

# Analyses of Reaction Schemes Using De Donder Relations

J. A. Dumesic

*Department of Chemical Engineering, University of Wisconsin—Madison, Madison, Wisconsin 53706*

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The use of De Donder relations is addressed for analysis of reaction schemes to describe the kinetics of overall reactions. These relations provide a simple means of determining the number of kinetic parameters required to calculate the overall reaction rate. These 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. For surface reaction schemes, one additional kinetic parameter is required for each stable surface species that becomes abundant on the surface. De Donder relations offer a rigorous approach for assessing whether a reaction scheme contains a rate determining step, and they provide a convenient means of deriving a series of rate expressions for cases where specific steps are assumed to be rate determining. In addition, these 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.

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## INTRODUCTION

Studies of chemical kinetics typically involve analyses of reaction schemes, with the aim of describing the rate of the overall reaction in terms of contributions from individual elementary steps. In this respect, several issues become important. For example, how many kinetic parameters (e.g., preexponential factors and activation energies for elementary steps) are required in the most general case to calculate the overall rate from a reaction scheme? For the reaction conditions and kinetic parameters of interest, does the reaction scheme contain a rate determining step? In addition, with the rapid advances in the application of quantum-chemical techniques to identify the geometries, energetics and vibrational properties of transition states, we may add the following question: is it possible to determine whether a specific transition state may be involved in the overall reaction?

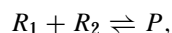
In the present note, we address the aforementioned issues by formulating the derivation of rate expressions from reaction schemes in terms of De Donder relations (1–5).

In addition, we show how the overall rates of gas-phase 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 we show that the overall rates are not controlled by the stabilities of the reaction intermediates. Finally, we show how De Donder relations may be used to derive a series of rate expressions from a reaction scheme for cases where specific steps are assumed to be rate determining.

We begin the analysis by considering an arbitrary gas-phase reaction. We then show how analysis of reaction schemes using De Donder relations can be generalized to include reactions on catalyst surfaces. The examples chosen in this respect are isobutene hydrogenation over Pt and ammonia synthesis over Fe catalysts.

## ARBITRARY GAS-PHASE REACTION

As our first general example, we consider the following arbitrary gas-phase reaction:



### OVERALL REACTION 1

which takes place according to a three-step reaction scheme,

1.  $R_1 \rightleftharpoons 2 I_1$
2.  $R_2 + I_1 \rightleftharpoons I_2$
3.  $I_1 + I_2 \rightleftharpoons P,$

### REACTION SCHEME 1

where  $R_1$  and  $R_2$  are reactants,  $P$  is the product, and  $I_1$  and  $I_2$  are reactive intermediates. We note that the energy transfer processes involved in these apparent unimolecular reactions are assumed to be quasi-equilibrated, such that these reactions can be written in their high-pressure limit. At lower pressures, step 1 would have to be written as a two-step process, involving the formation of an activated molecule through collision with another molecule (species  $M$ ), followed by reaction of the activated molecule to form two  $I_1$  species. In a similar fashion, steps 2 and 3 would have

to be written to include the participation of species  $M$  in the forward and reverse directions.

Holstein and Boudart (5) have recently shown how De Donder relations may be used to assess the consistency of reaction schemes containing closed cycles. In addition, Boudart has shown how De Donder relations may be used to illustrate the concept of kinetic coupling for the gas-phase chain reaction between  $H_2$  and  $Br_2$  to give  $HBr$  (6). The present example shows some of the advantages of using De Donder relations to analyze open cycles.

The steady state relations for reactive intermediates  $I_1$  and  $I_2$  are written in terms of the net rates,  $r_i$ , of the elementary steps as

$$\frac{dI_1}{dt} = 0 = 2r_1 - r_2 - r_3 \quad [1]$$

$$\frac{dI_2}{dt} = 0 = r_2 - r_3, \quad [2]$$

from which it follows that

$$r_1 = r_2 = r_3. \quad [3]$$

This result could have been written by inspection by noting that each of the stoichiometric coefficients for the three elementary steps is equal to unity, i.e., the overall reaction is equal to the simple sum of the three elementary steps in Scheme 1.

According to the De Donder relation, we write the net rate for elementary step  $i$  in terms of the forward rate of the step,  $r_i$ , and the affinity for the step,  $A_i$ ,

$$r_i = r_i \left[ 1 - \exp\left(\frac{-A_i}{RT}\right) \right], \quad [4]$$

where the affinity is equal to minus the change in the Gibbs free energy with respect to the extent of reaction (i.e., equal to the difference in the Gibbs free energies of the reactants and products of the elementary step at the reaction temperature and at the corresponding partial pressure for each reactant, product, and reaction intermediate). In general, the affinity,  $A_i$ , is expressed in terms of the standard state Gibbs free energies,  $G_j^\circ$ , and the activities,  $a_j$ , of the  $j$  reactants and products of the step,

$$A_i = - \sum_j v_{ij} G_j = - \sum_j v_{ij} [G_j^\circ + RT \ln(a_j)], \quad [5]$$

where  $v_{ij}$  are the stoichiometric coefficients for the  $j$  reactants and products of step  $i$ . This expression can be written in terms of the equilibrium constant for the step,  $K_{ieq}$ ,

$$\exp\left(\frac{-A_i}{RT}\right) = \frac{\prod_j a_j^{v_{ij}}}{K_{ieq}}, \quad [6]$$

since the equilibrium constant is determined by the change in the standard state Gibbs free energies:

$$K_{ieq} = \exp\left[\frac{-\sum_j v_{ij} G_j^\circ}{RT}\right]. \quad [7]$$

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

$$z_i = \exp\left(\frac{-A_i}{RT}\right) = \frac{\prod_j a_j^{v_{ij}}}{K_{ieq}}. \quad [8]$$

The value of  $z_i$  approaches zero as step  $i$  becomes irreversible and as  $z_i$  approaches unity as step  $i$  becomes quasi-equilibrated; therefore, this value of  $z_i$  may be termed the *reversibility* of step  $i$ . We note that the definition of the reversibility,  $z_i$ , in Eq. [8] is simply a transform of the affinity,  $A_i$ , in the De Donder relation for step  $i$ . We also note that the value of  $z_i$  remains bounded between 0 and 1 provided that step  $i$  proceeds in the forward direction. If step  $i$  changes direction, then the value of  $z_i$  becomes greater than 1. In such cases, it may be convenient to rewrite the step in the opposite direction so that the value of  $z_i$  remains less than 1.

For the three-step reaction scheme of this example, the values of  $z_i$  are equal to

$$z_1 = \frac{a_{I_1}^2}{K_{1eq} a_{R_1}} \quad [9]$$

$$z_2 = \frac{a_{I_2}}{K_{2eq} a_{R_2} a_{I_1}} \quad [10]$$

$$z_3 = \frac{a_P}{K_{3eq} a_{I_2} a_{I_1}}. \quad [11]$$

However, only two of these values are independent, because the product of the three values of  $z_i$  is controlled by the overall reversibility of the reaction,  $z_{total}$ ,

$$z_{total} = z_1 z_2 z_3 = \frac{a_P}{K_{eq} a_{R_1} a_{R_2}}, \quad [12]$$

where  $K_{eq}$  is the equilibrium constant for the overall reaction. This result follows from the relation that

$$A_{total} = A_1 + A_2 + A_3, \quad [13]$$

where  $A_{total}$  is the total change in affinity for the overall reaction, given by

$$A_{total} = -RT \ln\left[\frac{a_P}{K_{eq} a_{R_1} a_{R_2}}\right]. \quad [14]$$

The activities of intermediates  $I_1$  and  $I_2$  are now expressed in terms of  $z_i$  as

$$a_{I_1} = \sqrt{K_{1eq} a_{R_1} z_1} \quad [15]$$

$$a_{I_2} = \sqrt{K_{1eq} a_{R_1} z_1 K_{2eq} a_{R_2} z_2}, \quad [16]$$

and the net rates of the three reactions are given by

$$r_1 = k_1 a_{R_1} (1 - z_1) \quad [17]$$

$$r_2 = k_2 a_{R_2} a_{I_1} (1 - z_2) = \sqrt{K_{1eq}} k_2 a_{R_1}^{1/2} a_{R_2} z_1^{1/2} (1 - z_2) \quad [18]$$

$$r_3 = k_3 a_{I_1} a_{I_2} (1 - z_3) = K_{1eq} K_{2eq} k_3 a_{R_1} a_{R_2} z_1 z_2 \left(1 - \frac{z_{total}}{z_1 z_2}\right), \quad [19]$$

where  $k_i$  are the forward rate constants for the elementary reaction steps.

Finally, 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; i.e.,

$$\begin{aligned} k_1 a_{R_1} (1 - z_1) &= \sqrt{K_{1eq}} k_2 a_{R_1}^{1/2} a_{R_2} z_1^{1/2} (1 - z_2) \\ &= K_{1eq} K_{2eq} k_3 a_{R_1} a_{R_2} z_1 z_2 \left(1 - \frac{z_{total}}{z_1 z_2}\right). \end{aligned} \quad [20]$$

We may now address the issue of how many kinetic parameters are required in the most general case to calculate the overall rate from a reaction scheme. For the three-step reaction scheme of this example, we have three forward rate constants,  $k_i$ , and three reverse rate constants,  $k_{-i}$ . However, these rate constants must satisfy the overall equilibrium relation:

$$K_{eq} = \frac{k_1}{k_{-1}} \frac{k_2}{k_{-2}} \frac{k_3}{k_{-3}}. \quad [21]$$

Therefore, one may anticipate that five independent rate constants would be required to determine the overall rate of the reaction for the general case where no step is rate determining. However, the minimum number of kinetic parameters required to compute the rate for this three-step scheme is equal to 3, and these parameters,  $C_i$ , are

$$C_1 = k_1 \quad [22]$$

$$C_2 = \sqrt{K_{1eq}} k_2 \quad [23]$$

$$C_3 = K_{1eq} K_{2eq} k_3. \quad [24]$$

With values for these parameters, and from the known reaction conditions which specify  $a_{R_1}$ ,  $a_{R_2}$ ,  $a_P$ , and  $z_{total}$ , we may determine the unknown values of  $z_1$  and  $z_2$ .

It is useful to note the physical significance of the three  $C_i$  parameters. We use transition-state theory to express each rate constant  $k_i$  as

$$k_i = v^\ddagger K_i^\ddagger, \quad [25]$$

where  $v^\ddagger$  is a frequency factor (that may also include the standard state gas-phase concentration) and  $K_i^\ddagger$  is the equilibrium constant for the formation of the activated complex from the reactants of step  $i$ . We note that since conventional transition-state theory assumes quasi-equilibrium between

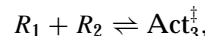
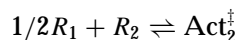
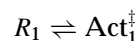
the reactants and the activated complex, this approach fails when the activation barrier is typically lower than  $5RT$  (e.g., 7, 8). In addition, this approach is not valid for situations where multiple crossings through the transition state take place or where quantum mechanical tunneling is important. In those common cases where transition-state theory is applicable, however, we may write the expressions for  $C_i$  as:

$$C_1 = v^\ddagger K_1^\ddagger \quad [26]$$

$$C_2 = v^\ddagger \sqrt{K_{1eq}} K_2^\ddagger \quad [27]$$

$$C_3 = v^\ddagger K_{1eq} K_{2eq} K_3^\ddagger. \quad [28]$$

We now note that a product of equilibrium constants for steps  $i$  can be expressed by a single equilibrium constant for an overall reaction that is a linear combination of these individual steps  $i$ . Therefore, it is apparent that  $C_1$ ,  $C_2$ , and  $C_3$  are controlled by the following lumped, quasi-equilibria:



#### TRANSITION STATE QUASI-EQUILIBRIA FOR SCHEME 1

where  $\text{Act}_1^\ddagger$ ,  $\text{Act}_2^\ddagger$ , and  $\text{Act}_3^\ddagger$  are the activated complexes for reactions 1, 2, and 3 of Scheme 1, respectively.

From the above equilibrium relations, we observe the important result that the rate of the overall reaction is controlled by quasi-equilibria between the reactants and/or products of the overall reaction with the activated complexes of the elementary steps. Importantly, the rate of the overall reaction is not controlled by the properties of the stable reactive intermediates,  $I_1$  and  $I_2$ .

The situation described above is illustrated in Fig. 1. This figure shows the Gibbs free energy changes,  $\Delta^\ddagger G_i^0$ , associated with the formation of the three activated complexes,  $\text{Act}_i^\ddagger$ , from the reactants and/or products of the overall reaction. To construct the plot in Fig. 1, we first determine the change in standard Gibbs free energies for each of the lumped, quasi-equilibria that describe the formation of activated complexes from reactants. For example, the value of  $\Delta^\ddagger G_2^0$  is given by

$$\Delta^\ddagger G_2^0 = G_{\text{act}_2}^0 - 0.5 G_{R_1}^0 - G_{R_2}^0, \quad [29]$$

where  $\text{act}_2$  refers to the second activated complex. We then note that the rate of step 2 is given by Eq. [18], which can

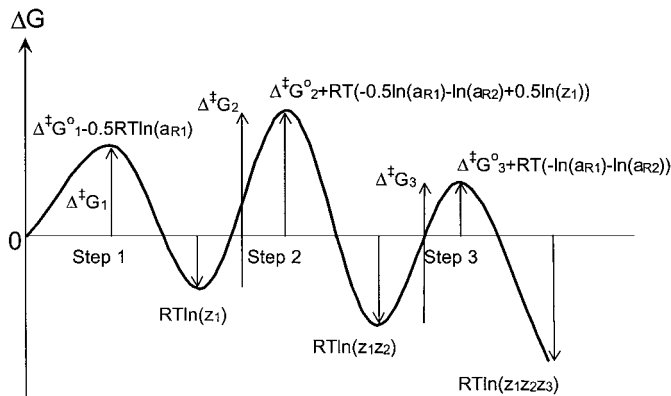


FIG. 1. Schematic representation of Gibbs free energy barriers for the elementary steps at particular reaction conditions. The highest barrier corresponds to the second activated complex, resulting in its kinetic parameters being the most sensitive for the rate of the overall reaction.

be written as

$$r_2 = v^\ddagger \exp \left[ \frac{-1}{RT} \left[ \Delta^\ddagger G_2^0 - \frac{1}{2} RT \ln(a_{R_1}) - RT \ln(a_{R_2}) - \frac{1}{2} RT \ln(z_1) \right] \right] (1 - z_2). \quad [30]$$

The value  $[\Delta^\ddagger G_2^0 - \frac{1}{2} RT \ln(a_{R_1}) - RT \ln(a_{R_2}) - \frac{1}{2} RT \ln(z_1)]$  corresponds to a Gibbs free energy barrier, and it is equal to the change in Gibbs free energy for the formation of the activated complex for the second step in its standard state, from the reactants  $R_1$  and  $R_2$  and the intermediate  $I_1$  at the reaction conditions. Since the Gibbs free energy decreases by  $RT \ln(z_1)$  after step 1, we note that the position of the maximum in the plot of Gibbs free energy versus reaction coordinate for step 2 is located at

$$\Delta^\ddagger G_2^0 - \frac{1}{2} RT \ln(a_{R_1}) - RT \ln(a_{R_2}) + \frac{1}{2} RT \ln(z_1). \quad [31]$$

After doing similar analyses for the first and third steps in Fig. 1, we find that the maxima for these steps in the plot of Gibbs free energy versus reaction coordinate are located at

$$\Delta^\ddagger G_1^0 - \frac{1}{2} RT \ln(a_{R_1}) \quad [32]$$

$$\Delta^\ddagger G_3^0 - RT \ln(a_{R_1}) - RT \ln(a_{R_2}). \quad [33]$$

The values of  $z_i$  are determined by solving the steady state equations, and the affinities for the three steps,  $A_i$ , are obtained from  $-RT \ln(z_i)$ . These affinities correspond to changes in the Gibbs free energies of the reactants and products of the elementary steps at the reaction conditions, e.g., at the reaction temperature and at the corresponding partial pressure for each reactant, product, and reaction intermediate. The rates of elementary steps are controlled

by their respective Gibbs free energy barriers. As indicated above, the rate of step 2 is controlled by a Gibbs free energy barrier,  $\Delta^\ddagger G_2$ , equal to  $\Delta^\ddagger G_2^0 - \frac{1}{2} RT \ln(a_{R_1}) - RT \ln(a_{R_2}) - \frac{1}{2} RT \ln(z_1)$ . We note that the  $(1 - z_i)$  terms in the rate expressions adjust the rates of the steps such that the net rates are equal at steady state. Thus, a step with a low Gibbs free energy barrier has a value of  $z_i$  that is near unity.

From Fig. 1 we observe that the formation of second activated complex has the highest Gibbs free energy barrier, which translates into a high sensitivity of the overall rate on the kinetic parameters for the formation of the second activated complex. A quantitative example of such a plot of Gibbs free energy is presented elsewhere for CO methanation on Ni(111) (9).

Having determined the values of  $z_i$  from the kinetic parameters  $C_i$  and the reaction conditions ( $a_i, z_{\text{total}}$ ), we may assess whether one of the steps is rate determining. In particular, a value of  $z_i$  near unity corresponds to an affinity near zero, and this situation indicates that step  $i$  is quasi-equilibrated. Therefore, a particular step  $j$  is rate determining if the value of  $z_j$  for that step is approximately equal to  $z_{\text{total}}$ , and all other values of  $z_i$  for the remaining steps are essentially equal to unity.

We may take advantage of this definition for the existence of a rate determining step to derive a series of rate expressions for the kinetics of the overall reaction for cases where specific steps are assumed to be rate determining. In particular, the rate of the overall reaction is calculated from the rate of the rate determining step by setting the value of  $z_j$  for this step equal to  $z_{\text{total}}$  and equating all other  $z_i$  terms to unity.

For example, if we assume that step 1 is rate determining, then the rate of the overall reaction,  $r_{\text{total}}$  is given by

$$r_{\text{total}, 1 \rightarrow \text{rds}} = k_1 a_{R_1} \left( 1 - \frac{a_P}{K_{\text{eq}} a_{R_1} a_{R_2}} \right). \quad [34]$$

The rate expression for the situation where step 2 is rate determining is

$$r_{\text{total}, 2 \rightarrow \text{rds}} = \sqrt{K_{1\text{eq}}} k_2 a_{R_1}^{1/2} a_{R_2} \left( 1 - \frac{a_P}{K_{\text{eq}} a_{R_1} a_{R_2}} \right). \quad [35]$$

The situation where step 3 is rate determining leads to the following rate expression:

$$r_{\text{total}, 3 \rightarrow \text{rds}} = K_{1\text{eq}} K_{2\text{eq}} k_3 a_{R_1} a_{R_2} \left( 1 - \frac{a_P}{K_{\text{eq}} a_{R_1} a_{R_2}} \right). \quad [36]$$

Next, we address whether it is possible to determine whether a specific transition state may be involved in the overall reaction. According to the above analyses, it is clear that the rate of any step  $i$  is given by

$$r_i = C_i F(a_1 \dots a_j) F(z_1 \dots z_k) (1 - z_i), \quad [37]$$

where  $a_j$  are the activities of the  $j$  reactants and products of the overall reaction,  $z_k$  are the values of  $z_k$  for the  $k$

elementary reactions, and  $C_i$  is controlled by a quasi-equilibrium relation between the reactants and/or products of the overall reaction with the particular activated complex under investigation. The maximum value of the rate  $r_i$  is found by equating all values of  $z_k$  to unity except  $z_i$  which is set equal to zero. This situation corresponds to the case where the activated complex is involved in an irreversible, rate determining step. As an example, the maximum rates of steps 1, 2, and 3 are

$$r_{1,\max} = C_1 a_{R_1} = v^\ddagger K_1^\ddagger a_{R_1} \quad [38]$$

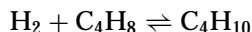
$$r_{2,\max} = C_2 a_{R_1}^{1/2} a_{R_2} = v^\ddagger \sqrt{K_{1\text{eq}}} K_2^\ddagger a_{R_1}^{1/2} a_{R_2} \quad [39]$$

$$r_{3,\max} = C_3 a_{R_1} a_{R_2} = v^\ddagger K_{1\text{eq}} K_{2\text{eq}} K_3^\ddagger a_{R_1} a_{R_2}. \quad [40]$$

Therefore, we can calculate the maximum rate at which a given transition state may contribute to the overall reaction by writing the appropriate quasi-equilibrium relation between the transition state and the reactants and/or products of the overall reaction. If this maximum rate is significantly lower than the observed overall rate, then the transition state does not participate in the overall reaction. On the other hand, if this maximum rate is higher than the observed overall rate, then the transition state may participate in the overall reaction. This maximum rate analysis provides a necessary, but not a sufficient, condition for assessing the participation in specific overall reactions of transition states identified by quantum-chemical calculations.

#### SURFACE REACTION: HYDROGENATION OF ISOBUTENE OVER Pt

We next consider the case of a reaction scheme for the hydrogenation of isobutene over a platinum catalyst (10).



#### OVERALL REACTION 2

This example shows the utility of De Donder relations for probing the kinetics of heterogeneous catalytic reactions. In this analysis we assume that the surface is uniform and follows Langmuirian kinetics. However, the principles developed here can be extended to nonuniform surfaces, for example, by allowing the kinetic parameters to depend on coverage.

A reaction scheme for isobutene hydrogenation is shown,

1.  $\text{H}_2 + 2^* \rightleftharpoons 2 \text{H}^*$
2.  $\text{C}_4\text{H}_8 + ^* \rightleftharpoons \text{C}_4\text{H}_8^*$
3.  $\text{C}_4\text{H}_8^* + \text{H}^* \rightleftharpoons \text{C}_4\text{H}_9^* + ^*$
4.  $\text{C}_4\text{H}_9^* + \text{H}^* \rightleftharpoons \text{C}_4\text{H}_{10} + 2^*$ ,

#### REACTION SCHEME 2

where \* represents a surface site. Steady state relations for surface species  $\text{H}^*$ ,  $\text{C}_4\text{H}_8^*$ , and  $\text{C}_4\text{H}_9^*$  indicate that the net rates of all reactions are equal.

The surface coverages by these species,  $\theta_i$ , can be expressed in terms of  $z_i$ , the equilibrium constants  $K_{i\text{eq}}$ , and the partial pressures of the reactants and products,  $P_i$ ,

$$\theta_{\text{H}} = \sqrt{K_{1\text{eq}} P_{\text{H}_2}} \sqrt{z_1} \theta_* \quad [41]$$

$$\theta_8 = K_{2\text{eq}} P_8 z_2 \theta_* \quad [42]$$

$$\theta_9 = \sqrt{K_{1\text{eq}} P_{\text{H}_2}} K_{2\text{eq}} P_8 K_{3\text{eq}} \sqrt{z_1 z_2 z_3} \theta_*, \quad [43]$$

where the subscripts 8 and 9 refer to  $\text{C}_4\text{H}_8$  and  $\text{C}_4\text{H}_9$ , respectively.

The value of the overall reversibility,  $z_{\text{total}}$ , is equal to

$$z_{\text{total}} = \frac{P_{10}}{K_{\text{eq}} P_{\text{H}_2} P_8}, \quad [44]$$

where  $P_{10}$  refers to the pressure of isobutane.

The rates of steps 1–4 are given by

$$r_1 = k_1 P_{\text{H}_2} \theta_*^2 (1 - z_1) \quad [45]$$

$$r_2 = k_2 P_8 \theta_* (1 - z_2) \quad [46]$$

$$r_3 = \sqrt{K_{1\text{eq}}} K_{2\text{eq}} k_3 P_{\text{H}_2}^{1/2} P_8 z_1^{1/2} z_2 \theta_*^2 (1 - z_3) \quad [47]$$

$$r_4 = K_{1\text{eq}} K_{2\text{eq}} K_{3\text{eq}} k_4 P_{\text{H}_2} P_8 z_1 z_2 z_3 \theta_*^2 \left( 1 - \frac{z_{\text{total}}}{z_1 z_2 z_3} \right). \quad [48]$$

The primary difference between these relations and those derived above for gas-phase reactions is the presence of  $\theta_*$  for the surface reactions. This fraction of the surface that is not covered by adsorbed species is given by a site balance:

$$\theta_* = 1 - \theta_{\text{H}} - \theta_8 - \theta_9. \quad [49]$$

Substitution of the relations for  $\theta_{\text{H}}$ ,  $\theta_8$ , and  $\theta_9$  into the site balance gives

$$\theta_* = \frac{1}{1 + \sqrt{K_{1\text{eq}} P_{\text{H}_2}} \sqrt{z_1} + K_{2\text{eq}} P_8 z_2 + \sqrt{K_{1\text{eq}} P_{\text{H}_2}} K_{2\text{eq}} P_8 K_{3\text{eq}} \sqrt{z_1 z_2 z_3}}. \quad [50]$$

It is important to note that this expression for  $\theta_*$  is given in terms of  $z_i$ , the equilibrium constants  $K_{i\text{eq}}$ , and the partial pressures of the reactants and products,  $P_i$ . Therefore, we may determine the unknown values of  $z_1$ ,  $z_2$ ,  $z_3$ , and  $\theta_*$  by solving the steady state relations that  $r_1 = r_2 = r_3 = r_4$  along with the site balance.

For this case, we see that the expressions for  $r_1$  through  $r_4$  are controlled by the following four kinetic

parameters,  $C_i$ :

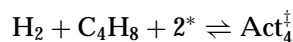
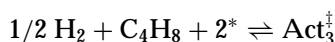
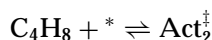
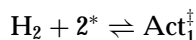
$$C_1 = k_1 \quad [51]$$

$$C_2 = k_2 \quad [52]$$

$$C_3 = \sqrt{K_{1\text{eq}}} K_{2\text{eq}} k_3 \quad [53]$$

$$C_4 = K_{1\text{eq}} K_{2\text{eq}} K_{3\text{eq}} k_4 \quad [54]$$

These kinetic parameters,  $C_1$  through  $C_4$ , are controlled by the four following lumped quasi-equilibria.



#### TRANSITION STATE QUASI-EQUILIBRIA FOR SCHEME 2

As we showed for gas-phase reactions, the four kinetic parameters  $C_1$  through  $C_4$  are determined by quasi-equilibria between the reactants and/or products of the overall reaction with the transition states. In this case for a surface reaction scheme, however, the overall reaction rate is also controlled by the value of  $\theta^*$ , which contains equilibrium constants for abundant surface species. This expression for  $\theta^*$ , therefore, introduces one additional kinetic parameter for each stable surface species that becomes abundant on the surface (and thus blocks surface sites). Accordingly, the overall reaction rate is controlled by four kinetic parameters ( $C_1$  through  $C_4$ ) plus one additional kinetic parameter for each stable surface species that becomes abundant on the surface.

We now derive a series of rate expressions corresponding to cases where each of the steps in the reaction scheme is assumed sequentially to be rate determining. As above, we set the value of  $z_i$  for the rate determining step equal to  $z_{\text{total}}$  and equate all other  $z_i$  terms to unity. If we assume that step 1 is rate determining, then the rate of the overall reaction,  $r_{\text{total}}$ , is equal to

$$r_{\text{total},1 \rightarrow \text{rds}} = \frac{k_1 P_{\text{H}_2} \left(1 - \frac{P_{10}}{P_{\text{H}_2} P_8 K_{\text{eq}}}\right)}{\left[1 + \sqrt{\frac{P_{10}}{K_{2\text{eq}} K_{3\text{eq}} K_{4\text{eq}} P_8}} + K_{2\text{eq}} P_8 + \sqrt{\frac{K_{2\text{eq}} K_{3\text{eq}} P_8 P_{10}}{K_{4\text{eq}}}}\right]^2}, \quad [55]$$

where we have used the result that

$$K_{\text{eq}} = K_{1\text{eq}} K_{2\text{eq}} K_{3\text{eq}} K_{4\text{eq}}. \quad [56]$$

If step 2 is rate determining, then

$$r_{\text{total},2 \rightarrow \text{rds}} = \frac{k_2 P_8 \left(1 - \frac{P_{10}}{P_{\text{H}_2} P_8 K_{\text{eq}}}\right)}{\left[1 + \sqrt{K_{1\text{eq}} P_{\text{H}_2}} + \frac{P_{10}}{P_{\text{H}_2} K_{1\text{eq}} K_{3\text{eq}} K_{4\text{eq}}} + \frac{P_{10}}{\sqrt{K_{1\text{eq}} P_{\text{H}_2} K_{4\text{eq}}}}\right]^2}. \quad [57]$$

The case where step 3 is rate determining leads to

$$r_{\text{total},3 \rightarrow \text{rds}} = \frac{\sqrt{K_{1\text{eq}}} K_{2\text{eq}} k_3 P_{\text{H}_2}^{1/2} P_8 \left(1 - \frac{P_{10}}{P_{\text{H}_2} P_8 K_{\text{eq}}}\right)}{\left[1 + \sqrt{K_{1\text{eq}} P_{\text{H}_2}} + K_{2\text{eq}} P_8 + \frac{P_{10}}{\sqrt{K_{1\text{eq}} P_{\text{H}_2} K_{4\text{eq}}}}\right]^2}. \quad [58]$$

Finally, if step 4 is the rate determining process,

$$r_{\text{total},4 \rightarrow \text{rds}} = \frac{K_{1\text{eq}} K_{2\text{eq}} K_{3\text{eq}} k_4 P_{\text{H}_2} P_8 \left(1 - \frac{P_{10}}{P_{\text{H}_2} P_8 K_{\text{eq}}}\right)}{\left[1 + \sqrt{K_{1\text{eq}} P_{\text{H}_2}} + K_{2\text{eq}} P_8 + \sqrt{K_{1\text{eq}} P_{\text{H}_2} K_{2\text{eq}} K_{3\text{eq}} P_8}\right]^2}. \quad [59]$$

We note that the rate expressions in Eqs. [55], [57], [58], and [59] are, in fact, traditional Langmuir–Hinshelwood relations. The advantage of using De Donder relations in these analyses is that this approach provides a convenient means of deriving Langmuir–Hinshelwood relations from the more general case where multiple steps are not in quasi-equilibrium.

Table 1 presents kinetic parameters that have been reported from experimental studies of isobutane dehydrogenation and isobutene hydrogenation over Pt catalysts (10). These studies involved measurements of overall reaction rates at steady state, isotopic tracing measurements collected with mixtures of  $\text{C}_4\text{H}_{10}$  and  $\text{D}_2$ , and microcalorimetric measurements of heats of adsorption of isobutene and  $\text{H}_2$  over Pt catalysts.

As an example of typical reaction conditions for isobutene hydrogenation, we consider the case where the

TABLE 1  
Kinetic Parameters for Isobutene Hydrogenation  
over Pt (Scheme 2) (10)

| Step | $A_{\text{for}}^a$    | $A_{\text{rev}}^a$    | $E_{\text{for}}^b$ | $E_{\text{rev}}^b$ |
|------|-----------------------|-----------------------|--------------------|--------------------|
| 1    | $6.30 \times 10^5$    | $4.50 \times 10^{10}$ | 0.0                | 78.0               |
| 2    | $3.00 \times 10^4$    | $1.10 \times 10^{12}$ | 0.0                | 118.0              |
| 3    | $1.90 \times 10^9$    | $7.60 \times 10^{11}$ | 71.9               | 41.6               |
| 4    | $1.30 \times 10^{12}$ | $2.90 \times 10^4$    | 85.0               | 41.6               |

<sup>a</sup> Forward and reverse preexponential factors,  $A_{\text{for}}$  and  $A_{\text{rev}}$ , respectively, in units of  $\text{atm}^{-1} \text{s}^{-1}$  for adsorption steps and  $\text{s}^{-1}$  for desorption and surface reaction steps.

<sup>b</sup> Forward and reverse activation energies,  $E_{\text{for}}$  and  $E_{\text{rev}}$ , in units of kJ/mol.

reaction temperature is 673 K, and the partial pressures of  $H_2$ ,  $C_4H_8$ , and  $C_4H_{10}$  are 0.6, 0.2, and 0.2 atm, respectively. For these conditions, the values of  $z_i$  can be determined to be

$$z_1 = 0.9993$$

$$z_2 = 0.9962$$

$$z_3 = 0.9977$$

$$z_4 = 0.0125$$

$$z_{\text{total}} = 0.0124$$

and the corresponding values of  $A_i$  are equal to

$$A_1 = 0.004 \text{ kJ/mol}$$

$$A_2 = 0.021 \text{ kJ/mol}$$

$$A_3 = 0.013 \text{ kJ/mol}$$

$$A_4 = 24.52 \text{ kJ/mol}$$

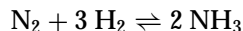
$$A_{\text{total}} = 24.56 \text{ kJ/mol.}$$

The fraction of the Pt surface that is free of adsorbed species,  $\theta^*$ , is equal to 0.084 for these conditions. The most abundant surface intermediates are adsorbed  $H^*$  and  $C_4H_8^*$ , indicating that the only kinetic parameters in the expression for  $\theta^*$  that are significant are  $K_{1\text{eq}}$  and  $K_{2\text{eq}}$ .

It is clear from these values of  $z_i$  that steps 1, 2, and 3 are quasi-equilibrated ( $z_i \sim 1$  or  $A_i \sim 0$ ) and step 4 is rate determining ( $z_4 \sim z_{\text{tot}}$  or  $A_4 \sim z_{\text{total}}$ ) for these reaction conditions.

### SURFACE REACTION: AMMONIA SYNTHESIS OVER Fe

We next consider the synthesis of ammonia over an iron catalyst (11).



#### OVERALL REACTION 3

The reaction scheme for this reaction can be written as

1.  $N_2 + 2^* \rightleftharpoons 2 N^*$
2.  $H_2 + 2^* \rightleftharpoons 2 H^*$
3.  $N^* + H^* \rightleftharpoons NH^* + ^*$
4.  $NH^* + H^* \rightleftharpoons NH_2^* + ^*$
5.  $NH_2^* + H^* \rightleftharpoons NH_3^* + ^*$
6.  $NH_3^* \rightleftharpoons NH_3 + ^*$ ,

#### REACTION SCHEME 3

where  $^*$  represents a vacant surface site and  $N^*$ ,  $H^*$ , and  $NH_x^*$  represent surface adsorbed species. This reaction il-

lustrates the case where the stoichiometric numbers of the elementary steps are not all equal, i.e., the stoichiometric numbers for steps 1–6 are equal to 1, 3, 2, 2, 2, and 2, respectively.

The net rates of the 6 elementary steps are equal to

$$r_1 = k_1 P_{N_2} \theta_*^2 - k_{-1} \theta_N^2 \quad [60]$$

$$r_2 = k_2 P_{H_2} \theta_*^2 - k_{-2} \theta_H^2 \quad [61]$$

$$r_3 = k_3 \theta_N \theta_H - k_{-3} \theta_{NH} \theta_* \quad [62]$$

$$r_4 = k_4 \theta_{NH} \theta_H - k_{-4} \theta_{NH_2} \theta_* \quad [63]$$

$$r_5 = k_5 \theta_{NH_2} \theta_H - k_{-5} \theta_{NH_3} \theta_* \quad [64]$$

$$r_6 = k_6 \theta_{NH_3} - k_{-6} P_{NH_3} \theta_* \quad [65]$$

The steady state equations take the form

$$r_1 = \frac{1}{3} r_2 = \frac{1}{2} r_3 = \frac{1}{2} r_4 = \frac{1}{2} r_5 = \frac{1}{2} r_6 \quad [66]$$

and the site balance is

$$1 = \theta_* + \theta_N + \theta_H + \theta_{NH} + \theta_{NH_2} + \theta_{NH_3} \quad [67]$$

We now write expressions for all surface coverages in terms of the values of  $z_i$  for the steps of the reaction scheme, and these expressions are solved for individual surface coverages in terms of the values of  $z_i$  and  $\theta^*$ :

$$\theta_N = \sqrt{K_{1\text{eq}} P_{N_2}} \sqrt{z_1} \theta_* \quad [68]$$

$$\theta_H = \sqrt{K_{2\text{eq}} P_{H_2}} \sqrt{z_2} \theta_* \quad [69]$$

$$\theta_{NH} = \sqrt{K_{1\text{eq}} P_{N_2}} \sqrt{K_{2\text{eq}} P_{H_2}} K_{3\text{eq}} \sqrt{z_1 z_2 z_3} \theta_* \quad [70]$$

$$\theta_{NH_2} = \sqrt{K_{1\text{eq}} P_{N_2}} K_{2\text{eq}} P_{H_2} K_{3\text{eq}} K_{4\text{eq}} \sqrt{z_1 z_2 z_3 z_4} \theta_* \quad [71]$$

$$\theta_{NH_3} = \frac{P_{NH_3}}{K_{6\text{eq}} z_6} \theta_* \quad [72]$$

The following relation holds for the overall reversibility,  $z_{\text{total}}$ :

$$z_{\text{total}} = \frac{P_{NH_3}^2}{K_{\text{eq}} P_{N_2} P_{H_2}^3} = z_1 z_2^3 z_3^2 z_4^2 z_5^2 z_6^2 \quad [73]$$

The site balance is used to express  $\theta^*$  in terms of the values of  $z_i$ :

$$\begin{aligned} \theta_*^{-1} = & 1 + \sqrt{K_{1\text{eq}} P_{N_2}} \sqrt{z_1} + \sqrt{K_{2\text{eq}} P_{H_2}} \sqrt{z_2} + \frac{P_{NH_3}}{z_6 K_{6\text{eq}}} \\ & + \sqrt{K_{1\text{eq}} P_{N_2}} \sqrt{K_{2\text{eq}} P_{H_2}} K_{3\text{eq}} \sqrt{z_1 z_2 z_3} \\ & + \sqrt{K_{1\text{eq}} P_{N_2}} K_{2\text{eq}} P_{H_2} K_{3\text{eq}} K_{4\text{eq}} \sqrt{z_1 z_2 z_3 z_4} \end{aligned} \quad [74]$$

Next, we may write expressions for the net rates of all steps in terms of the values of  $z_i$ :

$$r_1 = k_1 P_{N_2} \theta_*^2 [1 - z_1] \quad [75]$$

$$r_2 = k_2 P_{H_2} \theta_*^2 [1 - z_2] \quad [76]$$

$$r_3 = k_3 \sqrt{K_{1eq} P_{N_2}} \sqrt{K_{2eq} P_{H_2}} \sqrt{z_1 z_2} \theta_*^2 [1 - z_3] \quad [77]$$

$$r_4 = k_4 \sqrt{K_{1eq} P_{N_2}} K_{2eq} P_{H_2} K_{3eq} \sqrt{z_1 z_2 z_3} \theta_*^2 [1 - z_4] \quad [78]$$

$$r_5 = k_5 \sqrt{K_{1eq} P_{N_2}} (K_{2eq} P_{H_2})^{3/2} \times K_{3eq} K_{4eq} \sqrt{z_1 z_2} z_3 z_4 \theta_*^2 [1 - z_5] \quad [79]$$

$$r_6 = k_6 \frac{P_{NH_3}}{z_6 K_{6eq}} \theta_* [1 - z_6]. \quad [80]$$

In general, the steady state rate of the overall reaction is determined by solving for the 7 unknown values  $z_1$  through  $z_6$  and  $\theta^*$  from the steady state relations, the site balance, and the expression for  $z_{total}$ . We now consider the case where step 1 is rate determining, and therefore, all other steps are quasi-equilibrated. According to this assumption, we write

$$z_1 = z_{total} = \frac{P_{NH_3}^2}{K_{eq} P_{N_2} P_{H_2}^3} \quad [81]$$

and all other values of  $z_i$  are equal to unity. The rate expression for the overall reaction is equal to the rate of step 1, which is given by the following expression:

$$r_{1 \rightarrow rds} = r_1 = k_1 P_{N_2} \theta_*^2 [1 - z_1] = k_1 P_{N_2} \theta_*^2 \left( 1 - \frac{P_{NH_3}^2}{K_{eq} P_{N_2} P_{H_2}^3} \right), \quad [82]$$

where  $\theta^*$  is equal to:

$$\begin{aligned} \theta_*^{-1} = 1 + & \sqrt{\frac{K_{1eq}}{K_{eq} P_{H_2}^3}} P_{NH_3} + \sqrt{K_{2eq} P_{H_2}} \\ & + \frac{P_{NH_3}}{K_{6eq}} + \sqrt{\frac{K_{1eq} K_{2eq}}{K_{eq}}} K_{3eq} \frac{P_{NH_3}}{P_{H_2}} \\ & + \sqrt{\frac{K_{1eq}}{K_{eq}}} K_{2eq} K_{3eq} K_{4eq} \frac{P_{H_2} P_{NH_3}}{P_{H_2}^{1/2}}. \end{aligned} \quad [83]$$

Next, we consider the case where step 3 is rate determining, and therefore, all other steps are quasi-equilibrated. The value of  $z_i$  for the rate determining step is equal to

$$z_3 = z_{total}^{1/2} = \frac{P_{NH_3}}{\sqrt{K_{eq} P_{N_2} P_{H_2}^3}} \quad [84]$$

and all other values of  $z_i$  are equal to unity. The rate expression for the overall reaction is equal to the rate of step

3 divided by 2, which is given by the expression

$$\begin{aligned} r_{3 \rightarrow rds} = \frac{r_3}{2} = & \frac{k_3}{2} \sqrt{K_{1eq} K_{2eq}} \sqrt{P_{N_2} P_{H_2}} \theta_*^2 \\ & \times \left[ 1 - \frac{P_{NH_3}}{\sqrt{K_{eq} P_{N_2} P_{H_2}^3}} \right], \end{aligned} \quad [85]$$

where  $\theta^*$  is equal to

$$\begin{aligned} \theta_*^{-1} = 1 + & \sqrt{K_{1eq} P_{N_2}} + \sqrt{K_{2eq} P_{H_2}} + \frac{P_{NH_3}}{K_{6eq}} \\ & + \sqrt{\frac{K_{1eq} K_{2eq}}{K_{eq}}} K_{3eq} \frac{P_{NH_3}}{P_{H_2}} \\ & + \sqrt{\frac{K_{1eq}}{K_{eq}}} K_{2eq} K_{3eq} K_{4eq} \frac{P_{NH_3}}{\sqrt{P_{H_2}}} \end{aligned} \quad [86]$$

We now address the situation where steps 1 and 3 are reversible but not quasi-equilibrated, while all other steps are quasi-equilibrated. The values of  $z_1$  and  $z_3$  are related by

$$z_1 z_3^2 = z_{total} = \frac{P_{NH_3}^2}{K_{eq} P_{N_2} P_{H_2}^3} \quad [87]$$

and all remaining values of  $z_i$  are equal to unity. At steady state, the net rate of step 1 is equal to half the net rate for step 3, and we obtain the following expression after eliminating the value of  $z_3$  using Eq. [87]:

$$k_1 P_{N_2} [1 - z_1] = \frac{k_3}{2} \sqrt{K_{1eq} P_{N_2}} \sqrt{K_{2eq} P_{H_2}} [\sqrt{z_1} - \sqrt{z_{total}}]. \quad [88]$$

This steady state relation can be written as

$$(1 - z_1) = F_1 (\sqrt{z_1} - \sqrt{z_{total}}), \quad [89]$$

where  $F_1$  is defined as

$$F_1 = \frac{k_3 \sqrt{K_{1eq} K_{2eq} P_{H_2}}}{2k_1 \sqrt{P_{N_2}}}. \quad [90]$$

Solution of the steady state equation gives

$$\sqrt{z_1} = \frac{1}{2} [-F_1 + \sqrt{4 + F_1^2 + 4F_1 \sqrt{z_{total}}}], \quad [91]$$

We use this result for  $z_1$  to determine the value for  $z_3$ ; and we then evaluate  $\theta^*$  and determine the overall rate expression from either  $r_1$  or  $r_3$ .

Table 2 presents kinetic parameters that have been reported from experimental studies of ammonia synthesis over Fe catalysts (11). These studies involved, for example, measurements of  $N_2$  sticking coefficients, as well as various TPD and spectroscopic studies of iron single crystal surfaces.



TABLE 2  
Kinetic Parameters for Ammonia Synthesis  
over Fe (Scheme 3) (11)

| Step           | $A_{\text{for}}^a$    | $A_{\text{rev}}^a$    | $E_{\text{for}}^b$ | $E_{\text{rev}}^b$ |
|----------------|-----------------------|-----------------------|--------------------|--------------------|
| 1 <sup>c</sup> | $5.80 \times 10^1$    | $1.32 \times 10^9$    | -14.6              | 154.8              |
| 2              | $7.01 \times 10^6$    | $3.24 \times 10^{13}$ | 0.0                | 93.7               |
| 3              | $1.83 \times 10^9$    | $1.15 \times 10^7$    | 81.2               | 23.0               |
| 4              | $1.31 \times 10^{13}$ | $1.38 \times 10^{12}$ | 36.4               | 0.0                |
| 5              | $3.88 \times 10^{13}$ | $2.33 \times 10^{13}$ | 38.5               | 0.0                |
| 6              | $3.67 \times 10^{12}$ | $1.81 \times 10^8$    | 39.3               | 0.0                |

<sup>a</sup> Forward and reverse preexponential factors,  $A_{\text{for}}$  and  $A_{\text{rev}}$ , in units of  $\text{atm}^{-1} \text{s}^{-1}$  for adsorption steps and  $\text{s}^{-1}$  for desorption and surface reaction steps.

<sup>b</sup> Forward and reverse activation energies,  $E_{\text{for}}$  and  $E_{\text{rev}}$ , in units of kJ/mol.

<sup>c</sup> Kinetic parameters for the forward direction of step 1 include contributions from a weakly adsorbed, molecular precursor species.

As an example of typical reaction conditions for ammonia synthesis in laboratory reactors, we consider the case where the reaction temperature is 723 K, and the partial pressures of  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{NH}_3$  are 0.75, 0.25, and 0.116 atm, respectively (corresponding to approximately 50% of the equilibrium conversion at this temperature). For these conditions, the values of  $z_i$  can be determined to be

$$z_1 = 0.2508$$

$$z_2 = 0.9993$$

$$z_3 = 0.99854$$

$$z_4 = 1.000$$

$$z_5 = 1.000$$

$$z_6 = 0.9998$$

$$z_{\text{total}} = 0.2500$$

and the corresponding values of  $A_i$  are equal to

$$A_1 = 8.315 \text{ kJ/mol}$$

$$A_2 = 4 \times 10^{-4} \text{ kJ/mol}$$

$$A_3 = 0.0088 \text{ kJ/mol}$$

$$A_4 = 7 \times 10^{-8} \text{ kJ/mol}$$

$$A_5 = 1 \times 10^{-6} \text{ kJ/mol}$$

$$A_6 = 1 \times 10^{-4} \text{ kJ/mol}$$

$$A_{\text{total}} = 8.335 \text{ kJ/mol}$$

The fraction of the Fe surface that is free of adsorbed species,  $\theta^*$ , is equal to 0.014 for these conditions. The most abundant surface intermediate is adsorbed  $\text{N}^*$ , indicating

that the only kinetic parameter in the expression for  $\theta^*$  that is significant is  $K_{1\text{eq}}$ .

It is clear from these values of  $z_i$  that steps 2–6 are quasi-equilibrated ( $z_i \sim 1$  or  $A_i \sim 0$ ) and step 1 is rate determining ( $z_1 \sim z_{\text{tot}}$  or  $A_1 = A_{\text{total}}$ ) for these reaction conditions.

## CONCLUSIONS

We have shown that De Donder relations provide a simple means of determining the number of kinetic parameters required to calculate the overall reaction rate from a reaction scheme. De Donder analyses thereby provide a useful starting point for conducting sensitivity analyses of kinetic parameters in fitting reaction kinetics data. We have shown that the kinetic parameters identified by De Donder analyses 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. For surface reaction schemes, one additional kinetic parameter is required for each stable surface species that becomes abundant on the surface. Therefore, results from spectroscopic and/or theoretical studies of the reaction intermediates are necessary to determine kinetic parameters that control the surface coverages of stable surface species that become abundant on the surface.

As stressed by Boudart (6), De Donder relations offer a rigorous approach for assessing whether a reaction scheme contains a rate determining step. We have also shown that these relations provide a convenient means to derive a series of rate expressions for cases where specific steps are assumed to be rate determining. Importantly, we have shown that De Donder 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. We believe that this application of De Donder relations will be particularly useful in the future as the quantum-chemical calculations become used more extensively in catalysis research.

## ACKNOWLEDGMENTS

We thank Professor Boudart for suggesting that we use De Donder relations to identify rate determining steps in reaction schemes. More generally, we thank Professor Boudart for his continued efforts in addressing the advantages as well as the limitations of using reaction schemes of elementary steps to analyze experimental observations, including reaction kinetics data. We also thank Randy Cortright and Ram Watwe for many discussions on these topics, and we thank Thatcher Root and Manuel Natal-Santiago for critical reading of the manuscript. In addition, we thank Ram Watwe for his contributions to the concepts contained in Fig. 1.

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