VIRTUAL PRESSURE AND VIRTUAL FUGACITY IN CATALYSIS
AND ELECTROCATALYSIS

M. BOUDART

Department of Chemical Engineering, Stanford University, Stanford, California 94305, U.S.A.

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De Donder equation for multistep reactions, virtual pressure or fugacity in electrocatalytic reactions

The generalized De Donder equation and the generalized Butler-Volmer equation can be used to understand and calculate so-called virtual pressure or virtual fugacity of reactants or products in catalytic and electrocatalytic cycles respectively. This illustrates the usefulness of general relations between kinetics and thermodynamics in sub-fields of catalysis that differ in their methodology.

1. Catalysis

Catalysts differ in their complexity: from a proton to a Wilkinson rhodium coordination complex, from a platinum gauze to a shape selective zeolite, from a supramolecular assembly to an enzymatic site. This increasing complexity dictates differences in methodology, scientific jargon, and professional grouping. Yet there exist concepts that are common to homogeneous, heterogeneous and enzymatic catalysis, as they consist of general relations between thermodynamics and kinetics of any catalytic cycle.

One of these relations is the generalized expression of De Donder for a multistep catalytic reaction running at the steady state. It relates the ratio of forward to reverse rate $\nu/\bar{v}$ to the thermodynamic driving force $A/\sigma RT$ of the reaction:

$$\frac{\nu}{\bar{v}} = \exp\left(\frac{A}{\sigma RT}\right)$$

(1)

where $A = (\delta G/\delta \xi)_{T,p}$ is the affinity of the overall reaction defined as the partial derivative of the Gibbs free energy $G$ with respect to the extent of reaction $\xi$ at constant temperature $T$ and pressure $p$, and $\sigma$ is the stoichiometric number of the rate determining step, if there is one, of the catalytic cycle. There exists a rate determining step in the cycle if all of the others are in quasi-equilibrium. Then $\sigma$ is the number of times that the rate determining step must proceed for the cycle to turnover once, corresponding to the stoichiometric equation for the reaction, as written. How to obtain eq. (1) is described elsewhere [1].

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The purpose of this letter is to recall a useful consequence of eq. (1), namely the concept of virtual pressure and to apply this concept to an electrocatalytic reaction by means of the electrochemical equivalent of eq. (1).

In catalytic reactions, the concept of virtual pressure or virtual fugacity of a reactant or product was first conceived fifty years ago by Temkin and Pyzhev in connection with ammonia synthesis and decomposition [2]. If we write the stoichiometric equation for decomposition as

\[ 2\text{NH}_3 = \text{N}_2 + 3\text{H}_2 \]  

(2)

the rate determining step at pressures near atmospheric and, say, 673 K is the associative desorption of adsorbed atomic nitrogen \( \text{N}^* \) that is the most abundant reactive intermediate at the surface:

\[ \text{N}^* + \text{N}^* \rightarrow \text{N}_2 + 2^* \]  

(3)

and \( \sigma \) is equal to unity. According to eq. (1), the ratio of the rates of desorption and adsorption \( \frac{v_d}{v_a} \), equal to to \( \frac{\tilde{v}}{\tilde{u}} \) is given simply by

\[ \frac{v_d}{v_a} = \exp\left(\frac{A}{RT}\right) \]  

(4)

since \( \sigma \) is unity.

But it can be shown readily [3] and in all generality without any assumption on the non-ideality of surface kinetics on a non-uniform surface, that

\[ \frac{v_d}{v_a} = \frac{[\text{N}_2]_v}{[\text{N}_2]_{ss}} \]  

(5)

where \( [\text{N}_2]_{ss} \) is the actual pressure (or fugacity) of \( \text{N}_2 \) in the reacting system at the steady state and \( [\text{N}_2]_v \) is the virtual pressure (or fugacity) of \( \text{N}_2 \) defined as the pressure or fugacity of \( \text{N}_2 \) that would be necessary to reach a surface concentration \( [\text{N}^*]_{ss} \) prevailing during the steady-state of the reaction, if \( \text{N}_2 \) were in equilibrium with the surface.

Now, \( A \) can be evaluated readily from the equilibrium constant \( K \) of reaction (2) and the steady state pressures of \( \text{N}_2, \text{H}_2, \) and \( \text{NH}_3 \). If all three are at 1 bar, the virtual pressure of \( \text{N}_2 \) is equal to 6400 bar at 673 K. Thus, while ammonia is decomposed at 1 bar, everything happens as if the catalyst were submitted to very high pressures of \( \text{N}_2 \). In particular, with an iron catalyst, a bulk nitride is formed that would not be stable in \( \text{N}_2 \) at 1 bar and 673 K. The experimentally determined amount of nitrogen dissolved on an iron catalyst as a result of ammonia decomposition on its surface has been shown to correspond to that in equilibrium with the corresponding pressure of \( \text{N}_2 \) [3]. The notion of virtual pressure is well established in catalysis [4] and can provide useful mechanistic information even when it cannot be calculated [5].

2. Electro catalysis

The generalized De Donder relation (1) can be obtained [1] for any catalytic sequence at the steady state, thus also for electrocatalysis at an electrode. When