

# Application of the De Donder Relation to the Mechanism of Catalytic Reactions

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The principle of microscopic reversibility at equilibrium is often invoked in the context of the feasibility of postulated kinetic mechanisms. In this context, it is argued that the De Donder relation  $A\nu \geq 0$ , relating the affinity  $A$  and the net rate  $\nu$  of a chemical reaction, appears to be particularly incisive, as it clearly applies to nonequilibrium systems, at the steady state or the quasi-steady state. In particular, when reactions or elementary steps are involved in closed cycles, application of the De Donder relation leads to informative restrictions concerning postulated mechanisms.

## Introduction

If a mechanism is postulated for a catalytic reaction, what are the thermodynamic restrictions on its validity? This question has been addressed theoretically in the context of the principle of microscopic reversibility (PMR),<sup>1–6</sup> which states that, at equilibrium, the forward and reverse rates of elementary steps are equal. This principle was put forth by Tolman in 1924,<sup>7,8</sup> and can be shown to result from the invariance of the equations of motion under time reversal. PMR leads to the additional conclusions that at equilibrium the reverse and forward rates of all chemical reactions—irrespective of the mechanism or number of elementary steps involved—are identical and that the reverse reaction proceeds through the identical series of elementary steps as the forward reaction. This is frequently called the principle of detailed balance (PDB). When reactions are away from equilibrium, the situation is not clear, although the kinetics of forward and reverse reactions seems to proceed in a manner similar to that expected if both PMR and PDB did apply.<sup>9,10</sup> Our purpose is to address ourselves to situations away from equilibrium by applying a thermodynamic relation to chemical kinetics away from equilibrium, as presented by De Donder in 1927.<sup>11</sup> The De Donder equation relates the rates of the forward and backward reactions of an elementary step,  $\bar{\nu}$  and  $\bar{\nu}$ , to the affinity of the reaction  $A$ , as a straightforward consequence of transition state theory, as explained in the secondary reference:<sup>11</sup>

$$\bar{\nu}/\bar{\nu} = \exp(A/RT) \quad (1)$$

The affinity  $A$  is defined as  $(-\partial G/\partial \xi)_{T,p}$  where  $G$  is the Gibbs free energy and  $\xi$  is the extent of reaction. At equilibrium,  $A = 0$ , and eq 1 leads directly to the principle of microscopic reversibility:  $\bar{\nu} = \bar{\nu}$ . Equation 1 also leads to the better known De Donder relation relating the net rate of the reaction  $\nu = \bar{\nu} - \bar{\nu}$  to its affinity

$$A\nu \geq 0 \quad (2)$$

This relation, half of which is often called the De Donder inequality, holds both at equilibrium (where  $A$  and  $\nu$  are both zero) and away from equilibrium. Both  $A$  and  $\nu$  are positive

for an elementary step with a net positive rate and both negative for a net negative rate.

Strictly speaking, relations 1 and 2 are applicable only to elementary steps, not overall reactions taking place through closed cycles of elementary steps, such as chain and catalytic reactions. For such reactions

$$A = \sum_i \sigma_i A_i \quad (3)$$

where the summation is over the  $i$  steps of the cycle, each one weighted with a stoichiometric number,  $\sigma_i$ , defined as the number of times that the  $i$ th step must take place at each turnover of the cycle. The steady-state rate  $\nu = \bar{\nu} - \bar{\nu}$  is then

$$\sigma_i \nu = \nu_i = \bar{\nu}_i - \bar{\nu}_i \quad (4)$$

and the De Donder relations 1 and 2 still apply but together with eqs 3 and 4. In particular, if all steps in the cycle are in quasi-equilibrium except one called the rate determining step with subscript  $d$ ,  $A = \sigma_d A_d$  and  $A$  must be replaced by  $A/\sigma_d$  in the relation of De Donder, eq 1, as shown in ref 12.

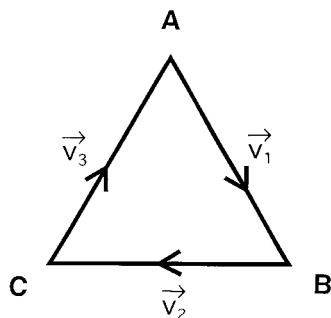
The De Donder relations are more general than the principle of microscopic reversibility since they apply away from—as well as at—equilibrium. The formalism of De Donder leads to additional information regarding the rate of chemical reactions near equilibrium, where the net rate is linearly dependent on the affinity,<sup>12,13</sup> and it is useful in the calculation of virtual fugacities in catalytic and electrocatalytic reactions.<sup>14</sup>

Application of the principle of microscopic reversibility to the study of the feasibility of reaction mechanisms has been limited to the study of isotopic exchange reactions, where if one neglects kinetic isotope effects, the mechanisms and rates must be identical in both the forward and reverse directions. PMR has been applied to the study of several homogeneous reactions, including the kinetics and mechanism of carbonyl exchange reactions in  $M(\text{CO})_5\text{X}$ , where  $M$  is a transition metal atom such as Mn or Re and  $X$  is a halogen,<sup>15–17</sup> and of electrophilic substitution reactions involving organometallic compounds.<sup>18,19</sup> It has also been applied to heterogeneously catalyzed hydrogen–deuterium exchange reactions in hydrocarbons.<sup>20–22</sup> For all of these cases, PMR has been used to rule out proposed reaction mechanisms for symmetrical reaction

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## SCHEME 1



paths. Burwell and Pearson<sup>23</sup> have extended the theoretical foundation to asymmetrical reactions with multiple paths.

The De Donder inequality has more general applicability for the study of kinetic mechanisms than does the principle of microscopic reversibility. It has been used to differentiate between thermodynamic coupling and kinetic coupling in chain and catalytic reactions. While the former plays no role, the latter enables some reactions to proceed by displacing the equilibrium of thermodynamically unfavorable steps.<sup>24</sup> The De Donder inequality provides a theoretical underpinning for examining the potential role of stable intermediates in complex reactions. Examples of its use in this manner include the platinum-catalyzed C-H<sub>2</sub>O reaction, where it has been shown that formation of CH<sub>4</sub> does not proceed through a CO intermediate,<sup>25</sup> and the iron-catalyzed formation of filamentous carbon from methanol, which has been shown not to occur through disproportionation of a CO intermediate.<sup>26</sup> In the discussion below, we apply the De Donder inequality to the study of reaction mechanisms involving closed reaction cycles.

### Reaction Mechanisms with Closed Reaction Cycles: Triangular Reactions

The De Donder relations, eqs 1 and 2, provide additional direct insight in the first classical example consisting of a triangular network of one way reactions, i.e., kinetically irreversible reactions, as shown in Scheme 1.

According to the principle of microscopic reversibility, such a triangular network is ruled out at equilibrium.<sup>4</sup> If all three reactions take place at equilibrium, the reactions must be two-way reactions, i.e., kinetically reversible, with the rates of each reaction being identical in the forward and reverse direction.

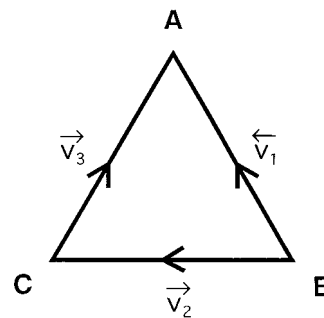
Away from equilibrium, we can use the De Donder inequality to arrive at the same conclusion regarding the prohibition of Scheme 1, where the arrows point in the direction of the positive reaction rate. We make use of the fact that Gibbs free energy is a state property. Thus, the affinity of a closed cycle of reactions is zero, and as Scheme 1 is written

$$A_1 + A_2 + A_3 = 0 \quad (5)$$

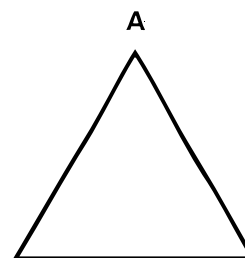
since by definition  $A_1 = \mu_A - \mu_B$ ,  $A_2 = \mu_B - \mu_C$ , and  $A_3 = \mu_C - \mu_A$ , where  $\mu_A$ ,  $\mu_B$ , and  $\mu_C$  are the chemical potentials of components A-C, respectively. Clearly  $A_1$ ,  $A_2$ , and  $A_3$  cannot all be positive. From the De Donder inequality (eq 2),  $v_1$ ,  $v_2$ , and  $v_3$  also cannot all be positive.

At least one term in the sum must be negative, say  $A_1$ . Hence, from the De Donder inequality, the reaction from A to B will actually be in the direction from B to A (Scheme 2). As time goes on, two possibilities arise. The first one is that components B and C will be consumed while only component A remains and equilibrium is reached (Scheme 3). The second possibility

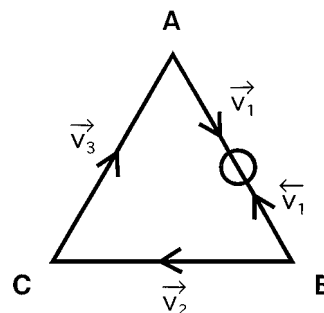
## SCHEME 2



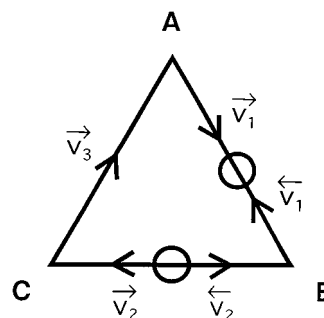
## SCHEME 3



## SCHEME 4



## SCHEME 5

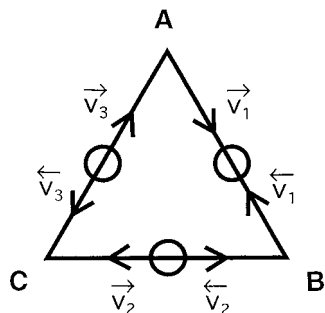


is that equilibrium will be reached, say between components A and B, and  $A_1 = -A_1 = 0$ , with  $\bar{v}_1 = \bar{v}_1$  (Scheme 4), where the symbol zero denotes equilibrium (zero net rate). But, then, to account for the necessity of  $A_2 + A_3$  being equal to zero, either  $A_2$  or  $A_3$  will have to be negative, say  $A_2$ . Then again we will reach equilibrium as time goes on (Scheme 5) with  $A_2 = -A_2 = 0$  and  $\bar{v}_2 = \bar{v}_2$ . Then finally  $A_3$  will also be equal to zero as the equilibrium between B and C is reached. So, at the steady state which is also the equilibrium state (Scheme 6), the principle of microscopic reversibility applies, as is well-known for the triangular reaction network.

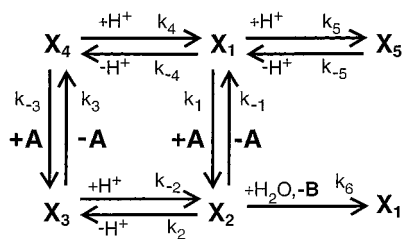
### Networks Including Closed Cycles of Reactions

As a second example of the application of the De Donder inequality to the study of reaction mechanisms, we consider

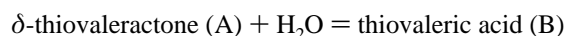
## SCHEME 6



## SCHEME 7



the hydrolysis of  $\delta$ -thiovaleractone (A) catalyzed by imidazole ( $X_1$ ).<sup>4,27,28</sup> The overall reaction is



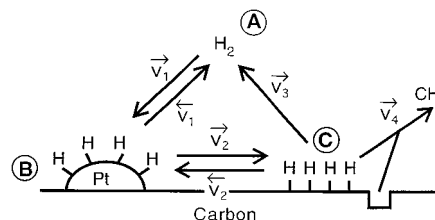
A mechanism was proposed by Bruice and Bruno;<sup>27</sup> it is sketched in Scheme 7, where  $X_1$  is imidazole and  $X_2$ ,  $X_3$ ,  $X_4$ , and  $X_5$  are other catalytic intermediates, with  $X_2$  representing both the normal and zwitterionic forms of the same intermediate. To fit the data, the authors proposed that (1)  $k_1 \gg k_{-3} \{k_{-4}/(k_4[H^+])\}$  and (2)  $k_3\{k_2/k_{-2}[H^+]\} \approx k_{-1}$ , where  $k_i$  and  $k_{-i}$  are the rate constants of the forward and reverse reactions. As later shown by Westheimer and Bender,<sup>28</sup> if both of these statements were true, then  $k_1k_2k_3k_4 \neq k_{-1}k_{-2}k_{-3}k_{-4}$ , which is a violation of the principle of microscopic reversibility. Thus, the proposed reaction mechanism is not allowed. However, strictly speaking, since the principle of microscopic reversibility only applies at equilibrium, this conclusion is only applicable at equilibrium.

Since the kinetics of the hydrolysis of  $\delta$ -thiovaleractone (A) was studied far from equilibrium, the feasibility of the reaction mechanism is better analyzed with the De Donder relations than with the principle of microscopic reversibility. From Scheme 7, it is clear that reactions 1–4 form a closed reaction cycle. Thus, as in the case of the triangular cycle,

$$A_1 + A_2 + A_3 + A_4 = 0 \quad (6)$$

Bruice and Bruno assume that steps 2 and 4 are reversible and rapid. This corresponds to  $A_2 \approx 0$  and  $A_4 \approx 0$ . The two kinetic approximations of Bruice and Bruno stated above yield  $A_1 \gg 0$  and  $A_1 \gg |A_3|$ , although no constraint on the sign of  $A_3$  is made. Even so, eq 6 cannot hold, and the previously noted kinetic assumptions of Bruice and Bruno cannot be valid. The unacceptability of Scheme 7 is made more definitive when, later in their paper, the authors hypothesize that thiovaleric acid (B) is produced from  $\delta$ -thiovaleractone (A) through the intermediate  $X_2$  according to reactions 1 and 6 but that some of the intermediate  $X_2$  is recycled back to  $X_1$  through reactions 2, 3, and 4. This catalytic sequence corresponds to  $v_1 > 0$  and  $v_2 = v_3 = v_4 > 0$ . From the De Donder inequality, eq 4, this yields  $A_1, A_2, A_3, A_4 > 0$ , which is inconsistent with eq 6. Therefore, the kinetic mechanism is thermodynamically prohibited, as

## SCHEME 8



already concluded by Westheimer and Bender from the principle of microscopic reversibility at equilibrium.

## Catalytic Cycle Including a Triangular Cycle

A third example is based on a proposed mechanism to form methane from carbon and hydrogen, as shown in Scheme 8.<sup>29</sup> In this mechanism, molecular hydrogen is reversibly and dissociatively chemisorbed onto the surface of platinum particles located on the surface of carbon, which serves both as a support and as a reactant. The hydrogen atoms then *spill over* onto the carbon in a reversible step.<sup>30,31</sup> According to the proposed mechanism, the hydrogen atoms which spill over onto the carbon can be transferred back to the platinum particles, react with the carbon to form methane, or recombine and desorb as  $H_2$ .

A closed reaction cycle is contained within the overall reaction mechanism of Scheme 8, since there are two routes whereby hydrogen chemisorbed on carbon can recombine to form molecular hydrogen. The first is the direct recombination and desorption from carbon, which occurs at a rate  $\bar{v}_3$ , and the second is reverse spillover of chemisorbed atomic hydrogen from carbon to platinum followed by its recombination and desorption as molecular hydrogen, which occurs at a rate  $\bar{v}_1$ .

If the overall reaction of hydrogen with carbon to form methane is occurring at a net positive steady-state rate, it follows that  $v_1 = v_2 > 0$ . Therefore, from eq 2,  $A_1$  and  $A_2 > 0$ , but for the closed cycle involving reactants A–C, we have  $A_1 + A_2 + A_3 = 0$ . As a result,  $A_3$  must be negative together with  $v_3$ . Thus, the uncatalyzed desorption of hydrogen from carbon cannot proceed irreversibly in the direction as proposed by Olander and Balooch<sup>29</sup> and written in Scheme 8. Indeed, if this step occurs at all, it must take place at a net *negative* rate as written in Scheme 8; that is, the uncatalyzed chemisorption of hydrogen onto carbon must occur at a faster rate than the uncatalyzed desorption under conditions where methane is produced at a net positive rate. An alternate reaction mechanism has been proposed that is not subject to the above criticism. For this mechanism that is beyond the scope of this paper, the interested reader is referred to the published paper.<sup>32</sup>

The conclusions reached above can be applied generally to other types of spillover reactions.<sup>33–35</sup> Thus, if adsorption of a reactant onto the surface of a support occurs through a catalytic route, then desorption of the adsorbed gas under the same conditions must take place through a series of steps which are identical with—but reverse from—those occurring for the catalyzed adsorption. Away from equilibrium, adsorption cannot be occurring at a net positive rate by one mechanism while desorption is simultaneously taking place at a net positive rate through a different mechanism.

## Conclusion

In a lucid exposé of the principles of *The Thermodynamics of the Steady State*,<sup>36</sup> Denbigh, quoting Onsager, notes that “In the more general situation of several reactions, the statement that each equilibrium constant is equal to the ratio of the forward

and backward velocity constants can only be proved by the use of microscopic reversibility as an additional basic principle."

In this paper, we use the De Donder equation (eq 1) and its companion in eq 2 as the additional basic principle that follows from irreversible thermodynamics and is valid away from equilibrium. But, it must be also noted that a consequence of eq 1 is that, for any elementary step, the ratio of velocity constants  $\bar{k}_i$  and  $\bar{k}_i$  in the forward and backward directions is equal to the equilibrium constant  $K_i$ . Indeed, application of eq 1 for values of the thermodynamic activity at the standard state (superscript  $\circ$ ) yields

$$\bar{v}_i^\circ/\bar{v}_i^\circ = \bar{k}_i/\bar{k}_i = \exp(A_i^\circ/RT) = K_i$$

Another reflection suggested by our paper is that chemical kineticists frequently simplify complex kinetics by assuming that the backward rate can be neglected for some of the elementary steps. This leads to unavoidable trouble as equilibrium is approached. In other words, according to the De Donder equation, there is no "one way" or "irreversible" step or reaction. The simplification in kinetics consisting of assuming one way steps or reactions is of course very useful, but only sufficiently far away from equilibrium. This *caveat* is just another expression of the De Donder equation that was forgotten or overlooked for the past 70 years, until its recent revival.<sup>13,14,24</sup>

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