

LETTER TO THE EDITOR

Finding the Rate-Determining Step in a Mechanism

Comparing DeDonder Relations with the “Degree of Rate Control”

In a recent paper (J. A. Dumesic, *J. Catal.* **185**, 496 (1999)), Dumesic argued that “DeDonder relations offer a rigorous approach for assessing whether a reaction scheme contains a rate determining step.” Here, we argue that, while analysis with DeDonder relations is a very powerful approach that has many advantages, it has a limitation with respect to finding the rate determining step, and another method, previously proposed by this author (C. T. Campbell, *Topics Catal.* **1**, 353 (1994)) involving the “degree of rate control,” is preferable in that particular respect. An approach for extending this latter method to transient kinetic conditions is also suggested. © 2001 Elsevier Science

I. INTRODUCTION

The “rate-determining step” (RDS) is a very common concept in discussing the kinetics of reaction mechanisms and is one frequently treated in papers and textbooks on this subject (1–13). Nevertheless, the definition of the RDS and how one determines which step it is in a complex mechanism are still subject to some controversy (1, 2, 7, 10, 13). Prescriptions for defining the rate determining step have been discussed on numerous occasions (1, 2, 7, 10, 13). Most recently, Dumesic has defined it on the basis of the DeDonder relation for the affinities of elementary steps (1). It is shown here that this definition is not as general as that offered previously by Campbell on the basis of his concept called the degree of rate control of elementary steps (2). The *degree of rate control* of a step, as mathematically defined by Campbell (2), is useful in kinetic modeling, and in putting terms such as *rate-controlling step* and *rate-limiting step* into a more rigorous framework. It includes essential information about the activation free-energy barrier for the RDS ignored by Dumesic’s method for finding the rate determining step (which involves only the thermodynamic driving force).

II. DUMESIC’S METHOD FOR SPECIFYING THE RATE DETERMINING STEP INVOLVING DEDONDER AFFINITIES (FROM (1))

The net rate for an elementary step i , r_i , is defined as its forward rate, \mathbf{r}_i , minus its reverse rate. The affinity for

step i is simply its thermodynamic driving force, i.e., the difference in Gibbs free energies of the reactants minus that for the products

$$A_i = -\sum_j (v_{ij} \cdot \mu_j), \quad [1]$$

where v_{ij} is the stoichiometric coefficient for species j in step i (negative for reactants and positive for products), μ_j is the chemical potential of species j , and the sum is over all species j involved in that step as reactants or products. The affinity of i therefore can be expressed also in terms of the activities of the species present in the reaction mixture

$$A_i = -RT \cdot \ln \left\{ \left[\prod_j (a_j^{v_{ij}}) \right] / K_{\text{eq},i} \right\}, \quad [2]$$

where a_j is the activity of species j (related closely to its concentration), $K_{\text{eq},i}$ is the equilibrium constant for step i , and the product runs over all species j involved in step i as reactants or products. Dumesic defined the *reversibility* of step i , z_i , as

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

Note that z_i equals zero when there are not yet any products for step i , and it approaches unity as that reaction step approaches equilibrium. Dumesic also defined the overall reversibility of the net (overall) reaction, z_{total} , as

$$z_{\text{total}} = \left[\prod_j (a_j^{v_j}) \right] / K_{\text{eq}}, \quad [4]$$

where K_{eq} is the equilibrium product for the overall reaction and the product runs over the products and reactants of the overall reaction.

According to the DeDonder relation, we may write the net rate of step i in terms of its forward rate and the affinity for step i

$$r_i = \mathbf{r}_i \cdot [1 - \exp(-A_i/RT)]. \quad [5]$$

Dumesic (1) defined the existence of a rate determining step by saying that “a particular step m is rate determining if the value of z_m is approximately equal to z_{total} , and all other values of z_j for the remaining steps are essentially equal to unity.” He further showed beautifully that this is quite a useful definition that can be applied to advantage in many circumstances to analyze reaction schemes. We argue, however, that this way of finding the rate determining step is too limiting in that the reversibility of a step addresses only its thermodynamic driving force, and in no way contains information about the activation barrier involved. One must in some way include these essential kinetic details in a definition of the rate determining step if one wishes to locate the overall reaction’s bottleneck step in a completely general way for complex reaction mechanisms. We further argue that one can learn the location of a bottleneck in any complex reaction with an analysis that compares the “degree of rate control” of the elementary steps, which is like performing a sensitivity analysis to learn which elementary rate constant(s) most sensitively influence the overall reaction’s rate.

We emphasize that this minor limitation of Dumesic’s method for reaction analysis in no way should detract from the many, very powerful tools it provides in understanding and simplifying kinetics. It is a method that should be embraced, as it can be utilized to great advantage.

III. CAMPBELL’S METHOD FOR SPECIFYING THE RATE DETERMINING STEP INVOLVING THE DEGREE OF RATE CONTROL

Frequently in analyzing the kinetics of a complex reaction mechanism, one would like to evaluate the extent or degree to which a particular step controls the overall reaction rate. Campbell (2) pointed out that this can be easily done within a kinetic model using a type of sensitivity analysis, by simply increasing both the forward and reverse rate constants for that step by 1% (thus not changing its equilibrium constant), and calculating the resulting fractional increase in the overall rate. The step whose increase leads to the greatest increase in overall rate, R , is then the most rate-controlling. The degree to which a step controls the overall rate is just the percentage increase in the overall rate divided by this 1%. To be more rigorous, one must take the limit of this ratio as this 1% change shrinks to zero. To put this concept on a more rigorous, differential calculus basis, Campbell (2) defined the degree at rate control for step i , $X_{\text{rc},i}$, as

$$X_{\text{rc},i} = (k_i/R) \cdot (\delta R/\delta k_i), \quad [6]$$

where the partial derivative, $\delta R/\delta k_i$, is taken holding constant the equilibrium constant for step i and the rate constants k_j for all other steps j . Here, keeping $K_{\text{eq},i}$ constant just means that the rate constant for the reverse

of step i must also be changed when taking this derivative (i.e., $\delta k_i/k_i = \delta k_{-i}/k_{-i}$). Note that the partial derivative in this expression can easily be calculated from an analytical expression for the net rate R involving the various elementary steps’ equilibrium constants and rate constants, if such an expression is available or can be derived from the mechanism under study. Much more importantly in the modern computer age, it can also be calculated by numerical methods if no analytical expression can be derived, simply by changing the values for both of the parameters k_i and k_{-i} by a small amount (e.g., by +1%, for which $\delta k_i/k_i = 0.01$) and seeing how much this affects the net rate R established at steady state ($\delta R/R$). The steady-state rate can be solved by any computerized solution to the series of differential equations defined by the elementary-step rate equations and initial conditions (e.g., by finite-difference methods). The reader who has dealt with such computer simulations will recognize that the complexity of interconnected reactions that can be dealt with in this way is almost limitless. Care should be taken, of course, to ensure that the change in k_i is small enough that the response in R is linear, yet not so small that the response is computationally inaccurate or imprecise.

Campbell (2) further suggested a new definition for rate-determining step as that step m in a mechanism which has a degree of rate control ($X_{\text{rc},m}$) equal to unity. This definition gives the same RDS as that obtained by the definition of RDS proposed by Dumesic for all the example mechanisms considered by Dumesic in (1). Furthermore, this definition gives the same RDS as that obtained by the definition of RDS proposed by Boudart and Tamaru for all the example mechanisms considered by Boudart and Tamaru in (7). For all those mechanisms considered by both Boudart and Tamaru (7) and Dumesic (1), where there was a single RDS, the degree of rate control for that step is found to be 1.0, and it is zero for all other steps. Campbell postulated that this is generally true (2), and we show further evidence that suggests it is true below.

Note that an analytical expression for the rate equation for the overall reaction is needed in the Boudart/Tamaru definition of the RDS but not in Campbell’s definition. Campbell’s definition is easy to apply in complex reactions, where computer modeling is necessary and analytical expressions for the overall rate equation may not be available.

Campbell proposed (2) that a *rate-controlling step* or *slow step* be defined as any step i with a non-zero $X_{\text{rc},i}$. There can be more than one rate-controlling step in certain mechanisms. He further proposed that steps where the degree of rate control is positive be called *rate-limiting steps*. This definition clearly identifies steps where an increase in rate constant would be beneficial, and where catalyst improvement would be effective. Of course, there can be more than one rate-limiting step in certain mechanisms, and some steps will be more rate-limiting than others (those with larger

X_{rc}). He proposed that steps where the degree of rate control is negative be called *inhibition steps*. The degree of rate control should be a useful concept in catalyst design, and in evaluating how closely reaction conditions approach a situation where there is a single RDS. A step would, for example, be nearly rate determining if its X_{rc} value were between 0.6 and 1.0. We propose a practical limit for X_{rc} of 0.95, above which a step is considered to be the rate determining step, since a value of exactly unity is only achieved in limiting cases not realizable in the laboratory.

The value of Campbell's concept of the degree of rate control has been demonstrated by Baranski (10) in three selected example mechanisms (a) a series of any number of consecutive steps, (b) the shrinking-core model of gas–solid interactions, and (c) a catalytic reaction on the surface of a solid. Baranski also proved for mechanisms of type (a) that, if a rate determining step, i , exists with a degree of rate control equal to unity (i.e., $X_{rc,i} = 1$), then the degree of rate control for all other steps j is zero ($X_{rc,j \neq i} = 0$).

Stoltze (11) supported the use of the degree of rate control in microkinetic modelling. Sriramulu (14) also showed that it is powerful in analyzing kinetics and mechanisms in complex electrocatalytic reactions.

The degree of rate control of a step quantifies the importance of that step in determining the overall reaction rate for the whole, complex mechanism, independent of the equilibrium constant for that step. It answers the question: If one could find a catalyst which accelerated only that one step (without affecting its equilibrium constant or the rate constants of other steps, for example, by stabilizing its transition state), then how much would this affect the overall reaction rate? This is obviously of practical importance since, in a complex industrial process, finding a good catalyst for any step with a large degree of rate control would lead to a faster net reaction. It thus helps one identify the bottlenecks in a process and highlights those steps where one should concentrate the most effort in process improvement. It is easiest to imagine this in a multistep reaction mechanism or process which is not initially catalytic, where it simply identifies the step(s) where a catalyst is needed. Of course, it is harder to imagine such a "catalyst" when one is already dealing with a catalytic mechanism where almost all species are already adsorbed on a surface. It thus becomes a thought experiment, analogous to finding a surface additive which somehow magically stabilizes the transition state to that one elementary step without affecting the energies of any other adsorbed species. Strictly speaking, this is probably impossible experimentally. Still, in many real surface mechanisms, it may be possible to achieve a similar improvement in net rate with an additive (or surface structural change) which stabilizes both the transition state and the product of that step, or which destabilizes the reactant and, to a lesser extent the transition state of that step. If the transition state has a different charge or dipole moment

than the reactant or product, it is not hard to imagine a surface additive (e.g., an electropositive or electronegative adatom) that might do this, without too dramatically changing the other elementary steps. This might also be useful in selectivity improvement, by finding selective poisons for the rate-controlling step(s) in the net rate to an undesirable side product, or by promoting its inhibition step (if one exists).

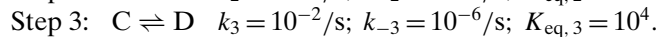
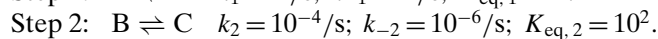
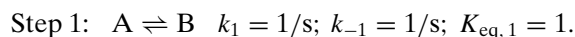
A criticism might be that surface additives surely affect the energies of all surface species (13). However, as our knowledge of surface chemistry grows, so too will our ability to identify surface additives or surface structural changes which affect more strongly the energies of some types of species compared to others. At the very least, identifying the steps with large degrees of rate control should give us good ideas for catalyst improvement. Also, if one is interested in microkinetic modeling, the steps with large degrees of rate control are the steps whose rate constants most sensitively affect the net rate. The degree of rate control thus identifies those steps where one should concentrate the most effort in measuring accurate rate constants. In summary, the degree of rate control is a powerful concept in many ways.

The ratio of the net rate to the forward rate of step i , which has been used previously in kinetic analyses (8, 9), is somewhat similar to the degree of rate control in some mechanisms, but it can be quite different too, depending on the mechanism.

IV. COMPARISON OF CAMPBELL'S AND DUMESIC'S METHODS

One very obvious difference between Campbell's and Dumesic's methods for ascertaining the RDS appears whenever the mechanism includes the slow step followed by a fast step. In such cases, both these steps will initially have a value for z_i that is much less than unity. Therefore, in such cases, Dumesic's method would fail to identify a RDS, but Campbell's method would identify the slow step as rate determining. Depending upon the relative equilibrium constants for these two steps, it is possible to have the value of z_i for the last step be smaller than that for the slow step. This would be the opposite of the ordering of the relative degree of rate control for those two steps!

Let us analyze a simple, concrete example reaction mechanism, which highlights this difference between Campbell's and Dumesic's methods for ascertaining the RDS. Consider the mechanism:



Net reaction: $A \rightleftharpoons D$.

One can see from the magnitudes of these rate constants that the first step will be fast to equilibrium, and that the

second step will be slow and rate determining. Step 3 is fast, but remains very far from equilibrium for a long time (until the overall reaction is >99.99% complete).

Consider the simplified case wherein the above reaction occurs in an ideal solution of fixed volume (i.e., as a batch reaction), with the activity of each species n then just being its molar concentration, $[n]$. Consider starting the reaction at time $t = 0$ with $[A]_0 = 2.000$ molar, and $[B] = [C] = [D] = 0$. In just a few seconds, the equilibrium in step 1 is established, and $[B] = K_{eq,1} [A] = K_{eq,1}([A]_0 - [B])$. This can be rearranged to give

$$[B] = K_{eq,1}[A]_0/(1 + K_{eq,1}) = [A]_0/2 = 1.000 \text{ M.} \quad [7]$$

Note that step 2 is so slow that almost no C nor D has yet been made. The concentrations of A and B remain at ~ 1.0 M for $\sim 10^3$ s, but they eventually get consumed significantly by step 2 on a slower time scale. Since $k_3 \gg k_{-2}$, one can write

$$d[C]/dt = k_2[B] - k_3[C] + k_{-3}[D]. \quad [8]$$

The last term can be ignored as long as $[D]$ remains $\ll K_{eq,3} [C]$ (which will be true for $>10^3$ s). At such times, this can be solved to give

$$[C] = (k_2/k_3)[B]\{1 - \exp(-k_3t)\}. \quad [9]$$

Since $[B] = 1.0$ M at such times, we see that $[C]$ grows rapidly until it reaches a nearly steady-state concentration $[C] = (k_2/k_3)[B] = 10^{-2}$ M, after ~ 250 s. It remains near this concentration until A and B start to get significantly consumed (only after $\sim 2 \times 10^3$ s). One can also write

$$d[D]/dt = k_3[C] - k_{-3}[D], \quad [10]$$

which gives

$$[D] = K_{eq,3}[C]\{1 - \exp(-k_{-3}t)\}. \quad [11]$$

At times less than $\sim 10^3$ s, this reduces to a linear growth in $[D]$

$$[D] = k_3[C]t = k_2[B]t = k_2([A]_0/2)t = (10^{-4} \text{ M/s}) \cdot t. \quad [12]$$

This holds approximately true as long as the intermediate C holds a reasonably steady-state concentration (i.e., from ~ 250 to $\sim 2 \times 10^3$ s). While this steady-state approximation holds, the net reaction rate is approximately

$$\begin{aligned} R &= d[D]/dt = k_2\{[A]_0/(1 + K_{eq,1})\} \\ &= k_2([A]_0/2) = (10^{-4} \text{ M/s}). \end{aligned} \quad [13]$$

From this analytical expression, one can see that the degree of rate control is unity for step 2 and zero for all other

steps:

$$X_{rc,1} = (k_1/R) \cdot (\delta R/\delta k_1) = (k_1/R) \cdot 0 = 0. \quad [14]$$

$$\begin{aligned} X_{rc,2} &= (k_2/R) \cdot (\delta R/\delta k_2) = (k_2/R) \cdot ([A]_0/2) \\ &= k_2/\{k_2([A]_0/2)\} \cdot ([A]_0/2) = 1.00. \end{aligned} \quad [15]$$

$$X_{rc,3} = (k_3/R) \cdot (\delta R/\delta k_3) = (k_3/R) \cdot 0 = 0. \quad [16]$$

Step 2 is thus the rate-determining step in this mechanism according to Campbell's criterion. This agrees with intuition.

However, this is not obvious from Dumesic's method since, during this steady-state period, both steps 2 and 3 have values for their reversibilities (z_i), which are far below unity, but neither is equal to the net reversibility:

$$z_1 = \left[\prod_j (a_j^{v_{ij}}) \right] / K_{eq,1} = ([B]/[A])/K_{eq,1} = 1.0. \quad [17]$$

$$z_2 = ([C]/[B])/K_{eq,2} = (k_2/k_3)/(10^2) = 10^{-4}. \quad [18]$$

$$\begin{aligned} z_3 &= ([D]/[C])/K_{eq,3} = (k_3[C]t/[C])/(10^4) = (10^{-6} \text{ s}^{-1}) \cdot t \\ &= 2.5 \times 10^{-4} \text{ to } 10^{-3} \text{ in this time range.} \end{aligned} \quad [19]$$

Note that $z_{total} = ([D]/[A])/K_{eq} = z_1 z_2 z_3 = 2.5 \times 10^{-8}$ to 10^{-7} in this time range. Thus, neither z_1 , z_2 nor z_3 equals z_{total} , so there is no obvious RDS according to Dumesic's criterion, in contrast to the conclusion by Campbell's method. Clearly, Campbell's criterion is more general in that it also identifies the RDS even in these types of mechanisms where the slow step is followed by fast steps.

Note that a catalyst that accelerated only step 2 would increase the net reaction rate proportionally. A catalyst that accelerated only step 1 or only step 3 would have absolutely no effect on the net reaction rate. This is consistent with the definition of RDS based on Campbell's criterion involving the degree of rate control of the involved steps.

V. USING CAMPBELL'S METHOD IN TRANSIENT KINETICS

Campbell's method was mainly intended for application to kinetics where a steady-state or quasi-steady state rate has been established, as, for example, in a flow reactor, or for low conversion rates in batch reactors. However, it can be applied to transient kinetics within some microkinetic models as follows:

1. Using the microkinetic model's true kinetic parameters, numerically simulate the kinetic transient, starting from its initial steady-state condition at time $t = 0$ when the perturbation occurs up to some time of interest after perturbation, t .

2. Starting at time t , increase both the forward and reverse rate constants for step i by 1% (thus not changing its

equilibrium constant), and let the reaction simulation proceed from time t with these new, altered rate constants. The concentrations of some intermediate(s) consequently will change. If these concentrations change to new, quasi-steady-state levels quickly, meaning on a time scale dt that is short compared to t (i.e., $dt \ll t$), then it is possible to estimate the resulting incremental change in the net reaction rate at time $t + dt$, $\delta R(t + dt)$, due to this incremental increase in rate constant, $\delta k_i/k_i = 0.01$. Thus,

$$\delta R(t + dt) = R'(t + dt) - R(t + dt), \quad [20]$$

where $R'(t + dt)$ and $R(t + dt)$ are the net rates at time $t + dt$ calculated by the simulation with and without this incremental increase in rate constants for step i (and $-i$) at time t , respectively.

3. Calculate the resulting fractional change in the net rate at time $t + dt$, $\delta R(t + dt)/R(t + dt)$, and the degree of rate control of step i , $X_{rc,i}$, using Eq. [6] with $\delta k_i/k_i = 0.01$. The resulting value of $X_{rc,i}$ applies most accurately at time $t + (dt/2)$, which is very close to time t . This degree of rate control can be calculated similarly for all the elementary steps. Their values rank these steps with respect to the sensitivity of the net reaction rate at that time to their rate constants, and identifies which step(s) are kinetic bottlenecks for product formation at that time during the transient.

4. If necessary, repeat steps 1–3 with smaller and smaller incremental increases (instead of the 1% above) until this approaches a true differential limit.

VI. CONCLUSIONS

The degree of rate control is a powerful concept in that it identifies the step(s) in a complex mechanism where one can gain the most by accelerating the rate (for example, by identifying a selective catalyst or catalyst additive to accelerate that step) or by studying the rate further (for example, when developing a microkinetic model). Note that an analytical expression for the net rate is not needed to determine the degree of rate control. It can be done easily in even the most complex mechanisms by using finite

difference or other numerical methods which can be easily implemented with a desktop computer. The degree of rate control is also pedagogically instructive, in that it is easy to define and calculate, and it easily identifies the step(s) whose rate constant(s) enter explicitly into the analytical expression for the net rate (and not just indirectly in the form of equilibrium constants).

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REFERENCES

1. Dumesic, J. A., *J. Catal.* **185**, 496 (1999).
2. Campbell, C. T., *Topics Catal.* **1**, 353 (1994). [Proc. of Topsoe/Nielsen Symp., 1993]
3. Atkins, P., "Physical Chemistry." Freeman, New York, 1978.
4. Levine, I. N., "Physical Chemistry." McGraw-Hill, New York, 1978.
5. Boudart, M., "Kinetics in Chemical Processes." Prentice Hall International, Engelwood Cliffs, NJ, 1968.
6. Laidler, K. J., "Chemical Kinetics." Harper Collins, New York, 1987.
7. Boudart, M., and Tamaru, K., *Catal. Lett.* **9**, 15 (1991).
8. Aparicio, L. M., and Dumesic, J. A., *Topics Catal.* **1**, 233 (1994).
9. Dumesic, J. A., Rudd, D. F., Aparicio, L. M., Resoske, J. E., and Trevino, A. A., "The Microkinetics of Heterogeneous Catalysis." Am. Chem. Soc. Washington, DC, 1993.
10. Baranski, A., *Solid State Ionics* **117**, 123 (1999).
11. Stoltze, P., *Prog. Surf. Sci.* **65**, 65 (2000).
12. Holstein, W. L., and Boudart, M., *J. Phys. Chem.* **101**, 9991 (1997).
13. Boudart, M., *Topics Catal.* **14** (2001).
14. Sriramulu, S., Dissertation. Chemical Engineering Department, Univ. of Washington Press, Seattle, 1999.

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