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In a recent Viewpoint published in this journal,[1] Kozuch and Martin attempted to clarify the concepts of turnover frequency (TOF) and turnover number (TON), which are often used in catalysis research. The present comment has been written to debate some of the views put forward by them and also to point out a number of inaccuracies. The authors wrote that "Despite its utility and common use, the TOF concept is still not well-defined and leads to confusion." I agree with this statement, except that I think the utility of TOF is highly questionable, and this is, in fact, the main reason why the IUPAC has given no definition of this concept thus far.

In a comment published in the electronic version of Science magazine, the present author briefly described major reservations against the use of TOF values.[2] These comments, although originally intended to be very general in nature, were misunderstood to be critical of a single paper.[3] The authors of that paper ended their rebuttal by noting that "[TOFs are] an additional characterization tool for characterizing catalysts even though they do not fit into the pure concept of chemical kinetics."

This sentence alone, by contrasting pure chemical kinetics and characterizing catalysts, illustrates quite clearly that catalysis research and kinetics (which is usually considered together with mechanism research) have developed to be distinct disciplines within the chemical sciences. This is a very surprising and unfortunate state of affairs (at least to the present author). No expert would deny that catalysis is a kinetic phenomenon! It appears that catalysis researchers are interested mainly in preparing new catalysts for target reactions, but seldom do kinetic experiments in any acceptable detail to determine rate laws or to propose mechanisms that would be considered well established within the kinetics and mechanisms community. In contrast, researchers focusing on kinetics often face the criticism of not discovering anything new and studying only processes that are already well-known. I feel that the lack of understanding between the two groups is already a major obstacle to further scientific advance.

Kozuch and Martin correctly describe several of the pitfalls of determining and comparing TOF values, and their recommendations often sound very much like calls to follow good kinetic practice in experimental design; however, they also make some highly debatable points, objections to which will be raised in the following paragraphs. These will be focused on TOF (which gives kinetic information) as opposed to TON (stoichiometric information), in line with the emphasis of the original Viewpoint.

1. The concept of standardized, universally comparable TOF values used to characterize catalytic efficiency, seems to reflect the desire of some experimenters rather than scientific reality. A full characterization of catalytic activity can and should be made by determining the rate law of the catalyzed process. In such a system, the rate law almost invariably contains multiple rate constants. It is just impossible to give a fair representation of a rate law with a single physical property, however standardized it might be, without losing essential information.

2. Thermodynamic concepts should not be misused in kinetics. In the Viewpoint, the prime example of this mistake is the use of standard states, which are necessary in thermodynamics primarily because of working with state functions. Standard states are also used in defining thermodynamic activities, which express the dependence of the chemical potential on the composition of a system. None of these ideas is transferable to chemical kinetics, which does not work with state functions or chemical potentials. Just because it is routine (and correct) to think that activities replace concentrations in exact thermodynamic relationships, the same is not true in any of part chemical kinetics. In kinetics, the variables are concentrations and not activities: a concentration unit is inherently needed, but not a standard state.

3. Stoichiometric coefficients are included in the usual definition of the rate of reaction. In the first paragraph of section 2.1, an example is given that is supposed to give a reason for distinguishing TOF from the ratio of the rate of reaction and the catalyst concentration (reactions "R → P" and "2R → P"), yet the authors make no distinction between the rates of concentration change for particular reactants or products and the rate of reaction,[4] which contains a division by the stoichiometric coefficients exactly to solve the noted problem, that is, to be independent of the identity of the species that is used for its determination.

4. The difference between turnover frequency and rates or rate constants of reactions cannot be as sharp as the article claims. In fact, the authors themselves use the ratio of the rate of reaction and the catalyst concentration to give TOF values in their derivation leading to eqs 5, 6, 7, 9, and 10. In eq 11, however, TOF is used as the left-hand side of the Eyring equation, where a first-order rate constant should be. I think the supposed sharp distinction between closely related quantities originates mainly from a failure to use the concept of the rate of reaction correctly (as mentioned in point 3). It is not possible for a catalytic turnover to occur without consuming reactants and forming products (it would not be called a turnover). On the other hand, and this remark is notably absent from the Viewpoint, product formation is not impossible without the intervention of the catalyst (i.e., without a turnover) because only spontaneous processes can be catalyzed. Therefore, calculating catalytic efficiency must always allow for the noncatalyzed route in some way. This is also the reason why I think the representation focusing on reactants and products should be preferred in Scheme 1 of the Viewpoint, although its graphic appeal is undeniably lower than that of the alternative.

5. The Eyring equation should be used only for giving the temperature dependence of the rate constants of elementary reactions, but not directly for other kinetic quantities. Equations 11 and 12 in section 3.2 of the Viewpoint give what the authors call the "energetic span approximation", which is, in fact, identical to the classical Eyring equation[5] with some of the quantities renamed. It is a very well understood property of the Eyring equation that it gives a theoretical framework for describing the rate constants of elementary reactions, but it

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cannot be used for combinations of rate constants or rates in its original form. On a conceptual level, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ mean the enthalpy and the entropy of the transition state in an elementary reaction. In an overall reaction containing several elementary reactions, the number of characteristic pairs of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values is equal to the number of transition states (e.g., Figure 3 in the Viewpoint shows two consecutive transition states). It is impossible to condense the information content of several pairs of physical quantities into a single pair. Even if eq 11 gives an acceptable phenomenological description of the temperature dependence of TOF within a (usually narrow) temperature range, no theoretical information content should be associated with the determined parameters; neither should they be used for extrapolation.

6. Section 2.4 in the original Viewpoint calls for determining TOF values under conditions when they are independent of the substrate concentration. Although the text states that "... reaching saturation may be impossible for some reactions", this is a very weak statement. In fact, most typical rate laws do not imply the possibility of such saturation.[4] In this regard, a major source of possible conceptual error stems from confusing rates and rate constants. Rate constants typically do have theoretical maximum values (e.g., the diffusion-controlled rate constant in solution kinetics), but rates are limited only by physical constraints on the concentration values.[4] Although I feel there are some conceptual problems within the arguments in this session, I do not debate the wisdom of the final recommendation ("... TOF should be expressed at saturation whenever possible, but still the concentrations must be declared") as long as someone feels inclined to report TOF values.

7. Steady state assumptions must be declared and their validity range described. In section 2.4, eq 5 is claimed to give the TOF on the basis of the chemical scheme shown in eq 4. Equation 9 relates to eq 8 in a very similar fashion a little later. In fact, eqs 5 or 9 are valid only if steady-state conditions prevail for species C_1 and C_2.[4] These conditions pose a limitation on the values of both the concentrations and the rate constants k_1 and k_2, which cannot be left without a note at the very least.

8. Section 2.3 gives a clear description of changes in TOF from one time instant to another. This sequence of thought is so trivial that it is not even described in any detail by textbooks of chemical kinetics, but it is the very reason why the rate of reaction is defined in terms of differentials (or derivates) and not finite differences.[4]

9. The Viewpoint contains a rather troubling misuse of the word "bimolecular". The intended meaning of the authors was probably a reaction consuming (or producing) two identical molecules. In fact, the word bimolecular is used for an elementary reaction that occurs between two reagent molecules (identical or not).[4]

Overall, I think Kozuch and Martin describe many of the reservations kineticists nurture about the concept of TOF. To the authors' credit, they try to make suggestions to resolve the problems. Many of these recommendations are actually about taking more extensive kinetic measurements, most of which are exactly the ones that are necessary to establish a rate law. It is difficult to understand why the researcher should make a futile attempt to condense the information content of these measurements into a single physical quantity instead of reporting the rate law and the rate constants directly.

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Notes

The authors declare no competing financial interest.

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