

Response reactions: An interpretive concept in chemical thermodynamics

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Abstract: In a series of papers (ref. 1-13) we have recently elaborated the concept of “response reactions”, in order to interpret and rationalize the changes taking place in multiple-equilibrium systems, when the control parameters (pressure, temperature, initial amounts of substances) are altered. The concept helps to interpret certain unusual phenomena – frequently encountered in multiple-equilibrium systems – by decomposing the sensitivity coefficients in a linear way into terms uniquely assigned to response reactions. It has also been shown that the “configurational” or “relaxational” part of many important first derivatives in chemical thermodynamics may be expressed as a sum of terms, assigned to response reactions. The concept of response reactions opens a new way to formulate the change of the thermodynamic potential functions in terms of affinities. As a result, coupling between reactions appears in a natural and straightforward manner. The equations derived may be extended into the domain of irreversible thermodynamics.

Introduction

There are two equivalent approaches to describe a reacting chemical system. The first is the original Gibbs formulation (ref. 14):

$$dG_{(T,P)} = \sum_{i=1}^q \mu_i dn_i \quad (= 0 \text{ at equilibrium})$$

and the second is based on De Donder's theory (ref 15):

$$dG_{(T,P)} = - \sum_{j=1}^m A_j d\xi_j \quad (= 0 \text{ at equilibrium})$$

where

- q = number of species,
- m = number of stoichiometrically independent reactions (SIRs),
- ξ_j = extent of the j -th SIR,
- μ_i = chemical potential of the i -th species,
- n_i = amount of the i -th species,
- $A_j = -(\partial G / \partial \xi_j)_{(T,P)}$ = affinity of the j -th SIR,
- $q - m$ = number of components.

The presentation in this article is based on examples, in order to reveal the “chemistry” behind the sometimes complicated mathematical expressions, given in full detail in our previous papers. As an example we consider a homogeneous system containing CH₄, H₂O, CO, CO₂, and H₂, at 1000 K. One possibility to describe the chemical transformations in this system is the following:



$$K_1 = 26.12 \quad ; \quad \Delta H_1^\ominus = 225.39 \text{ kJ mol}^{-1}$$



$$K_2 = 35.73 \quad ; \quad \Delta H_2^\ominus = 190.62 \text{ kJ mol}^{-1}$$

Denote the initial amount of the i -th species by n_i° and its equilibrium amount by n_i^e . The total amount is denoted by $n_{tot}^e = \sum n_i^e$ at equilibrium and by $n_{tot}^\circ = \sum n_i^\circ$ in the initial state. Then the following two systems of equations may be used to calculate the composition of the equilibrium state at a given total pressure P_{tot} . The Gibbs approach:

$$K_1 = \frac{P_{CO}(P_{H_2})^3}{P_{CH_4}P_{H_2O}} = \frac{n_{CO}^e(n_{H_2}^e)^3}{n_{CH_4}^e n_{H_2O}^e} \times \frac{(P_{tot})^2}{(n_{tot}^e)^2}$$

$$K_2 = \frac{P_{CO_2}(P_{H_2})^4}{P_{CH_4}(P_{H_2O})^2} = \frac{n_{CO_2}^e(n_{H_2}^e)^4}{n_{CH_4}^e(n_{H_2O}^e)^2} \times \frac{(P_{tot})^2}{(n_{tot}^e)^2}$$

supplemented with the elementary abundance (mass-conservation) conditions:

$$\text{for carbon: } n_{CH_4}^\circ + n_{CO}^\circ + n_{CO_2}^\circ = n_{CH_4}^e + n_{CO}^e + n_{CO_2}^e$$

$$\text{for oxygen: } n_{CO}^\circ + 2n_{CO_2}^\circ + n_{H_2O}^\circ = n_{CO}^e + 2n_{CO_2}^e + n_{H_2O}^e$$

$$\text{for hydrogen: } 4n_{CH_4}^\circ + 2n_{H_2O}^\circ + 2n_{H_2}^\circ = 4n_{CH_4}^e + 2n_{H_2}^e + 2n_{H_2O}^e$$

We have five equations and five unknowns, their solution is a standard numerical procedure.

The second possibility is to employ the De Donder approach:

$$K_1 = \frac{(n_{CO}^\circ + \xi_1)(n_{H_2}^\circ + 3\xi_1 + 4\xi_2)^3}{(n_{CH_4}^\circ - \xi_1 - \xi_2)(n_{H_2O}^\circ - \xi_1 - 2\xi_2)} \times \frac{(P_{tot})^2}{(n_{tot}^\circ + 2\xi_1 + 2\xi_2)^2}$$

$$K_2 = \frac{(n_{CO_2}^\circ + \xi_2)(n_{H_2}^\circ + 3\xi_1 + 4\xi_2)^4}{(n_{CH_4}^\circ - \xi_1 - \xi_2)(n_{H_2O}^\circ - \xi_1 - 2\xi_2)^2} \times \frac{(P_{tot})^2}{(n_{tot}^\circ + 2\xi_1 + 2\xi_2)^2}$$

Here we have two equations and two unknowns, the solution of which is also straightforward.

The two procedures are equivalent, as far as the calculation of the equilibrium composition is concerned. When using De Donder's method, the mass-balance conditions are involved in ξ_1 and ξ_2 . The difference between the two approaches becomes transparent if we consider the linear transformation of the equations (1) and (2). Any - linearly independent - combination of these equations may be used in case of the Gibbs approach; the latter three equations (mass-balance) will always be the same, and the same quantities (n_i^e) are calculated.

In case of the De Donder approach, we have only two equations, but the price is that new quantities (extents of reactions of SIRs) are introduced. The disadvantage is that if we start with another choice of SIRs, then the calculated extents will be different. Before proceeding further, we have to elaborate on the meaning of the extents of reactions, because it is crucial to understand how the extents of different reactions change by changing the control parameters.

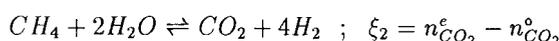
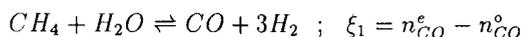
Extents of reactions

In case of a single reaction, the change of the extent has two different meanings:

- ξ is a mathematical tool for taking into account the mass balance;
- ξ means that $\nu_i \xi$ is the amount of the i -th species, transported between the two sides of the stoichiometric equation, where ν_i is the respective stoichiometric number (negative for reactants and positive for products).

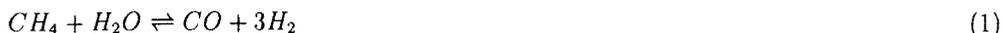
The shift of the extent of a single reaction when the control-parameters are changed is unequivocally determined by the Le Chatelier principle.

The situation which we encounter in multiple-equilibrium systems is also illustrated through the example chosen:



It is evident that the extent of the first reaction at equilibrium state **must be** the change in the amount of CO, as this species is missing from the second equilibrium. Similar reasoning applies for the extent of the second reaction at equilibrium. It is interesting to realize, that the extent of a given reaction is determined by the species which is **missing** from the other!

Any two (independent) linear combinations of the equations (1) and (2) may serve as a set of SIRs of the same system, for instance:



$$K_1 = 26.12 ; \quad \Delta H_1^\ominus = 225.39 \text{ kJ mol}^{-1} ; \quad \xi_1 = n_{CH_4}^\circ - n_{CH_4}^e$$



$$K_3 = (K_1/K_2) = 0.731 ; \quad \Delta H_3^\ominus = \Delta H_1^\ominus - \Delta H_2^\ominus = 34.77 \text{ kJ mol}^{-1} ; \quad \xi_3 = n_{CO_2}^\circ - n_{CO_2}^e$$

It is seen that the extent of reaction (1) depends on the second reaction chosen and not on its own characteristics. It may be stated, therefore, that in multiple-equilibrium systems the concept of "extent of reaction" is a useful mathematical tool for book-keeping purposes, but **its second meaning is lost**. Consequently, without performing a full-scale numerical calculation, we are unable to predict how the extents are shifted by changing the control parameters.

Sensitivity coefficients in multiple-equilibrium systems

Taking reactions (1) and (2) – for example – one can easily see that in each of them the sign of the sensitivity coefficient $\partial n_{H_2O}/\partial T$ is negative. In view of this one would be inclined to predict that their joint effect has the same sign (H_2O is on the reactant side of both endothermic reactions). Let us compare this prediction with results depicted in Figure 1, where $\partial n_{H_2O}/\partial T$ is plotted as a function of pressure. It is seen that the prediction is fulfilled only in a narrow intermediate range of pressure.

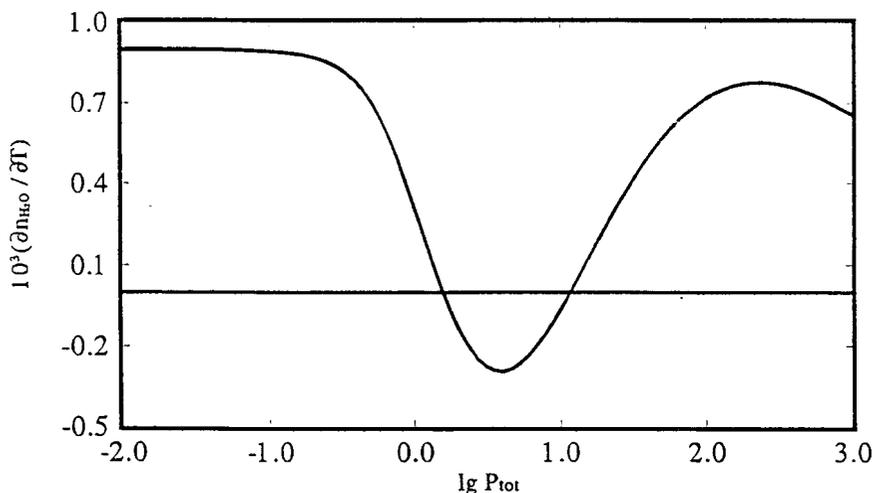


Figure 1.

$\partial n_{H_2O}/\partial T$ as a function of pressure, at initial composition: $n_{CH_4} = 1$, $n_{H_2O} = 1$, $n_{CO_2} = 1$, $n_{H_2} = 1$ and $n_{CO} = 2$ mol.

A similar consideration shows that if the reactions (1) or (2) are regarded individually, then the sign of $\partial n_{H_2O}/\partial P$ must be positive. Moreover, it may be concluded that at very low pressure, in each reaction n_{H_2O} should approach 0. The respective joint effect is seen in Figure 2, exhibiting just the opposite features: a non-zero and constant amount of water at low pressure and its decrease at high pressure.

Let us try to predict the pressure-dependence of n_{H_2O} if the system is described by the following two equations, derived from (1) and (2) by simple linear combination:



$$K_3 = 0.731 ; \quad \Delta H_3^\ominus = 34.77 \text{ kJ mol}^{-1}$$



$$K_4 = 0.0980 ; \Delta H_4^\ominus = -329.7 \text{ kJ mol}^{-1}$$

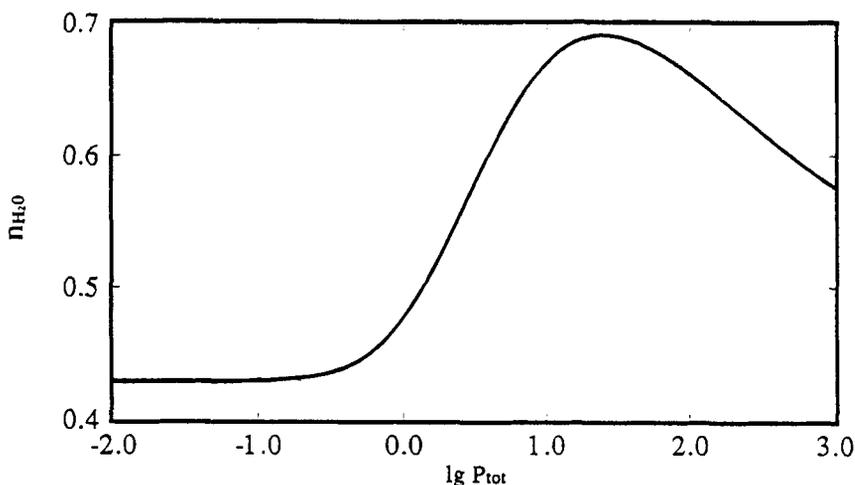


Figure 2.

n_{H_2O} as a function of pressure at the same initial conditions as in Figure 1.

Based on equations (3) and (4), some of the features of Figures 1 and 2 become understandable. It should be stressed again that equations (1) and (2) are **equivalent** to equations (3) and (4) if our aim is calculating the equilibrium composition. If, on the other hand, we want to **understand the behaviour of the system**, i.e., if we want to know how the equilibrium is shifted by changing a control parameter, **none of them gives correct result**.

In some pressure range the system behaves as if equilibria (1) and (2) would be valid, whereas in some other range as if equilibria (3) and (4) prevail.

One may find a number of similar phenomena, namely that the response of a multiple-equilibrium system cannot be rationalized by considering the expected response of the reactions selected to carry out the calculations. In particular:

- Unusual concentration distribution in complex equilibrium systems in solutions (ref. 16).
- Dilution of a solution increases the concentration of some of the species (ref. 10).
- Decrease of the concentration of a coordinatively saturated complex (ML_N) with increasing concentration of the ligand (L) (ref. 2).
- Two exothermic reactions together behave as if they were endothermic (example given in this paper).
- The increase of pressure decreases the amount of some substance in all reactions; their joint effect is, however, just the opposite (example given in this paper).
- Precipitation by dilution (ref. 17).

It may be stated that the behaviour of multiple-equilibrium systems is **unpredictable**. As far as sensitivity coefficients of multiple equilibrium systems are concerned, **we can calculate everything, but we do not understand anything**.

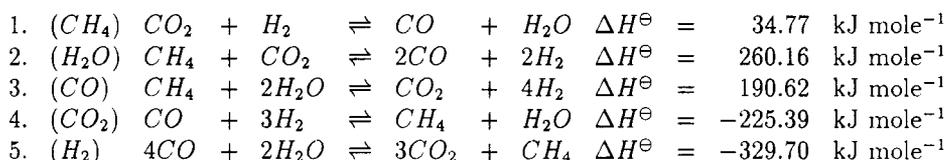
Response reactions

In view of the above examples, the most important task is to identify the reactions responsible for the response of a multiple-equilibrium system when the control parameters are changed. Detailed mathematical analysis (ref. 1-9) of the Hessian matrices of the Gibbs functions, defined in terms of the amounts of species, in terms of the extents of reactions, in terms of mole fractions of the species, and the use of Binet-Cauchy formula (ref. 18) led us to the definition of **response reactions**. The response reactions have the remarkable property that all conceivable sensitivity coefficients are sums of terms uniquely associated with them. In other words – as far as their sensitivity is concerned – multiple-equilibrium systems behave as if their thermodynamic properties were simple linear combinations of pertinent contributions coming from individual reactions.

Instead of the complicated definition of response reactions, we present here an algorithm for their derivation from the stoichiometrically independent reactions. The algorithm reads as follows:

- Choose $m - 1$ species which are missing from the given response reaction.
- Construct $q - m + 1$ identical $m \times (m - 1)$ matrices, containing the stoichiometric coefficients of the $m - 1$ missing species in the m stoichiometrically independent reactions.
- As a last column, add to these matrices, one-by-one, the stoichiometric coefficients of the $q - m + 1$ remaining species. By this, $(q - m + 1)$ distinct square matrices of order m are constructed.
- Calculate the determinants of these matrices. The resulting numbers are the stoichiometric coefficients of the species by which the respective $m \times (m - 1)$ matrices were supplemented.
- Repeat the above procedure for all possible choices of $m - 1$ species. The resulting $\binom{q}{m-1}$ reactions are the response reactions.

Carrying out the algorithm for the above example, we arrive at the following set of response reactions (the missing species are denoted in brackets):



It should be stressed again that for any thermodynamic calculation, any two of the five reactions are **sufficient**, the remaining three equilibria being redundant. If however, we want to interpret the behaviour of the system, then it is **necessary** to take into account all response reactions. Figure 3 shows the distribution of the species in our example, together with the decomposition of $\partial n_{H_2O}/\partial T$.

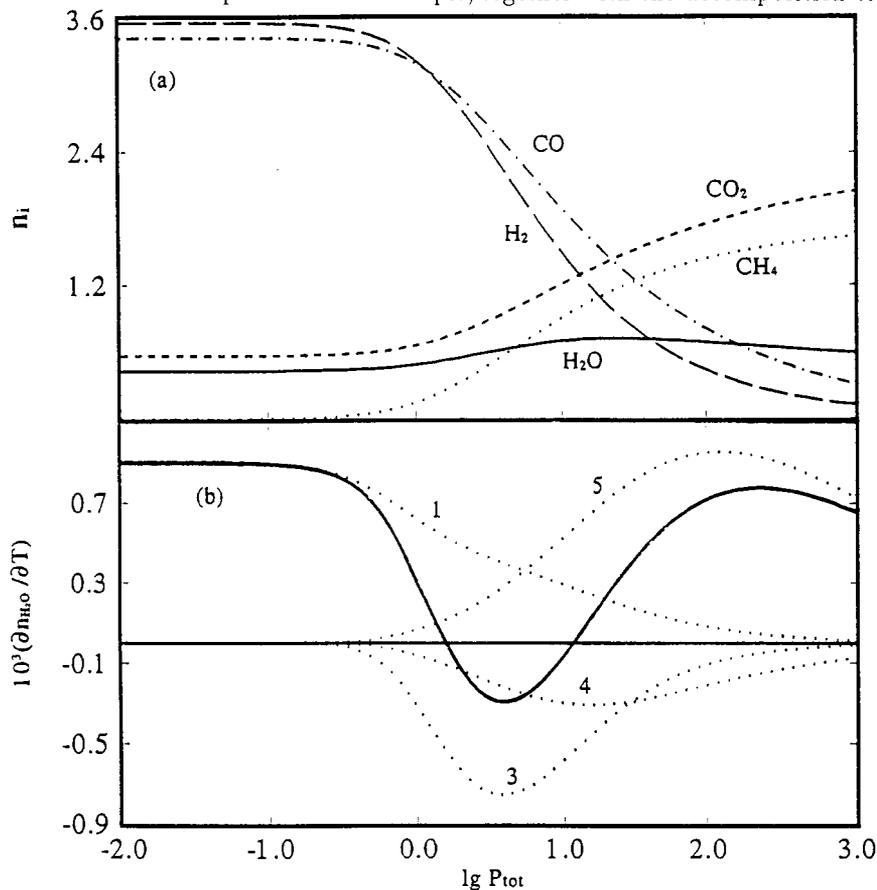


Figure 3.

- a. Distribution of the species as a function of pressure.
- b. Decomposition of $\partial n_{H_2O}/\partial T$.

Comparison of the distribution of the species with the decomposition shows that CH_4 is – practically – missing at low pressure. Therefore response reaction (1) is the dominant one, leading to positive $\partial n_{H_2O}/\partial T$. (Water is on the product side of an endothermic reaction.) Parallel with the formation of methane by increasing pressure, the role of response reactions (3) and (4) becomes more and more important. Both of them are acting in opposite direction. This leads to the decrease of the coefficient and in a narrow range causes the change of its sign. Finally at high pressure, where H_2 is practically missing, response reaction (5) dominates, where the water is on the reactant side of an exothermic reactions. Therefore $\partial n_{H_2O}/\partial T$ becomes positive again. Note that the response reaction (2) has no effect as water does not participate in it.

In a completely analogous way, it is easy to interpret the rather complicated change of n_{H_2O} as a function of pressure (Figure 2).

In addition to providing a simple means for interpreting the sensitivity coefficients of multiple-equilibrium systems, the response reactions have the following noteworthy characteristics:

- They are defined by $(m-1)$ “missing species”.
- Their number is always $\binom{q}{m-1}$.
- The number of linearly independent response reactions is equal to the number of SIRs (ref. 7).
- Any starting set of SIRs results in the same set of response reactions (ref. 7).
- The coupling between response reactions appears in a natural, unambiguous manner and it disappears in the case of solution equilibria (ref. 9).
- The participating species may be “latent”, i.e., the above algorithm might yield zero stoichiometric coefficient for those species which are not missing by definition.
- Phenomena – unusual at the first sight – which are in **apparent** contradiction with the Le Chatelier principle may be explained.

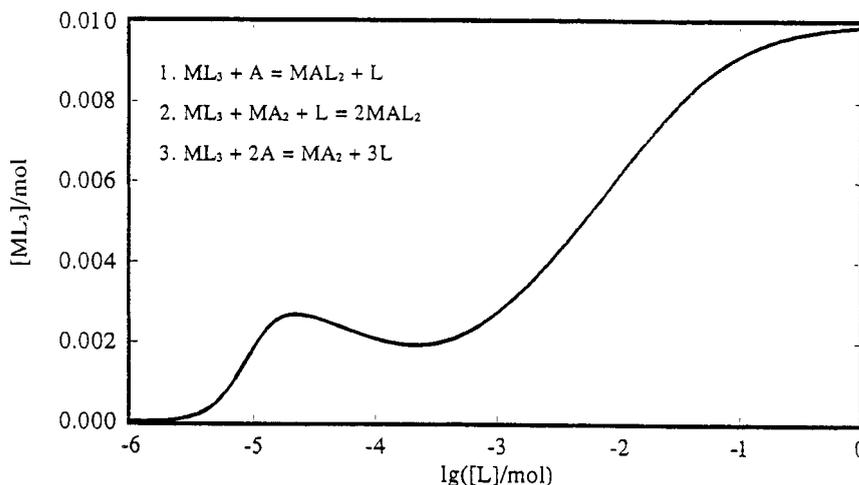


Figure 4.

Distribution of the saturated ML_3 complex as a function of $-\lg[L]$ in a metal ion (M), ligand A , ligand B system. Total concentrations: $T_M = 0.01$; $T_A = 0.01$ M. Formation constants: $\lg\beta_{MA_2} = 10.0$, $\lg\beta_{ML_3} = 15.0$, $\lg\beta_{MAL_2} = 15.0$.

Figure 4 shows – for example – the distribution of a coordinatively saturated ML_3 complex in a model system as a function of the concentration of the free ligand. The equilibria through which the change of $[L]$ may affect $[ML_3]$ are also given. It is easy to realize that the second equilibrium shown in Figure 4 is responsible for the strange decrease of $[ML_3]$ in the intermediate concentration range. L and ML_3 are found on the same side of the equilibrium. Therefore, in a range where this equilibrium dominates, the increase of $[L]$ must increase $[ML_3]$. The concept of response reactions has been also utilized to interpret unusual dilution effects (ref. 10).

Geometric representation

In case of three-component systems, the composition of the participating species may be characterized on a usual triangle diagram, as it is illustrated in Figure 5. The thick solid lines on Figure 5 outline that

range of composition – in terms of mole fractions of the three components – which may be composed from the given species. The dotted lines drawn between two species show the composition which may be achieved by mixing them. The points of intersections correspond to chemical reactions between the four species involved. Every point of intersection determines a response reaction, the numbers at these points refer to the serial number of the response reaction in the previous example. This representation convincingly suggests that – as far as the response of the system is regarded – all the five reactions must have an effect on it, even if any two of them are sufficient for calculations.

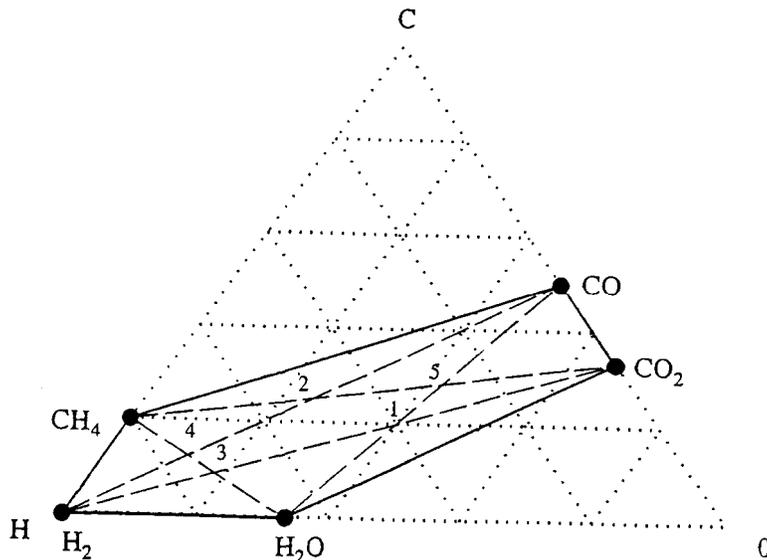


Figure 5.

Geometric representation of the composition of the species and the response reactions (1) – (5) in a triangle diagram.

Fundamental equations in terms of response reactions

As we have seen, in multiple-equilibrium systems the extent of reaction is an ambiguous quantity. At the same time the affinities are defined as partial derivatives of the Gibbs function with respect to the extents of reactions. It has been proven (ref. 12) that in spite of the ambiguity of the extents, the respective partial derivatives are well defined, their numerical values are independent of the choice of SIRs. Consequently, the change of the Gibbs function (as well as of other thermodynamic potentials) may also be defined in terms of affinities (ref. 9), either in terms of SIRs or in terms of response reactions. In terms of response reactions it reads:

$$\delta G = -S\delta T + V\delta P + \sum_{i=1}^M \sum_{j=1}^M L(i, j)_{T,P} A_i (\delta A_j)_{T,P}$$

where

$$M = \binom{q}{m-1} = \text{number of response reactions}$$

and

$$L(i, j)_{T,P} = \left(\frac{\partial^2 G}{\partial A_i \partial A_j} \right)_{T,P} = \text{coupling coefficient.}$$

$L(i, j)$ is a measure of the thermodynamic coupling between the i -th and the j -th response reaction. It has been demonstrated (ref. 9) that $L(i, j)$ disappears in solution equilibria whenever $i \neq j$.

The extension of the concept to the fundamental equations of irreversible thermodynamics is also possible^{8,9}. The point is that the time derivative of affinity plays the role of flux. By this, the inadequacy of the standard approach, caused by different transformation rules for affinities (forces) and velocities (fluxes) is avoided.

The results presented previously and briefly outlined here open a way to build up a complete set of equations of chemical thermodynamics based on response reactions. The main features of this new approach are the following:

- It provides a stoichiometrically unique representation of the multiple-equilibrium systems.
- The coupling between response reactions is defined unequivocally.
- All sensitivity coefficients and the relaxational part of the majority of first derivatives may be decomposed into terms uniquely associated with response reactions.
- Its application to nonequilibrium thermodynamics is straightforward, without any additional assumption or transformation.

Acknowledgement: This work was supported by the National Science Foundation of Hungary (OTKA, No. 4207).

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