

Response Reactions: Equilibrium Coupling

Eufrozina A. Hoffmann[†] and István Nagypál*

Department of Physical Chemistry, University of Szeged, P.O. Box 105, H-6701 Szeged, Hungary

Received: February 14, 2006; In Final Form: March 23, 2006

It is pointed out and illustrated in the present paper that if a homogeneous multiple equilibrium system containing k components and q species is composed of the reactants actually taken and their reactions contain only $k + 1$ species, then we have a unique representation with $(q - k)$ stoichiometrically independent reactions (SIRs). We define these as coupling reactions. All the other possible combinations with $k + 1$ species are the coupled reactions that are in equilibrium when the $(q - k)$ SIRs are in equilibrium. The response of the equilibrium state for perturbation is determined by the coupling and coupled equilibria. Depending on the circumstances and the actual thermodynamic data, the effect of coupled equilibria may overtake the effect of the coupling ones, leading to phenomena that are in apparent contradiction with Le Chatelier's principle.

1. Introduction

In a reactive system, detectable intermediate(s), undetectable transient species, and species in the state of activated complex are present beside the reactant(s) and product(s). The description of a reactive system requires stoichiometric equations showing the actual rearrangement of all the species participating in the reactions. In this case the equations show the actual transformation and rate constant may be assigned to them. All the above species are also present, in negligible concentration, in the equilibrium state; therefore an equilibrium system may be characterized with the perfect description of a reactive system. The perfect description correctly represents the kinetics of the system in reactive state, the thermodynamics and the dynamics of equilibrium in the equilibrium state. The perfect description contains elementary steps only. All of them run in the direction of decreasing free energy, there is no coupling between them.

The perfect description is unattainable in most of the cases as the composition and the thermodynamic data for the transient species and intermediates are not known. Therefore only the reactants and the products are taken into account to calculate the composition of the equilibrium state and its response to perturbations (sensitivity coefficients). The calculation is based either on the direct minimization of the free energy or on the equilibrium constants of the stoichiometrically independent reactions (SIRs, see below). The elimination of the transients in the case of the calculations based on SIRs leads to two apparent contradictions. The first one is that some reactions run in the direction of increasing free energy, which is overcompensated by the free energy decrease of the others. This phenomenon is treated in the framework of the theoretically criticized^{1–3} but practically useful concept of thermodynamic coupling.⁴ The second one is that the response of the equilibrium state upon perturbations may contradict the predicted response based on Le Chatelier's principle, considering SIRs only. This contradiction is explained by the concept of equilibrium coupling introduced in the present work. The concept is based on the recently elaborated theory of response reactions (RERs),^{5–8} by

unequivocally defining the SIRs as coupling equilibria and the remaining response reactions as coupled equilibria. It is pointed out and illustrated with examples that, under certain conditions, the response of the equilibrium state upon perturbations is primarily determined by the coupled equilibria. It should be mentioned that if the calculations are based on the direct minimization of free energy, then the coupling—neither in thermodynamic nor in equilibrium sense—does not appear.

2. Stoichiometrically Independent Reactions

SIRs are, by definition, a set of reactions in which none of the members can be expressed as a linear combination of the others. Their main characteristics are as follows:

- They are ambiguous. That is, any of the infinite number of their linear combinations can be used for thermodynamic calculation.
- Their number in a given system is fixed: $q - k$, where q is the number of species and k is the number of components.

The species⁹ is a chemical entity distinguishable from other such entities by its molecular formula; or failing that, by its molecular structure. The component is one of a set of k species of the chemical system, whose set of formula vectors $\{a_1, a_2, \dots, a_k\}$ satisfies $\text{rank}(a_1, a_2, \dots, a_k) = k$. The formula vector¹⁰ is a vector of subscripts (usually integers) to the elements in the molecular formula of species.

As an example, let us regard a protonated ligand (HL) that slightly dissociates in solution (charges are omitted for simplicity):



When a complex forming metal ion (M) is added to the system, ML complex is formed in equilibrium:

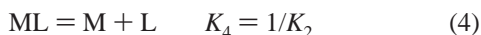


In this example, and in general in solution equilibria, the choice of components is straightforward, those species are the components that are unable to dissociate further (H, L and M). Their reaction produces the associates (HL and ML), and the number of stoichiometrically independent equilibria is equal to the number of associates which is two in the present case.

* Corresponding author. E-mail: nagypal@chem.u-szeged.hu. Phone: 36 62 544112. Fax: 36 62 544652.

[†] E-mail: efi@chem.u-szeged.hu.

There are many equivalent pairs of equations to describe the same equilibrium state, for instance:



Galán and Angulo,¹¹ on the basis of our formerly developed theory of RERs, have recently proven that all of the three equilibria mentioned above (eqs 1–3) must be taken into account when the relaxation experiments (*T*-jump for example) are evaluated, because all of them play role in the kinetics of the perturbed system, although only two of them are independent stoichiometrically. In general, they stated, all of the RERs should be taken into account if relaxation experiments are evaluated either in equilibrium or in stationary states. In other words, the SIRs are not sufficient to describe the response of a perturbed system.

3. Theory of Response Reactions

The complicated mathematics of the theory of response reactions was given in our previous papers. Originally it was developed from the stoichiometrically independent reactions, based on the species which are missing from them.^{5–7} Later on we redefined the response reactions on the basis of the composition of the species participating in the equilibrium.⁸ According to this RERs are defined as reactions in which the number of species exceeds the number of components by one. The redefinition made it possible to introduce the concept of equilibrium coupling, presented here. The redefined theory is based on the well-known fact that in an equilibrium system with *k* components unequivocal stoichiometric equations can be constructed from *k* + 1 (or less, see below) species. Formally correct stoichiometric equations may be constructed from *k* + 2, *k* + 3, etc. species also, but then the same reactants provide different amounts of the same products; i.e., the stoichiometry is not unequivocal. For example, 3ML + 2H = 3M + 2HL + L; 3ML + H = 3M + HL + 2L.

If the system contains *q* species, then we have $M = \binom{q}{k+1}$ possibilities to construct unequivocal stoichiometry. These are the RERs in the system. If we have a system composed of subsystems with less than *k* components, then (as in the H–L–M example) we arrive at the same stoichiometry whenever a species containing the “surplus” component is found among the chosen *k* + 1 species. For example either the H, L, HL, M or the H, L, HL, ML species are selected from H, L, HL, M, ML the unequivocal stoichiometric equation is in both cases H + L = HL. We named these degenerated reactions, which always appear if the whole system contains at least one subsystem with less than *k* components. In complicated systems with many subsystems, it may happen that more than one, otherwise correct, stoichiometry can be constructed from the *k* + 1 species chosen. These lead to zero reactions, in which the stoichiometric coefficients of all species become zero. Taking the degenerated reactions only once and omitting zero reactions, the number of remaining stoichiometrically unequivocal reactions is denoted by *R* ($R \leq M$).

These reactions are not independent stoichiometrically; *q* – *k* stoichiometrically independent reactions (SIRs), with the appropriate thermodynamic data, are sufficient to carry out any thermodynamic calculation, including the calculation of any sensitivity coefficients. Even if we have *R* – (*q* – *k*) redundant stoichiometric equations, all of them must be taken into account if we want to understand and rationalize the response of an equilibrium system upon perturbation.

According to the theory, any sensitivity coefficient of an equilibrium system is a simple sum of the sensitivity coefficients unequivocally assigned to *R* response reactions, and all RERs strictly obey Le Chatelier’s principle;¹² namely: “A system at equilibrium resists attempts to change its temperature, pressure, or concentration of a reagent.”

4. Equilibrium Coupling

In practice, the stoichiometric equations show the rearrangement of the reactants into (detectable) products. It is expedient therefore to construct SIRs from those reactants that are actually taken in an experiment or in an industrial process. The amount of initial reactants and the pressure and temperature unequivocally determine the equilibrium state, which means that it is always possible to construct SIRs containing the reactants only on their left-hand side. This way we arrive at an unequivocal definition of coupling reactions, and at a unique stoichiometric representation of a multiple equilibrium system, instead of the infinite possibilities derived purely from mathematical considerations. It follows that coupled reactions are those RERs in which there is at least one product on both sides. The restriction we made is that the coupling reactions must be chosen from the reactants actually taken in practice, which is in accordance with the chemical common sense.

As an example, let us consider a gas-phase equilibrium between CH₄, H₂O, CO, CO₂ and H₂ at 1000 K. It should be noted that some other species may also be formed in this system at 1000 K, but they are neglected to have as simple an example as possible. The rank of their atomic matrix is 3; i.e., it is a three-component system. The example shows a basic difference between the solution and gas-phase equilibria. In solutions the species unable to further dissociate are evidently taken as components and they are always present in the SIRs describing the system. In the gas phase it often happens that the “evident” components (C, H, O) are regarded as transients that are eliminated from the stoichiometric equations.

Five pairs of reactants may be chosen in the example (some of them are significant from the industrial and/or environmental point of view):

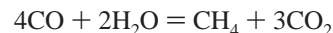
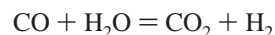
1. Reactants: CO and H₂. Products: CH₄, CO₂ and H₂O.

Coupling reactions:



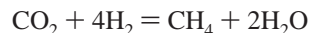
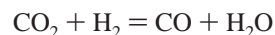
2. Reactants: CO and H₂O. Products: CH₄, CO₂ and H₂.

Coupling reactions:



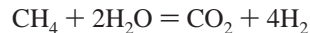
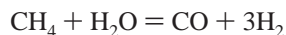
3. Reactants: CO₂ and H₂. Products: CH₄, CO and H₂O.

Coupling reactions:



4. Reactants: CH₄ and H₂O. Products: CO, CO₂ and H₂.

Coupling reactions:



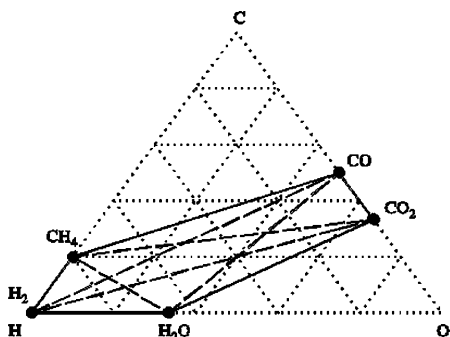
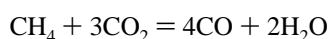
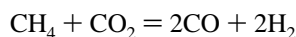


Figure 1. Geometric representation of the coupled and coupling reactions in the $\text{CH}_4\text{--H}_2\text{O--CO--CO}_2\text{--H}_2$ system.

5. Reactants: CH_4 and CO_2 . Products: CO , H_2 and H_2O .
Coupling reactions:



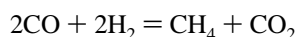
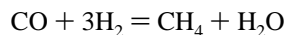
It is easy to realize that every equilibrium appears in both directions depending on the choice of the reactants. In other words, we have five RERs and the choice of two coupling reactions depends on the choice of the actual reactants.

The restriction of constructing coupling reactions only from reactants is illustrated on a triangle diagram representing this three-component system (Figure 1.). Taking the transient C, H, O as components, the composition of an equilibrium system may be any point within the solid lines. If, however, the reactants are defined, then the composition may change only along the lines connecting the reactants. The five crossing points represent the five RERs. The two crossing points in a line connecting the reactants chosen represent the coupling, the other three crossing points represent the coupled reactions.

In our papers dealing with the theory of response reactions some examples were provided, showing that an equilibrium system is shifted in the direction opposite that predicted by Le Chatelier's principle if the SIRs are analyzed only. The question is whether this contradiction comes from the arbitrariness of the choice of SIRs or appears even if the SIRs that are the coupling reactions are unequivocally determined as above. In other words, is it possible that the coupled reactions overtake the coupling reactions in determining the shift of an equilibrium system even if the coupling reactions are constructed from the reactants actually taken? The intuitive answer is yes, based on the following considerations. If we have two reactants and two coupling reactions, then the mole ratio of the reactants in the coupling reactions must be different. If one of them is in considerable excess, then the concentration (partial pressure) of the other will be relatively low in the equilibrium state. If there is a coupled equilibrium between the excess reactant and the products, then that equilibrium may determine the response of the system to perturbation.

5. Examples

5.1. Example. CO and H_2 may react in 1:3 and 1:1 mole ratios.



The increase of the pressure shifts both processes in the direction of the formation of the products. If the composition corresponds

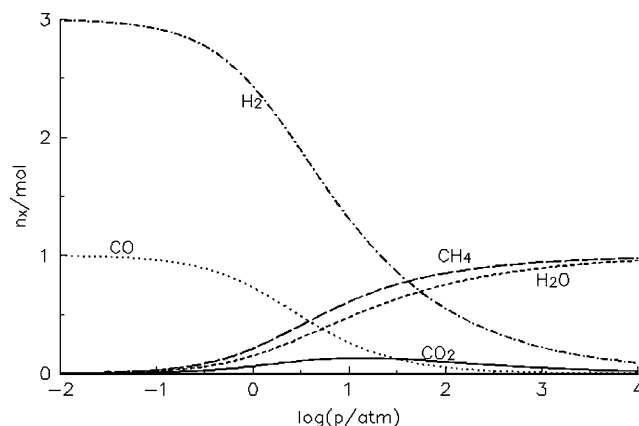


Figure 2. Distribution of the species as a function of the logarithm of pressure in the CO--H_2 system (Initial amounts: $n_{\text{H}_2}^0 = 3 \text{ mol}$, $n_{\text{CO}}^0 = 1 \text{ mol}$, $T = 1000 \text{ K}$).

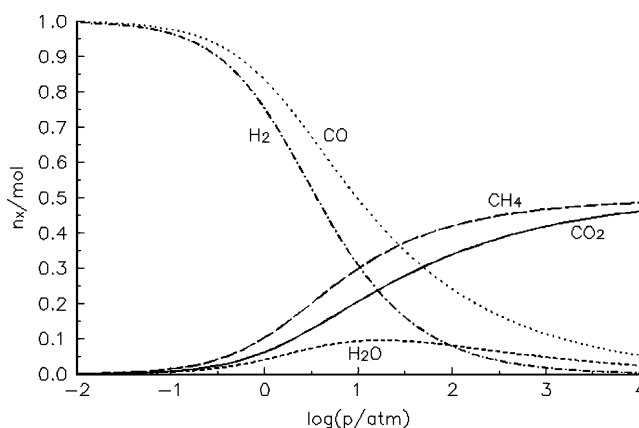
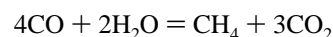
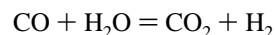


Figure 3. Distribution of the species as a function of the logarithm of pressure in the CO--H_2 system (Initial amounts: $n_{\text{H}_2}^0 = n_{\text{CO}}^0 = 1 \text{ mol}$, $T = 1000 \text{ K}$).

to a 1:3 mole ratio, then it may be predicted that CO will practically disappear at a pressure determined by the equilibrium constants, because CO is withdrawn from the system in a 1:1 ratio also. Therefore the coupled equilibrium between the remaining four species ($\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$) will dominate and will be shifted in the direction of decreasing the amount of CO_2 with an increase in pressure, in the direction opposite that which would be predicted from the SIRs only. If, however, the composition of the system corresponds to a 1:1 mole ratio, then H_2 will practically disappear and the equilibrium between the remaining four species ($4\text{CO} + 2\text{H}_2\text{O} = \text{CH}_4 + 3\text{CO}_2$) will dominate and will be shifted in the direction of decreasing the amount of H_2O , in the direction opposite that which would be predicted from the SIRs only. Figures 2 and 3 show the calculated distribution of the species as a function of pressure, in complete agreement with the prediction.

5.2. Example. The effect of the coupled reaction is not always opposite to the expected effect of the SIRs, and it may depend on the mole ratio. Analyzing the $\text{CO} + \text{H}_2\text{O}$ system in a similar way,

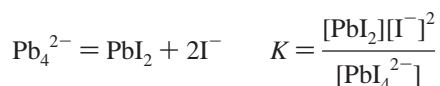


At a 2:1 mole ratio the amount of H_2O will practically disappear when the pressure is increased; thus the coupled equilibrium $2\text{CO} + 2\text{H}_2 = \text{CH}_4 + \text{CO}_2$ will dominate, which increases the amount of CO_2 with increasing pressure. At this mole ratio the coupled equilibrium has the same effect as one of the SIRs.

At 1:1 mole ratio, however, CO is expected to disappear first leading to the dominance of the coupled equilibrium $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$, which acts in the direction opposite to the effect of one of the SIRs. Calculations showed that at this mole ratio the coupled equilibrium cannot overcompensate the effect of the SIRs, but it could do it if H_2O is in even higher excess (1:3 mole ratio).

5.3. Example. A model system with a metal ion (M), two ligands (A and L) and with three complexes (MA_2 , MAL_2 and ML_3) showed that at constant total metal ion and ligand A concentration, increasing free L ligand concentration may decrease the concentration of the coordinatively saturated ML_3 complex. The SIRs are unequivocal in this case: the formation of the complexes from their components. Constructing the RERs, we find $\text{ML}_3 + \text{MA}_2 + \text{L} = 2\text{MAL}_2$ response equilibrium. In this equation ML_3 and L are also reactants; thus the increase of L concentration must decrease ML_3 and MA_2 and must increase MAL_2 concentration in accordance with Le Chatelier's principle.

5.4. Example. At high I^- concentration, PbI_4^{2-} complex is formed.¹³ The SIRs are the stepwise formation equilibria. Diluting the solution precipitates PbI_2 , which is evidently dissolved for further dilution. One of the response equilibria in the system is



Expressing $[\text{PbI}_2]$:
$$[\text{PbI}_2] = K \frac{[\text{PbI}_4^{2-}]}{[\text{I}^-]^2}$$

It is evident that the concentration of PbI_2 must be increasing in that range where the metal ion is mostly in PbI_4^{2-} form, as the decrease of $[\text{I}^-]$ by dilution has a quadratic effect in the denominator compared to the linear decrease of PbI_4^{2-} in the numerator.

6. Discussion

It is known that a multiple equilibrium system may be represented by an infinite number of linear combinations of the stoichiometrically independent reactions (SIRs). Taking into account that a stoichiometrically unequivocal reaction may contain $k + 1$ species only, where k is the number of components in the given stoichiometric equation, then we arrive at a finite number of possible representations. These reactions are called response reactions (RERs), as it has been proven before by us that all sensitivity coefficients of an equilibrium state are a sum of contributions unequivocally assigned to the response reactions.^{6–7} It has been proven by Galán and Angulo¹¹ that the response reactions must be considered when the relaxation kinetic experiments are evaluated. It is pointed out in the present paper that, if the reactants actually taken are used to create the SIRs and if the criterium is that they may contain only $k + 1$ species, then we arrive at a unique representation of an equilibrium system. These SIRs are called coupling reactions whereas all the RERs, which contain at least one of the products in both sides, are the coupled reactions. It is pointed out that the role of coupled reactions may be decisive in determining

the sign of the sensitivity coefficients when the system is perturbed. The sign of the sensitivity coefficient may be the same as or opposite of the sign predicted from SIRs only. If it is opposite, then we find phenomena that are in apparent contradiction with Le Chatelier's principle.

To sum up, the equilibrium coupling may be described as follows: If a homogeneous multiple equilibrium system containing k components and q species is composed of the reactants actually taken and if their reactions contain only $k + 1$ species, then we have a unique representation with $(q - k)$ stoichiometrically independent reactions, instead of the mathematically possible infinite number of representations. We define these as coupling reactions. All the other possible combinations with $k + 1$ species are the coupled reactions, which are in equilibrium when the $(q - k)$ SIRs are in equilibrium. The response of the equilibrium state to perturbation is determined by the coupling and coupled equilibria. Depending on the circumstances and the actual thermodynamic data, the effect of coupled equilibria may overtake the effect of the coupling ones, leading to phenomena that are in apparent contradiction with Le Chatelier's principle.

For the sake of completeness, it should be mentioned that in the case of the perfect (in most cases unattainable) description of an equilibrium system, the equilibrium coupling, as well as the thermodynamic coupling mentioned in the Introduction, disappears. In other words, both types of couplings appear only because we are not yet able to completely describe a reactive system that leads to the equilibrium state. Moreover, if the calculations are based on the direct minimization of the free energy, i.e., no reaction equations are considered at all, then the question of coupling—neither in the thermodynamic nor in equilibrium sense—does not even appear. Despite this, we believe that the definition and introduction of equilibrium coupling is a useful concept, because most of the chemists interpret their results in terms of chemical reactions.

Acknowledgment. This work was supported by the National Science Foundation of Hungary (OTKA T047031).

Supporting Information Available: An executable PC program to construct all the possible unequivocal stoichiometry from the composition of the species in an equilibrium system is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Koenig, F. O.; Horne, F. H.; Mohilner, D. M. *J. Am. Chem. Soc.* **1961**, *83*, 1029.
- (2) Keizer, J. J. *Theor. Biol.* **1975**, *49*, 323.
- (3) Boudart, M. *J. Phys. Chem.* **1983**, *87*, 2786.
- (4) Prigogine, I.; Defay, R. *Chemical Thermodynamics*; Longmans Green: New York, 1954.
- (5) Fishtik, I.; Nagypál, I.; Gutman, I. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3245.
- (6) Fishtik, I.; Nagypál, I.; Gutman, I. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 259.
- (7) Fishtik, I.; Gutman, I.; Nagypál, I. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3525.
- (8) Hoffmann, E. A.; Nagypál, I. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3107.
- (9) Smith, W. R.; Missen, R. W. *Chemical Reaction Equilibrium Analysis: Theory and Algorithms*; Wiley: New York, 1982.
- (10) Brinkley, S. P. *J. Chem. Phys.* **1946**, *14*, 563; erratum, p 686.
- (11) Galán, M.; Angulo, G. *Chem. Phys.* **2000**, *254*, 329.
- (12) Treptow, R. S. *J. Chem. Educ.* **1980**, *57*, 417.
- (13) Nagypál, I.; Beck, M. T. *Talanta* **1982**, *29*, 473.