{k, i_k}^{v_k}, \quad (6)$$

$$\Delta H_{i_1, i_2, \dots, i_n}^0 = RT^2 \frac{d}{dT} \ln K_{i_1, i_2, \dots, i_n}, \quad (7)$$

$$\begin{aligned} \Delta S_{i_1, i_2, \dots, i_n}^0 &= \\ &= R \ln K_{i_1, i_2, \dots, i_n} + \Delta H_{i_1, i_2, \dots, i_n}^0 \cdot T^{-1}, \end{aligned} \quad (8)$$

where  $p_{k, i_k}$  denotes a partial pressure of the  $A_k^{(i_k)}$  in the equilibrium mixture.

Let the observation of process (1) be so organized that for  $p_k$  in Eq. (2) it holds

$$p_k = \sum_{i_k=1}^{j_k} p_{k, i_k}. \quad (9)$$

If isomers are taken into consideration, the number of chemical components of the system is  $\sum_{k=1}^n j_k$  and the number of equilibrium constants (6) is  $\prod_{k=1}^n j_k$ . We shall limit ourselves to the following set of  $1 - n + \sum_{k=1}^n j_k$  independent equilibrium constants:

$$\begin{aligned} K_{i_1} &= K_{i_1, 1, 1, \dots, 1} \quad (i_1 = 1, 2, \dots, j_1) \\ K_{i_2} &= K_{1, i_2, 1, \dots, 1} \quad (i_2 = 1, 2, \dots, j_2) \\ &\vdots \\ K_{i_n} &= K_{1, 1, 1, \dots, i_n} \quad (i_n = 1, 2, \dots, j_n). \end{aligned} \quad (10)$$

The processes given by equilibrium constants (10) are associated with the following standard enthalpy and entropy changes:

$$\begin{aligned}\Delta H_{i_1}^0 &= \Delta H_{1,1,1, \dots, 1}^0 = RT^2 \, d \ln K_{i_1} / dT \\ \Delta H_{i_2}^0 &= \Delta H_{1,i_2,1, \dots, 1}^0 = RT^2 \, d \ln K_{i_2} / dT \\ &\vdots \\ \Delta H_{i_n}^0 &= \Delta H_{1,1,1, \dots, i_n}^0 = RT^2 \, d \ln K_{i_n} / dT,\end{aligned}\quad (11)$$

$$\begin{aligned}\Delta S_{i_1}^0 &= \Delta S_{1,1,1, \dots, 1}^0 = R \ln K_{i_1} + \Delta H_{i_1}^0 \cdot T^{-1} \\ \Delta S_{i_2}^0 &= \Delta S_{1,i_2,1, \dots, 1}^0 = R \ln K_{i_2} + \Delta H_{i_2}^0 \cdot T^{-1} \\ &\vdots \\ \Delta S_{i_n}^0 &= \Delta S_{1,1,1, \dots, i_n}^0 = R \ln K_{i_n} + \Delta H_{i_n}^0 \cdot T^{-1}.\end{aligned}\quad (12)$$

Provided that (9) is valid, our next task is to express  $K$ ,  $\Delta H^0$  and  $\Delta S^0$  (Eqs (2)–(4)) in terms of  $K_{i_k}$ ,  $\Delta H_{i_k}^0$  and  $\Delta S_{i_k}^0$  (Eqs (10)–(12)).

### General Relationships

According to (6) and (10) the partial pressure of the  $A_k^{(i_k)}$  component becomes:

$$p_{k,i_k} = K_{i_k}^{1/v_k} \prod_{\substack{j=1 \\ j \neq k}}^n p_{j,1}^{-v_j/v_k}.\quad (13)$$

On substituting this result into (2) and by assuming (9) one gets after some algebraic manipulation

$$K = K_{1,1,1, \dots, 1}^{-(n-1)} \prod_{k=1}^n \left( \sum_{i_k=1}^{j_k} K_{i_k}^{1/v_k} \right)^{v_k}.\quad (14)$$

From (3), (11) and (14) it follows

$$\begin{aligned}\Delta H^0 &= -(n-1) \Delta H_{1,1,1, \dots, 1}^0 + \\ &+ \sum_{k=1}^n \sum_{i_k=1}^{j_k} K_{i_k}^{1/v_k} \Delta H_{i_k}^0 / \sum_{i_k=1}^{j_k} K_{i_k}^{1/v_k}.\end{aligned}\quad (15)$$

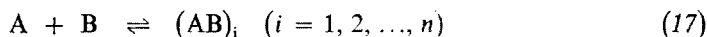
Furthermore, (4), (12) and (15) give us

$$\begin{aligned}\Delta S^0 &= -(n-1) \Delta S_{1,1,1, \dots, 1}^0 + \\ &+ \sum_{k=1}^n \sum_{i_k=1}^{j_k} K_{i_k}^{1/v_k} \left[ \Delta S_{i_k}^0 + R \ln \frac{\left( \sum_{i_k=1}^{j_k} K_{i_k}^{1/v_k} \right)^{v_k}}{K_{i_k}} \right] / \sum_{i_k=1}^{j_k} K_{i_k}^{1/v_k}.\end{aligned}\quad (16)$$

Relationships (14)–(16) are the desired expression for the effective characteristics (2)–(4) of the entire process by means of characteristics (10)–(12) of partial processes. The forms of (14)–(16) depend of course on the choice of the set (10); the equations given above represent thus only one way of expressing the conversion relationship. The set (10) was so chosen as to permit an easy passage to some special cases of interest.

### Special Cases

Processes noted in the introduction are mostly of the type



and represent thus a special case for which  $j_1 = 1, j_2 = 1, j_3 = n$ . For the sake of of simplicity we set

$$\begin{aligned} K_i &= K_{1,1,i} \\ \Delta H_i^0 &= \Delta H_{1,1,i}^0 \quad (i = 1, 2, \dots, n) \\ \Delta S_i^0 &= -\Delta S_{1,1,i}^0, \end{aligned} \quad (18)$$

which gives us (14)–(16) in the form

$$K = \sum_{i=1}^n K_i \quad (19)$$

$$\Delta H^0 = \sum_{i=1}^n \frac{K_i}{K} \Delta H_i^0 \quad (20)$$

$$\Delta S^0 = \sum_{i=1}^n \frac{K_i}{K} \left( \Delta S_i^0 + R \ln \frac{K}{K_i} \right). \quad (21)$$

On denoting the highest and the lowest values of the  $\Delta H_i^0$  set with  $\Delta H_{\max}^0$  and  $\Delta H_{\min}^0$ , respectively, it is possible to show by means of (20) that it holds

$$\Delta H_{\min}^0 \leq \Delta H^0 \leq \Delta H_{\max}^0. \quad (22)$$

It should be noted that an analogous relationship for  $\Delta S^0$  does not hold. Consider next a very simple case of the process (17), where equilibrium constants and enthalpy and entropy changes are of the same value for all  $n$  partial reactions. Hence, (19)–(21) become

$$K = nK_1 \quad (23)$$

$$\Delta H^0 = \Delta H_1^0 \quad (24)$$

$$\Delta S^0 = \Delta S_1^0 + R \ln n. \quad (25)$$

Obviously, the result (25) is a known expression for the entropy of mixing, applicable to the formation of the equimolar mixture of optical isomers<sup>14</sup>.

### *Applications and Conclusions*

The utility of formulas (14)–(16) interrelating characteristics of partial and total processes is twofold. Firstly, they make it possible to interpret observed effective  $K$ ,  $\Delta H^0$  and  $\Delta S^0$  by means of results of the theoretical treatment of partial processes *i.e.* by making use of thermodynamic characteristics  $K_{i_k}$ ,  $\Delta H_{i_k}^0$  and  $\Delta S_{i_k}^0$  appearing in (10)–(12). Secondly, they permit the determination of the standard enthalpy changes,  $\Delta H_{i_k,0}^0$ , for processes (10) at absolute zero from the observed temperature dependence of the equilibrium constant  $K$  of the total process (1). If molecular constants of all isomers  $A_k^{(i_k)}$  are available for the construction of partition functions, it is possible to evaluate their standard thermodynamic potentials<sup>14</sup>. For the sake of simplicity, consider only a process of the type (17). Its  $\Delta H_{i_0}^0$  can be determined by the least-square optimization of the following expression

$$\Delta = \sum_T \left[ K - \sum_{i=1}^n \exp \left( \frac{\Delta \Phi_i^0}{R} - \frac{\Delta H_{i_0}^0}{RT} \right) \right]^2. \quad (26)$$

Here  $\Delta \Phi_i^0$  denotes the changes in the standard thermodynamic potential associated with the processes (17). The summation in Eq. (26) runs over temperatures at which  $K$  was measured. Molecular constants for the construction of partition functions may originate from spectral measurements or quantum chemical calculations. Use can even be made of those quantum chemical methods that fail in providing a satisfactory account of enthalpies but give molecular constants accurate enough for calculations of entropy.

From the two applications noted the former is evidently more significant. If (15) and (20) are compared, the following important result emerges: Even if we limit ourselves in the treatments of processes of this type to the computation of the enthalpy term, we need to know their equilibrium constants. This implies a significance of calculations of equilibrium constants in cases of weak interactions<sup>9</sup>, where processes with isomeric reaction components occur rather often. If the enthalpies of partial processes are rather close in value, the effective  $\Delta H^0$  will not differ markedly from

them as documented by Eq. (22). On the contrary, with the entropy term the effect of the isomerism of components is more pronounced, which conforms to the special result represented by Eq. (25).

*The author is indebted to Dr R. Zahradnik for his interest and valuable discussions and Dr E. Erdös for critical comments on the manuscript.*

#### REFERENCES

1. Hougen O. A., Watson K. M.: *Chemical Process Principles. II. Thermodynamics*. Wiley, New York 1948.
2. Holub R.: *Chemická rovnováha plynných reakcí*. Academia, Prague 1972.
3. Slanina Z., Zahradník R.: Unpublished results.
4. Hirschfelder J. O., Curtiss C. F., Bird R. B.: *Molecular Theory of Gases and Liquids*. Wiley, New York 1954.
5. Kochanski E., Roos B., Siegbahn P., Wood M. H.: *Theoret. Chim. Acta* 32, 151 (1973).
6. Ewing G. E.: *Angew. Chem.* 84, 570 (1972).
7. Evett A. A., Margenau H.: *Phys. Rev.* 90, 1021 (1953).
8. Orgel L. E., Mulliken R. S.: *J. Am. Chem. Soc.* 79, 4839 (1957).
9. Hobza P., Zahradník R.: *This Journal* 39, 2866 (1974).
10. Johnson F. A., Colburn C. B.: *J. Am. Chem. Soc.* 83, 3043 (1961).
11. Colburn C. B., Johnson F. A., Haney C.: *J. Chem. Phys.* 43, 4526 (1965).
12. Burton J. J.: *Acta Metall.* 21, 1225 (1973).
13. Grimsrud E. P., Kebarle P.: *J. Am. Chem. Soc.* 95, 7939 (1973).
14. Janz G. J.: *Thermodynamic Properties of Organic Compounds*. Academic Press, New York 1967.

Translated by P. Čársky.