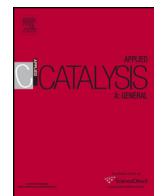




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Unraveling the mechanism of chemical reactions through thermodynamic analyses: A short review[☆]

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ABSTRACT

Basic thermodynamic analyses can provide in-depth knowledge of the mechanism of chemical reactions. This short review recalls first the definitions of the approach-to-equilibrium η , the reaction quotient Q and the thermodynamic equilibrium constant K . Thereafter, four case studies specifically dealing with gas-phase heterogeneously catalyzed reactions are reviewed: (i) alkane hydroisomerization, (ii) NO oxidation during the selective catalytic reduction of NO_x with propene, (iii) the steam reforming of methanol and (iv) ethanol condensation to butanol. These examples illustrate in different manners how a reaction mechanism can be supported or rejected based on rather simple analyses of the concentrations of reactants and products. While the examples used here are all referring to catalyzed reactions, it must be emphasized that the method can be applied to non-catalytic systems.

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1. Introduction

Chemical processes can be made more efficient by better understanding the various reaction steps involved in the conversion of a given feedstock into the desired products so that each step can be (i) promoted by a suitable catalyst and/or (ii) carried out under appropriate operating conditions as to push away the limiting conversion associated with the thermodynamics of the system. Insights into reaction mechanisms can be obtained, for instance, via studying the nature (e.g. acid/base [1], redox [2]) and structure [3,4] of the catalytic sites or by in situ and operando spectroscopy [5–8].

Thermodynamics is routinely used as a tool to determine favorable reaction conditions so that high yields of products can be achieved. However, it is less common to use thermodynamics to support or rule out a particular reaction step. The power of this method is recalled here, showing how details of complex reaction mechanisms can be unraveled. The method is based on the comparison of the proportions of reactants and products present in the reactor effluent to various thermodynamic equilibrium constants pertaining to the system.

This short review recalls first the definitions of the reaction quotient Q and the thermodynamic equilibrium constant K . The

calculation of these numbers will be detailed over a few examples, taken primarily from published work of the authors. The direct comparison of these two numbers (or the value of the ratio $Q/K = \eta$, so-called “approach-to-equilibrium” parameter) can be used to support or reject the relevance of a reaction step in a complex scheme.

It is important to stress that the method described here does not involve the thermodynamics of adsorbed species and therefore no inference can be made as to the nature and concentration of surface intermediates. The examples used in the present paper are dealing with gas-phase compounds and heterogeneous catalysis, but it is crucial to realize that the method can be applied to non-catalytic reactions and condensed systems, as long as activity coefficients are available.

The insights obtained in each of the examples enabled to derive better catalytic formulations or guide future catalyst development and improved reaction conditions. Numerical examples of calculus are given so that a reader not familiar with this topic should fully understand the whole procedure. Most calculations can actually be done on user-friendly commercially available thermodynamic softwares such as HSC Chemistry[®].

2. Definitions

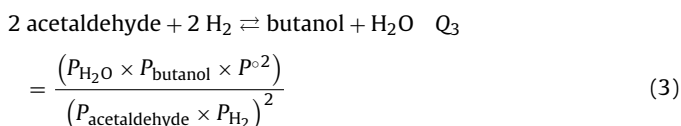
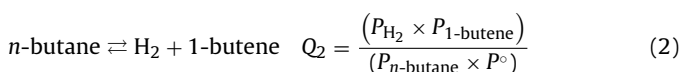
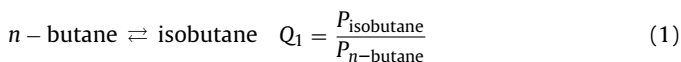
The reaction quotient Q for a given reaction is the ratio between the product of the (dimensionless) chemical activity of each of the

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products to that of the reactants, each raised to the power of the corresponding stoichiometric coefficient [9]. For reactions involving only gaseous compounds at moderate pressure, the chemical activities can be approximated to the pressures of reactants normalized to the standard pressure $P^\circ = 1$ bar (i.e. ideal case for which the gas fugacities are unity). Examples of expressions for Q are given below for some of the reactions discussed here [Eqs. (1)–(3)].



If no reaction product is present in the system (typically at the start of the reaction in a batch reactor or at the front of the bed in a plug flow reactor), the reaction quotient Q is equal to zero. If the system under study has reached the thermodynamic equilibrium the value of the reaction quotient is equal, by definition, to the reaction equilibrium constant K [Eq. (4)]. The value of K can be determined through the knowledge of the standard Gibbs free energy of reaction $\Delta_r G^\circ$ at the temperature considered, which is tabulated for common reactions and can be calculated in most thermodynamic softwares.

$$Q_{\text{equilibrium}} = K = \exp\left(\frac{-\Delta_r G^\circ}{RT}\right) \quad (4)$$

The approach-to-equilibrium (noted “ η ”) is the ratio between Q and K [Eq. (5)] and takes a maximum value of one as the system reaches equilibrium. The approach-to-equilibrium is commonly used as a means to obtain forward rates of reaction when the extent of backward reaction becomes significant [10]. The variation of Gibbs free energy of reaction $\Delta_r G$ can be written as follows [Eq. (6)]:

$$\eta = \frac{Q}{K} \quad (5)$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q = RT \ln \frac{Q}{K} = RT \ln \eta \quad (6)$$

The change of the Gibbs free energy of reaction must remain equal to or lower than zero at all stages of a spontaneous chemical conversion of the system. Therefore, the value of the approach-to-equilibrium η must remain lower or equal to unity, i.e. $\eta = Q/K \leq 1$. This is schematically represented in Fig. 1, in which the open circles are associated with allowed evolutions of the system, while the states in the red shaded zone are forbidden transformations.

The above paragraph recalls that the Gibbs free energy of the system at any point of a spontaneous transformation cannot be higher than its initial value. This is the realm of thermodynamics. This statement is not contradictory with the fact that at any time a minute fraction (determined by statistical thermodynamics) of the molecules will have a sufficiently high energy to overcome an activation barrier to form the products. This fraction of molecules that can react will be increased – and so will be the reaction rate – if the activation barrier of the transformation can be lowered by using a catalysts or a suitable solvent. This is the realm of kinetics.

The level of kinetic analysis used in the following examples is basic, mostly consisting in measuring the concentrations of reactants and products. Detailed kinetic analyses (e.g. based on the determination of reaction orders, primary and secondary reaction products, microkinetic models) are also a powerful tool to unravel reaction mechanism, but are not the point of the present contribution.

$$\Delta_r G(T) = RT \ln \eta$$

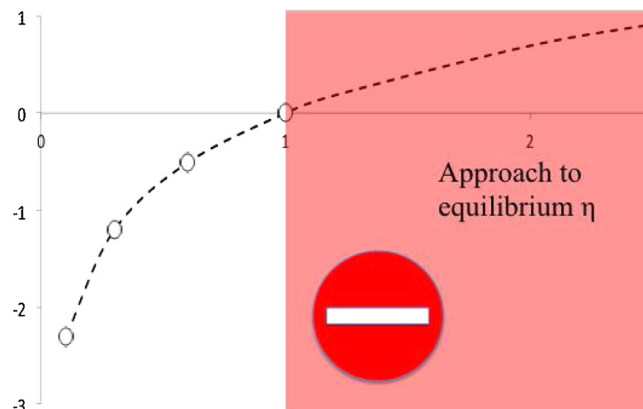


Fig. 1. Gibbs free energy of reaction as a function of the approach-to-equilibrium η . Only transformations associated with $\eta \leq 1$ are allowed.

3. Case studies

The calculation of η requires the determination of the reaction quotient Q , which implies measuring the partial pressure (or concentration) of each of the species appearing in the stoichiometric equation. If a reactant or product is in large excess, then the evolution of the reaction quotient can be satisfactorily monitored by only considering the variation of the concentration of the other compounds.

This is exemplified in the first two case studies described below dealing with alkane hydroisomerization and NO_x oxidation, for which the H₂ and O₂ concentrations, respectively, were considered to be constant. The thermodynamic analysis was there merely reduced to comparing two-term ratios (i.e. [A]/[B]) of pairs of concentrations of reactant and/or products.

The third case study dealing with methanol steam reforming shows how the thermodynamically relevant reaction pathway can be readily determined from the comparison between the measured molar fractions and those calculated at the thermodynamic equilibrium.

The final case study dealing with ethanol condensation involves the analysis of an intermediate reaction step based on the exact determination of the reaction quotient Q . The utilization of equilibrium diagrams is shown to be a useful guide in the search of possible reaction pathways and the rejection of forbidden routes.

3.1. Alkane hydroisomerization

Solids derived from tungsten and molybdenum carbides and oxides can be alternative to noble metals to catalyze reactions such as the reverse water–gas shift and alkane hydroisomerization [11–14]. The nature of the reaction mechanism of alkane hydroisomerization over molybdenum oxide-based catalysts had been a matter of debate. Katrib et al. [15] and Matsuda et al. [16] had proposed that a traditional bifunctional mechanism operated, involving alkenes as reaction intermediates. On the contrary, Bouchy et al. [17] had proposed a metallacyclobutane intermediate-based mechanism.

The hydroisomerization of *n*-butane to isobutane [Eq. (1)] over reduced MoO₃ provided a case study in which thermodynamics enabled to positively determine both the reaction mechanism and the rate-determining step (RDS) [18]. MoO₃ is not active for this reaction and the catalytically active phase (thought to be an oxyhydroxide of molybdenum [19]) is gradually formed under the reaction stream at 350 °C (Fig. 2). Note that the insertion of carbon

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