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PERSPECTIVES IN CATALYSIS

VIRTUAL PRESSURE AND VIRTUAL FUGACITY IN CATALYSIS AND ELECTROCATALYSIS

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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 $\vec{v}/\overleftarrow{v}$ to the thermodynamic driving force $A/\sigma RT$ of the reaction:

$$\vec{v}/\overleftarrow{v} = \exp(A/\sigma RT) \tag{1}$$

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 ξ at constant temperature T and pressure p, and σ 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 σ 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].

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

$$2NH_3 = N_2 + 3H_2 \tag{2}$$

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

$$N^* + N^* \leftrightarrows N_2 + 2^* \tag{3}$$

and σ is equal to unity. According to eq. (1), the ratio of the rates of desorption and adsorption v_d/v_a, equal to to $\vec{v}/\overleftarrow{v}$ is given simply by

$$v_d/v_a = \exp(A/RT) \tag{4}$$

since σ 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

$$v_d/v_a = [N_2]_v/[N_2]_{ss} \tag{5}$$

where $[N_2]_{ss}$ is the actual pressure (or fugacity) of N_2 in the reacting system at the steady state and $[N_2]_v$ is the *virtual pressure* (*or fugacity*) of N_2 *defined* as the pressure or fugacity of N_2 that would be necessary to reach a surface concentration $[N^*]_{ss}$ prevailing during the steady-state of the reaction, if 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 N_2, H_2, and NH_3. If all three are at 1 bar, the virtual pressure of 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 N_2. In particular, with an iron catalyst, a bulk nitride is formed that would not be stable in 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 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. Electrocatalysis

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 the electrochemical reaction is driven only by an overpotential η, the electrochemical equivalent of eq. (1) is:

$$\vec{i}/\overleftarrow{i} = \exp(\eta/\sigma RT) \tag{6}$$

where $\vec{i}$ and $\overleftarrow{i}$ are the opposite electronic currents at the electrode and the overall stoichiometric equation for the electrode reaction corresponds to the transfer of only one electron.

As happens frequently in different areas of catalysis, eq. (6) has been obtained independently from eq. (1) and is generally expressed in a different way. But the reader can check easily that eq. (6) can be obtained from the generalized form of the Butler-Volmer equation [6]:

$$i = i_0\left[\exp(\overleftarrow{\alpha}\eta/RT) - \exp(-\vec{\alpha}\eta/RT)\right] \tag{7}$$

where i_0 is the exchange current at equilibrium and $\vec{\alpha}$ and $\overleftarrow{\alpha}$ are so-called transfer coefficients that are related to σ through

$$\vec{\alpha} + \overleftarrow{\alpha} = 1/\sigma. \tag{8}$$

Let us apply eq. (6) to an electrode reaction for which the associative desorption of hydrogen is the rate determining step

$$H^* + H^* \leftrightarrows H_2 + 2^*. \tag{9}$$

Just as before, in the case of desorption of nitrogen, we define a *virtual pressure or fugacity* of hydrogen, $[H_2]_v$ as the pressure or fugacity that would be necessary to reach a surface concentration $[H^*]_{ss}$ prevailing during the steady-state of the electrode reaction taking place at a real pressure or fugacity of H_2, $[H_2]_{ss}$ if this virtual H_2 were in equilibrium with the electrode surface:

$$v_d = k_d f_d[(H^*)_{ss}] = v_a = k_a f_a[(H^*)_{ss}] \times [H_2]_v. \tag{10}$$

The kinetics of desorption and adsorption are expressed in perfectly general terms: there is no need to define rate constants k_d and k_a, or the functions f_d and f_a of the surface concentrations $[H^*]$ that can be expressed in terms of a thermodynamic activity on a thermodynamically and kinetically non-ideal surface. Then we proceed:

$$\frac{v_d}{v_a} = \frac{k_d f_d[(H^*)_{ss}]}{k_a f_a[(H^*)_{ss}] \times [H_2]_{ss}}. \tag{11}$$

Substitution of (10) into (11) yields:

$$v_d/v_a = [H_2]_v/[H_2]_{ss}. \tag{12}$$

Let us now apply eqs. (6) and (12) to the discharge of deuterium from alkaline solutions of heavy water on a palladium electrode:

$$D_2O + e^- + * \leftrightarrows D^* + OD^-$$

$$D^* + D^* \leftrightarrows D_2 + 2^*.$$

The overall reaction consisting of transfer of one electron is:

$$D_2O + e^- \leftrightarrows \tfrac{1}{2}D_2 + OD^-.$$

Assume now that the associative desorption of D_2 is the rate determining step. Its stoichiometric number σ is equal to 1/2. Since at the steady state:

$$\vec{i}/\overleftarrow{i} = v_d/v_a$$

we have, from eqs. (6) and (12):

$$[D_2]_v/[D_2]_{ss} = \exp(2\eta/RT). \qquad (13)$$

At 300 K and $[D_2]_{ss} = 1$ bar, the virtual pressure of D_2 at an overpotential of 0.8 eV or 0.8×23.06 kcal mol^{-1}, is 7.6×10^{26} bar in agreement with an unexplained statement of Fleischmann and Pons [7]: "attempts to attain this level (of overpotential) by compression of D_2 would require pressure in excess of 10^{26} atm." The above provides a clarification of this statement.

3. Postscript

Although the existence of high virtual pressures of N_2 in catalytic ammonia decomposition can be calculated and has been verified experimentally, the existence of very high virtual pressures of H_2 in electrocatalysis of palladium requires experimental confirmation. The calculation of such pressures is simple but rests on the assumption of a reaction mechanism, in particular of a rate determining step, at high values of overpotential. Nevertheless, the possibility of such virtual pressures is intriguing and deserves further investigation. The well-established precedent in the case of catalytic ammonia synthesis provides support of the concept of virtual pressure in electrocatalysis.

It is concluded that further applications of general macroscopic relations between kinetic and thermodynamic quantities in all of the subfields of catalysis might be fruitful. One may wonder why an attempt at doing this has taken so long. After all, the very concept of the stoichiometric number of the rate determining step was first enunciated properly fifty years ago by Horiuti for applications both in heterogeneous catalysis and in electrocatalysis as well [8]. And the concept of virtual pressure or virtual fugacity of adsorbed nitrogen in ammonia synthesis and decomposition is also fifty years old [2].

The important message conveyed by the concepts of stoichiometric number σ and *virtual pressure* or *virtual fugacity*, is that the latter would be ~ 13 orders of magnitude smaller as that calculated above if σ were equal to unity in the case just analyzed above. This is no trivial matter. Hence, the "mechanism" of the reaction as expressed by the stoichiometric number of the rate determining step is essential. The Nernst equation, in the electrocatalytic case, is not trustworthy, as it ignores reaction mechanism. This warning has been expressed many times in the literature of electrochemistry [9]. Similarly, just to define fugacity in terms of an equilibrium chemical potential does not define virtual fugacity, a concept pertaining to a situation far away from equilibrium. The generalized Butler-Volmer equation rather than the Nernst equation should be used in the calculation of virtual pressure or virtual fugacity.

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