

LETTER TO THE EDITOR

Reply to Finding the Rate-Determining Step in a Mechanism: Comparing DeDonder Relations with the “Degree of Rate Control”

INTRODUCTION

In (1), Campbell argues that the degree of rate control, $X_{RC,i}$, is a better tool, compared to the use of DeDonder relations, for assessing which steps in the reaction scheme limit the overall rate of a stoichiometric reaction. It is true that situations exist for which DeDonder relations implicate an upper limit for the number of reaction steps that may limit the overall reaction kinetics. In particular, the reversibility, z_i , of each irreversible step in a reaction scheme is equal to zero (where z_i is equal to the ratio of the reverse rate to the forward for step i); therefore, the DeDonder approach does not distinguish the relative importance of each step in this case. This situation is remedied by Campbell's degree of rate control. Importantly, however, there are other aspects of the reaction kinetics where the DeDonder approach provides essential insight. The following concepts, for example, are readily demonstrated using DeDonder relations (see (2)):

(i) DeDonder relations provide a simple means to determine the number of kinetic parameters required to calculate the overall reaction rate.

(ii) Kinetic parameters for gaseous reactions are controlled by quasi-equilibria between the reactants and/or products of the overall reaction with the transition states of the elementary steps, and they are not determined by the properties of the stable reaction intermediates.

(iii) Reaction kinetics for surface reaction schemes are controlled by concept (ii) above, plus one additional kinetic parameter for each stable surface species that becomes abundant on the surface.

(iv) DeDonder relations make it possible to calculate the maximum rate at which a given transition state may contribute to the overall reaction rate, providing a necessary condition for assessing the participation in the overall reaction scheme of transition states identified by quantum chemical calculations.

(v) DeDonder relations provide a convenient means for deriving rate expressions from reaction schemes for special cases where a limited number of steps are not quasi-equilibrated.

It is important to indicate that Campbell's degree of rate control (originally proposed in (3)) is a very useful tool to help identify the kinetically significant steps in a reaction scheme. More generally, however, I would suggest that DeDonder relations and Campbell's degree of rate control are highly complementary tools for analyzing reaction schemes. In particular, DeDonder relations have enormous utility for deriving general principles of reaction kinetics for reaction schemes, and Campbell's degree of rate control provides a nice quantitative tool for computing the sensitivities of each step in a reaction scheme when values for all of the rate constants are available.

In the following sections, we explore some interesting connections between DeDonder relations and Campbell's degree of rate control. These derivations are presented elsewhere in greater detail (2, 4).

IDENTIFICATION OF KINETIC PARAMETERS FROM DEDONDER RELATIONS

According to the formulation of DeDonder (5), the net rate, r_i , for elementary step i is expressed in terms of the forward rate of the step, \bar{r}_i , and the affinity for the step, A_i

$$r_i = \bar{r}_i \left[1 - \exp\left(\frac{-A_i}{RT}\right) \right], \quad [1]$$

where the affinity is equal to minus the change in the Gibbs free energy with respect to the extent of reaction. The affinity, A_i , can be expressed in terms of the standard state Gibbs free energies, G_j^o , and the activities, a_j , of the j reactants and products of the step

$$A_i = - \sum_j \nu_{ij} G_j = - \sum_j \nu_{ij} [G_j^o + RT \ln(a_j)], \quad [2]$$

where ν_{ij} are the stoichiometric coefficients for the j reactants and products of step i . This relation can be expressed in terms of the equilibrium constant for the step, $K_{i,eq}$:

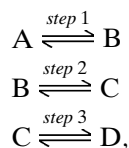
$$\exp\left(\frac{-A_i}{RT}\right) = \frac{\prod_j a_j^{\nu_{ij}}}{K_{i,eq}}. \quad [3]$$

For convenience, we define a dimensionless variable, z_i , equal to the exponential of $-A_i/RT$:

$$z_i = \exp\left(\frac{-A_i}{RT}\right) = \frac{\prod_j a_j^{v_{ij}}}{K_{ieq}}. \quad [4]$$

The value of z_i approaches zero as step i becomes irreversible, and z_i approaches unity as step i becomes quasi-equilibrated; therefore, this value of z_i may be termed the *reversibility* of step i .

Consider the three-step reaction scheme



where species B and C are reaction intermediates and the overall reaction is $\text{A} \rightleftharpoons \text{D}$. The values of z_i are equal to

$$\begin{aligned} z_1 &= \frac{a_B}{K_{1,eq}a_A} \\ z_2 &= \frac{a_C}{K_{2,eq}a_B} \\ z_3 &= \frac{a_D}{K_{3,eq}a_C}. \end{aligned} \quad [5]$$

The product of the three values of z_i is controlled by the overall reversibility of the reaction, z_{total} :

$$z_{total} = z_1 z_2 z_3 = \frac{a_D}{K_{eq}a_A}. \quad [6]$$

The activities of intermediates B and C are now expressed in terms of z_i , and the net rates of the three reactions are given by

$$\begin{aligned} r_1 &= k_1 a_A (1 - z_1) \\ r_2 &= K_{1,eq} k_2 a_A z_1 (1 - z_2) \\ r_3 &= K_{1,eq} K_{2,eq} k_3 a_A z_1 z_2 \left(1 - \frac{z_{total}}{z_1 z_2}\right). \end{aligned} \quad [7]$$

The unknown values of z_1 and z_2 are determined by requiring that the net rates of steps 1, 2, and 3 are equal. Therefore, the net rate of the overall reaction is again controlled by three-lumped kinetic parameters, K_{TSi} :

$$\begin{aligned} r_1 &= K_{TS1} a_A (1 - z_1) \\ r_2 &= K_{TS2} a_A z_1 (1 - z_2) \\ r_3 &= K_{TS3} a_A z_1 z_2 \left(1 - \frac{z_{total}}{z_1 z_2}\right). \end{aligned} \quad [8]$$

It can now be seen for the three-step reaction scheme of this example that the net rate of the overall reaction is

controlled by three kinetic parameters, K_{TSi} , that depend only on the properties of the transition states for the elementary steps relative to the reactants (and possibly the products) of the overall reaction. We note that the reaction scheme contains six individual rate constants k_i and k_{-i} , the product of which must give the equilibrium constant for the overall reaction. However, it is not necessary to determine values for five linearly independent rate constants to determine the rate of the overall reaction. In general, we conclude that the maximum number of kinetic parameters needed to determine the net rate of overall reaction is equal to the number of transition states in the reaction scheme (equal to 3 in the present case), since each kinetic parameter is related to a quasi-equilibrium constant for the formation of each transition state from the reactants and/or products of the overall reaction (2). To calculate rates for heterogeneous catalytic reactions, we note that an additional kinetic parameter is required for each surface species that is abundant on the catalyst surface. Specifically, the net rate of the overall reaction is determined by the intrinsic kinetic parameters K_{TSi} , as well as by the fraction of the surface sites, θ^* , that is available for the formation of the transition states, and the value of θ^* is determined by the extent of site blocking by abundant surface species.

In short, we note that DeDonder relations allow the overall reaction kinetics to be expressed in terms of quasi-equilibrium relations involving transition states, and the properties of these transition states can be related to activation barriers with respect to stable reaction intermediates. However, by expressing the reaction kinetics in terms of quasi-equilibria between transition states and the appropriate reactants and/or products, we eliminate the need to estimate the thermodynamic properties of reaction intermediates that are not abundant on the catalyst surface.

SENSITIVITIES OF THE NET RATE TO INDIVIDUAL RATE CONSTANTS

We again consider the three-step reaction scheme discussed above. The net rates for the three steps are given below in the DeDonder form:

$$\begin{aligned} r_1 &= k_1 a_A (1 - z_1) \\ r_2 &= \frac{k_1}{k_{-1}} k_2 a_A z_1 (1 - z_2) \\ r_3 &= \frac{k_1}{k_{-1}} \frac{k_2}{k_{-2}} k_3 a_A z_1 z_2 \left(1 - \frac{k_{-1} k_{-2} k_{-3}}{k_1 k_2 k_3} \frac{a_D}{z_1 z_2 a_A}\right). \end{aligned} \quad [9]$$

The sensitivity of the net rate with respect to k_1 is determined by first taking the derivative of r_1 , r_2 , and r_3 with

respect to k_1 , as shown below

$$\begin{aligned} \left(\frac{\partial r_1}{\partial k_1}\right)_{k_j} &= \left(\frac{\partial r_1}{\partial k_1}\right)_{k_j, z_i} + \left(\frac{\partial r_1}{\partial z_1}\right)_{k_i, z_2} \left(\frac{\partial z_1}{\partial k_1}\right)_{k_j} \\ \left(\frac{\partial r_2}{\partial k_1}\right)_{k_j} &= \left(\frac{\partial r_2}{\partial k_1}\right)_{k_j, z_i} + \left(\frac{\partial r_2}{\partial z_1}\right)_{k_i, z_2} \left(\frac{\partial z_1}{\partial k_1}\right)_{k_j} \\ &\quad + \left(\frac{\partial r_2}{\partial z_2}\right)_{k_i, z_1} \left(\frac{\partial z_2}{\partial k_1}\right)_{k_j} \\ \left(\frac{\partial r_3}{\partial k_1}\right)_{k_j} &= \left(\frac{\partial r_3}{\partial k_1}\right)_{k_j, z_i} + \left(\frac{\partial r_3}{\partial z_1}\right)_{k_i, z_2} \left(\frac{\partial z_1}{\partial k_1}\right)_{k_j} \\ &\quad + \left(\frac{\partial r_3}{\partial z_2}\right)_{k_i, z_1} \left(\frac{\partial z_2}{\partial k_1}\right)_{k_j}, \end{aligned} \quad [10]$$

where k_j refers to all rate constants except k_1 , k_i refers to all rate constants, and z_i refers to z_1 and z_2 .

At steady state, the three net rates r_i are equal to the overall rate, r . Therefore, we write

$$\left(\frac{\partial r_1}{\partial k_1}\right)_{k_j} = \left(\frac{\partial r_2}{\partial k_1}\right)_{k_j} = \left(\frac{\partial r_3}{\partial k_1}\right)_{k_j} = \left(\frac{\partial r}{\partial k_1}\right)_{k_j}, \quad [11]$$

which allows determination of the partial derivatives of z_1 and z_2 with respect to k_1

$$\left(\frac{\partial z_1}{\partial k_1}\right)_{k_j} = - \left[\frac{(k_2 k_3 + k_3 k_{-1} + k_{-1} k_{-2}) z_1 - k_{-1} (k_3 + k_{-2})}{k_1 (k_2 k_3 + k_3 k_{-1} + k_{-1} k_{-2})} \right] \quad [12]$$

$$\left(\frac{\partial z_2}{\partial k_1}\right)_{k_j} = \frac{[-(k_3 + k_{-2}) z_2 + k_{-2}] k_{-1}}{k_1 (k_2 k_3 + k_3 k_{-1} + k_{-1} k_{-2}) z_1}.$$

We now define the dimensionless sensitivity, s_1 , of the overall rate with respect to k_1 as

$$s_1 = \left(\frac{\partial r}{\partial k_1}\right)_{k_j} \frac{k_1}{r}. \quad [13]$$

Substitution of the relations for $\left(\frac{\partial z_1}{\partial k_1}\right)_{k_j}$ and $\left(\frac{\partial z_2}{\partial k_1}\right)_{k_j}$ into any of the expressions for the partial derivatives of r_i with respect to k_1 gives the sensitivity s_1 :

$$s_1 = \frac{k_2 k_3}{(k_2 k_3 + k_3 k_{-1} + k_{-1} k_{-2})(1 - z_1)}. \quad [14]$$

In a similar fashion, we may derive an expression for the dimensionless sensitivity, s_{-1} , of the overall rate with respect to k_{-1} as

$$s_{-1} = \left(\frac{\partial r}{\partial k_{-1}}\right)_{k_j} \frac{k_{-1}}{r} = \frac{-k_2 k_3 z_1}{(k_2 k_3 + k_3 k_{-1} + k_{-1} k_{-2})(1 - z_1)}.$$

The following expressions for s_2 , s_{-2} , s_3 , and s_{-3} may be derived according to the steps outlined above

$$\begin{aligned} s_2 &= \frac{k_2 k_3 z_1}{(k_2 k_3 + k_3 k_{-1} + k_{-1} k_{-2})(1 - z_1)} \\ s_{-2} &= \frac{-k_2 k_3 z_1 z_2}{(k_2 k_3 + k_3 k_{-1} + k_{-1} k_{-2})(1 - z_1)} \\ s_3 &= \frac{k_2 k_3 z_1 z_2}{(k_2 k_3 + k_3 k_{-1} + k_{-1} k_{-2})(1 - z_1)} \\ s_{-3} &= \frac{-k_2 k_3 z_{total}}{(k_2 k_3 + k_3 k_{-1} + k_{-1} k_{-2})(1 - z_1)}. \end{aligned} \quad [16]$$

It is now apparent that s_{-1} , s_{-2} , and s_{-3} are related to s_1 , s_2 , and s_3 by

$$\begin{aligned} s_{-1} &= -z_1 s_1 \\ s_{-2} &= -z_2 s_2 \\ s_{-3} &= -z_3 s_3. \end{aligned} \quad [17]$$

The above relations are specific cases of the more general result for any elementary step i :

$$s_{-i} = -z_i s_i. \quad [18]$$

This result indicates that the sensitivity of the overall rate to the reverse rate constant for a step depends on the reversibility of the step. For example, the sensitivity of the overall rate to the reverse rate constant is equal to zero for an irreversible step ($z_i = 0$) and it is equal to the negative value of the sensitivity of the overall rate to the forward rate constant for a quasi-equilibrated step ($z_i = 1$).

For this case, we also see that

$$\begin{aligned} s_2 &= z_1 s_1 \\ s_3 &= z_2 s_2. \end{aligned} \quad [19]$$

Accordingly, we see that the sensitivity of the overall rate to the forward rate constant for step 2 depends on the reversibility of the previous step 1 that produces the reaction intermediate used in step 2. Similarly, the sensitivity of the overall rate to the forward rate constant for step 3 depends on the reversibility of the previous step 2 that produces the reaction intermediate used in step 3. In these cases, the sensitivity of the overall rate to the forward rate constant for a step approaches zero as the previous step that produces the reaction intermediate becomes irreversible ($z_i = 0$). In contrast, the sensitivity of the overall rate to the forward rate constant for a step remains non-zero as the previous step that produces the reaction intermediate becomes reversible ($z_i > 0$).

CONSERVATION OF SENSITIVITY

The above relations suggest a conservation of sensitivity for the forward and reverse rate constants of a reaction

scheme that leads to a single overall reaction. Consider the following sum of sensitivities for the above three-step reaction scheme

$$\sum_{i=1,3} (s_i + s_{-i}) = [(1 - z_1) + z_1(1 - z_2) + z_1z_2(1 - z_3)]s_1, \quad [20]$$

which leads to the result that

$$\sum_{1,3} (s_1 + s_{-1}) = (1 - z_1z_2z_3)s_1. \quad [21]$$

The sensitivity s_1 was expressed above in terms of $(1 - z_1)$, and the value of $(1 - z_1)$ at steady state is equal to

$$(1 - z_1) = \frac{k_1k_2k_3a_A - k_{-1}k_{-2}k_{-3}a_D}{k_1a_A(k_2k_3 + k_3k_{-1} + k_{-1}k_{-2})}. \quad [22]$$

Thus, the sensitivity s_1 can be written as

$$s_1 = \frac{k_1k_2k_3a_A}{k_1k_2k_3a_A - k_{-1}k_{-2}k_{-3}a_D}. \quad [23]$$

We also note that

$$z_1z_2z_3 = z_{total} = \frac{a_D}{K_{eq}a_A} = \frac{k_{-1}k_{-2}k_{-3}a_D}{k_1k_2k_3a_A}. \quad [24]$$

Therefore, we see that

$$\begin{aligned} \sum_{1,3} (s_i + s_{-i}) &= \left(1 - \frac{k_{-1}k_{-2}k_{-3}a_D}{k_1k_2k_3a_A}\right) \\ &\times \frac{k_1k_2k_3a_A}{k_1k_2k_3a_A - k_{-1}k_{-2}k_{-3}a_D} = 1. \end{aligned} \quad [25]$$

A more general demonstration of this conservation of sensitivity is presented elsewhere for reaction schemes that lead to a single stoichiometric reaction (4).

CONNECTION TO CAMPBELL'S DEGREE OF RATE CONTROL

Campbell suggests that the kinetic importance of a particular step in a reaction scheme can be ascertained by computing the effect on the overall rate of increasing the forward and reverse rate constants for that step, while maintaining the same value of the equilibrium constant for the step. According to Campbell (1, 3), the "degree of rate control" for step i , $X_{RC,i}$ is equal to

$$X_{RC,i} = \frac{k_i}{r} \left(\frac{\delta r}{\delta k_i} \right)_{K_{i,eq}, k_j}, \quad [26]$$

where the equilibrium constant for step i ($K_{i,eq}$) and all other rate constants are held constant.

We now compute Campbell's degree of rate control in terms of the sensitivities for the forward and reverse rate constants. We compute the change in the overall rate, δr , resulting from a change in k_i by δk_i and a change in k_{-i} by $\delta k_{i,eq}$ to maintain the same equilibrium constant

$$\delta r = \left(\frac{\partial r}{\partial k_i} \right)_{k_j} \delta k_i + \left(\frac{\partial r}{\partial k_{-i}} \right)_{k_j} \frac{\delta k_i}{K_{i,eq}}, \quad [27]$$

where k_j are all rate constants other than k_i or k_{-i} , as appropriate.

We compute Campbell's degree of rate control as

$$X_{RC,i} = \frac{k_i}{r} \left(\frac{\delta r}{\delta k_i} \right)_{K_{i,eq}, k_j} = \frac{k_i}{r} \left[\left(\frac{\partial r}{\partial k_i} \right)_{k_j} + \left(\frac{\partial r}{\partial k_{-i}} \right)_{k_j} \frac{k_{-i}}{k_i} \right], \quad [28]$$

which leads to the following relation

$$X_{RC,i} = s_i + s_{-i}. \quad [29]$$

According to Eq. [18], we can also write

$$X_{RC,i} = (1 - z_i)s_i. \quad [30]$$

Since we showed earlier in Eq. [25] that the sum of the sensitivities for the forward and reverse rate constants of a reaction scheme is equal to unity for a reaction scheme that leads to a single overall reaction, we now see that the sum of $X_{RC,i}$ for the steps is also conserved

$$\sum_i X_{RC,i} = 1. \quad [31]$$

This result is in agreement with the work of Baranski (6) referenced by Campbell. In particular, Baranski showed for a series of consecutive steps that if a rate-determining step exists with $X_{RC,i} = 1$, then the degree of rate control for all other steps is equal to zero.

In the above example of a three-step reaction scheme, the values of $X_{RC,i}$ are equal to

$$\begin{aligned} X_{RC,1} &= (1 - z_1)s_1 \\ X_{RC,2} &= z_1(1 - z_2)s_1 \\ X_{RC,3} &= z_1z_2(1 - z_3)s_1 \\ \sum_{i=1,3} X_{RC,i} &= (1 - z_1z_2z_3)s_1 = 1. \end{aligned} \quad [32]$$

Therefore, we see that Campbell's degree of rate control, $X_{RC,i}$, provides an excellent measure of the sensitivity of the overall reaction rate to the kinetic parameters for each step. The value of $X_{RC,i}$ approaches zero as step i becomes quasi-equilibrated, and the value of $X_{RC,i}$ becomes small as the previous steps that produce the reaction intermediates for step i become irreversible.

CLOSING REMARKS

In summary, DeDonder relations and Campbell's degree of rate control are complementary tools for analyzing reaction schemes; e.g., DeDonder relations have utility for deriving general principles of reaction kinetics for reaction schemes, and Campbell's degree of rate control provides a quantitative tool for computing the sensitivities of each step in a reaction scheme when values for all of the rate constants are available.

Research in heterogeneous catalysis is currently experiencing an explosion in the applications of combinatorial chemistry and high throughput screening methodologies toward the discovery of new catalysts. In combination with these data-based techniques, it is appropriate to employ knowledge-based techniques to guide the discovery process. For example, at some point in the research and development process, it becomes useful to supplement these experimental studies with quantitative analyses of the reaction kinetics to compare and/or extrapolate the performance of different catalytic materials at various reaction conditions. In this respect, analyses of reaction pathways on heterogeneous catalysts are facilitated by formulation of kinetic models of the surface chemistry, since these models can be used to consolidate reaction kinetics data collected using various reactants and products over a wide range of reaction conditions. The kinetic models serve to describe product distributions obtained from different reactants in terms of a limited number of kinetic parameters for various reaction pathways. This small set of kinetic parameters then becomes a surrogate for the more complex set of reaction kinetics data, providing a framework to compare quantitatively the performances of different catalysts at different reaction conditions.

In addition to advances in combinatorial chemistry and high throughput screening techniques, the reliability of initial guesses for parameters in kinetic models of catalytic surface chemistry has been significantly improved

by advances in quantum chemical techniques and density functional theory, which provide information about the geometries and energetics of chemical species interacting with catalytic sites consisting of clusters or periodic arrangements of atoms. These recent advances in computational techniques, combined with improved computer performance, make it possible to conduct quantum chemical calculations on more realistic models of active sites and on more complex reaction intermediates.

In view of the aforementioned advances in combinatorial chemistry and high throughput screening techniques, combined with advances in the speed and reliability of quantum chemical calculations, we suggest that research in heterogeneous catalysis will see a growth in the applications of reaction kinetics analyses to probe more realistic reaction schemes with better initial guesses for kinetic parameters. These analyses will be aided by the judicious use of DeDonder relations and Campbell's degree of rate control.

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