

2 Definitions and Concepts

It is important that precise and unambiguous terms be used when dealing with rates of reaction and reaction modeling of a chemical system. Many of the definitions provided here have been taken from those provided by the IUPAC [1].

2.1 Stoichiometric Coefficients

A balanced chemical reaction can be expressed as

$$(2.1) \quad 0 = \sum_i \nu_i B_i$$

where ν_i is the stoichiometric coefficient (positive for products and negative for reactants) of any product or reactant B_i . Thus an example reaction between A and B



can be expressed as

$$(2.3) \quad 0 = -aA - bB + cC + dD$$

2.2 Extent of Reaction

This quantity is defined as

$$\xi(\text{mol}) = (N_i - N_{i_0})/\nu_i \quad (2.1)$$

where N_{i_0} and N_i are the quantities of substance B_i , expressed in mole, at time zero and at any other time, respectively; consequently, ξ can be viewed as a mole of reaction.

2.3 Rate of Reaction

An unambiguous rate of reaction, r , is defined by the number of occurrences of this stoichiometric event, such as that shown by reaction 2.2, per unit time. For a particular species, i , its rate of production, r_i , is related to r by the stoichiometric coefficient, i.e.,

$$r_i = \nu_i r \quad (2.2)$$

Rates of reaction can be expressed in terms of process variables associated with a given reactor type via relationships generated by material balances on that reactor. Because rate measurements are essentially always made in a reactor, a discussion of the rate of reaction can be initiated by considering a well-mixed, closed reactor system typically referred to as a batch reactor. In this system, the advancement of the reaction is measured by the molar extent of reaction, ξ , and the reaction rate is equivalent to the rate of change of the molar extent of reaction, i.e.,

$$r = \dot{\xi} = d\xi/dt = \nu^{-1} dN_i/dt \text{ (mol/time)} \quad (2.3)$$

where $r_i = dN_i/dt$ is the rate of formation (or disappearance) of compound B_i . To make this an intrinsic property, it is normalized to unit reactor volume to get r (mol time⁻¹ volume⁻¹) or, when a catalyst is used, to the unit volume, or unit mass, or unit area of the catalyst. Thus, choosing seconds as the unit of time, one can define a volumetric rate:

$$r = r_v = \left(\frac{1}{V}\right) d\xi/dt \text{ (mol s}^{-1} \text{ cm}^{-3}\text{)} \quad (2.4)$$

where V should be only the volume of the catalyst particles excluding the interparticle volume; or a specific rate:

$$r_m = \left(\frac{1}{m}\right) d\xi/dt \text{ (mol s}^{-1} \text{ g}^{-1}\text{)} \quad (2.5)$$

where m is the mass of the catalyst; or an areal rate

$$r_a = \left(\frac{1}{A}\right) d\xi/dt \text{ (mol s}^{-1} \text{ cm}^{-2}\text{)} \quad (2.6)$$

where A is the area of the catalyst. It should be specified whether A is the total surface area or the surface area of only the active component, such as the metal surface area of a dispersed metal catalyst. All subsequent rates in this book will be some form of an intrinsic rate.

2.4 Turnover Frequency or Specific Activity

When the reaction rate is normalized to the surface area of the active component in the catalyst, such as the metal surface area as just mentioned, it is frequently referred to as the specific activity. If this areal rate is further

normalized to the number of surface metal atoms present, or to another specified type of site that has been counted by some stated method, then a turnover frequency (TOF), based usually on a specified reactant, is obtained

$$\text{TOF} = \frac{1}{S} = \frac{N_{\text{Av}}}{S} dN_i/dt \quad (2.7)$$

where N_{Av} is Avogadro's number (6.023×10^{23} molecules/g mole) and S represents the number of sites in the experimental system and can be represented as

$$S = LA \quad (2.8)$$

where L is the number density of sites (per unit area, such as cm^{-2}). A TOF has units of reciprocal time and is typically expressed as s^{-1} .

Several aspects must be emphasized at this time. First, for all these representations of rate, all conditions of temperature, initial concentrations or partial pressures, and extent of reaction must be specified. Second, for appropriate comparisons among different catalysts, areal rates or TOF values must be reported to correct for variations in active surface area. Finally, precise TOFs for heterogeneous catalysts are not so readily definable as those in homogeneous or enzyme catalysis because adsorption sites typically measured by the chemisorption of an appropriate gas and used to count surface metal atoms, for example, do not necessarily correspond to 'active' sites under reaction conditions on a one-to-one basis. The exact atom or grouping of atoms (ensemble) constituting the active site is typically not known for any heterogeneous reaction and, in fact, it is very likely that a variety of active sites may exist, each with its own rate, thus the observed TOF then represents an average value of the overall catalyst activity. Regardless, if rates are normalized to the number of surface metal atoms, M_s , in a metal catalyst as determined by some adsorption stoichiometry, for example, this not only provides a lower limit for the true TOF, but it also allows meaningful comparison among various catalysts, as stated above, as well as rate data obtained in different laboratories. *Thus TOFs (or areal rates) must be reported whenever possible in any proper catalytic study.*

The number of times, n , that the overall reaction takes place through the catalytic cycle represents the number of turnovers, and the rate is then [2]

$$r = dn/dt(\text{s}^{-1}) = N_{\text{Av}}d\xi/dt \quad (2.9)$$

The turnover frequency, N , based on this value and expressed as s^{-1} , is:

$$N(\text{s}^{-1}) = \frac{1}{S} dn/dt \quad (2.10)$$

and its relationship to that defined by equation 2.7 is therefore

$$N = 1/\nu_i dN_i/dt \quad (2.11)$$

The number of turnovers a catalyst can produce is the best way to define the life of a catalyst, and in real systems this number can be very large, frequently exceeding 10^6 [2]. Because TOFs used in industrial processes are frequently near 1 s^{-1} , lifetimes of one month to one year can readily be achieved.

2.5 Selectivity

The term selectivity, S , is used to describe the relative rates of two or more competing reactions on a catalyst. Such competition includes different reactants undergoing simultaneous reactions or a single reactant involved in two or more reactions. In the latter case, a fractional selectivity, S_F , for each product is defined by the equation

$$S_F = \dot{\xi}_i / \sum_i \dot{\xi}_i = r_i / \sum_i r_i \quad (2.12)$$

and a relative selectivity, S_R , for each pair of products is defined by

$$S_R = \dot{\xi}_i / \dot{\xi}_j = r_i / r_j \quad (2.13)$$

2.6 Structure-Sensitive and Structure-Insensitive Reactions

For some reactions on metal surfaces, the activity of the catalyst depends only on the total number of surface metal atoms, M_s , available, and these are termed structure-insensitive reactions; consequently, the TOF is essentially independent of metal dispersion or crystal plane and varies over a very small range (within a factor of 5, for example). For other reactions, the TOF is much greater on certain surface sites, thus the activity can be dependent on metal dispersion, crystal plane, or defect structures. These are termed structure-sensitive reactions. Preceding these terms, such reactions have been referred to as facile and demanding reactions, respectively [3].

2.7 Elementary Step and Rate Determining Step (RDS)

An elementary step is a reaction written exactly as it occurs at the molecular level, and the stoichiometry defined by reaction 2.1 does not describe how the chemical transformation occurs unless it represents an elementary step. Thus an arbitrary choice of stoichiometric coefficients cannot be made; for example, the dissociative adsorption of a diatomic molecule such as H_2 must be written



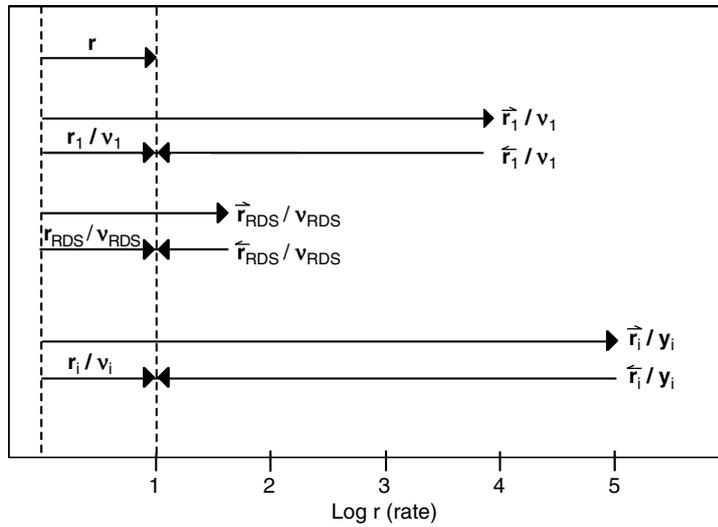


FIGURE 2.1. Relative rates and the net rate in a catalytic cycle, where RDS indicates a rate determining step.

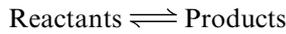
and it cannot be represented in a kinetic sequence as



in contrast to equations representing the equilibrium thermodynamics of reactions. Here * represents an active site involved in the catalytic sequence describing the overall reaction. The net rate of an elementary step, r , is the difference between the forward rate, \bar{r} , and the reverse rate, \bar{r} :

$$r = \bar{r} - \bar{r} \quad (2.14)$$

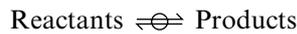
This step can be reversible when $\bar{r} \simeq \bar{r}$, which is represented by a double arrow:



or it can be irreversible if $\bar{r} \gg \bar{r}$, and this is represented by a single arrow:



Finally, this step may be essentially at equilibrium if \bar{r} and \bar{r} are both very large compared to the slow step(s) and if $\bar{r} \cong \bar{r}$, thus this quasi-equilibrated step is denoted by [2]:



Note that under reaction conditions with a net forward rate, this step cannot be exactly at equilibrium; it only requires that both the forward and reverse rates occur much more rapidly, typically orders of magnitude greater, than

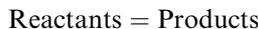
those associated with, if it exists, a rate determining step (RDS), i.e., an elementary step far from equilibrium that determines the overall rate of the catalytic cycle and is designated by



depending on whether it's irreversible or not. This latter step has its rate constant appearing in the rate expression and it is generally coupled with a quasi-equilibrated step [4]. Such a step can be envisioned schematically in Figure 2.1 using the designations defined previously.

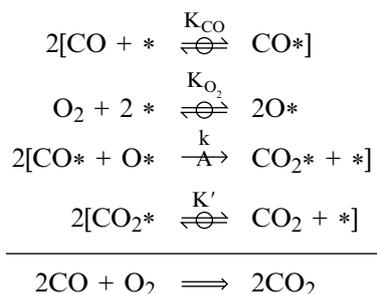
2.8 Reaction Pathway or Catalytic Cycle

A catalytic cycle is defined by a closed sequence of elementary steps, i.e., a sequence in which the active site is regenerated so that a cyclic reaction pattern is repeated and a large number of turnovers occurs on a single active site [5]. If the stoichiometric equation for each of the steps in the cycle is multiplied by its stoichiometry number, i.e., the number of times it occurs in the catalytic cycle, and this sequence of steps, the reaction pathway, is then added, the stoichiometric equation for the overall reaction is obtained. This equation must contain only reactants and products because all intermediate species must cancel out, and this overall reaction is represented by an equal sign:



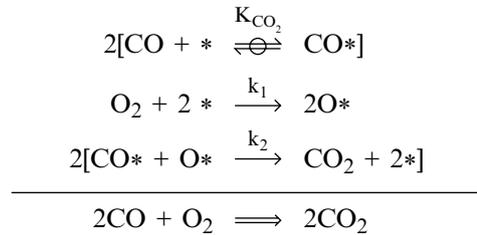
with \rightleftharpoons used if it is equilibrated and \Rightarrow used if it is far from equilibrium [2].

It should be stressed that a catalytic sequence representing the reaction pathway may not contain a RDS. As an example, consider the catalytic gas-phase oxidation of carbon monoxide. On some metals the surface reaction between adsorbed CO molecules and O atoms is the RDS, then, if * is an active site, the sequence can be represented as:



Here 2 represents the appropriate stoichiometric number in the cycle and all the reactive intermediates — *, CO* and O* — cancel out to give the bottom

overall equation. Alternatively, on other metals a RDS does not exist under certain conditions and the above sequence can become:



2.9 Most Abundant Reaction Intermediate (MARI)

If, under reaction conditions, one of the adsorbed species dominates on the surface and the fractional coverage of this intermediate on the catalytic sites is much greater than any other species, then it is said to be the most abundant reaction intermediate (MARI). Technically, it may not be the most abundant surface intermediate (MASI) because some adsorbed species may not be participating in the reaction sequence [2], although these two terms tend to be used interchangeably [1].

2.10 Chain Reactions

A chain reaction is a closed sequence which is created by the formation of active centers due to the thermal decomposition of a molecular species or to some external source such as light or ionizing radiation. A chain reaction must consist of at least four steps: one for initiation, one for termination and at least two for chain propagation, with the last steps being the principal pathway for product generation.

2.11 Reaction Rates in Reactors

In flow reactors, various quantities are related to the reaction rate. One important one is the space velocity, which is defined by the volumetric flow rate of the reactant stream, V_o , specified at the inlet conditions of temperature and pressure with zero conversion (unless otherwise noted), and the catalyst volume, V_c , to be:

$$\text{Space velocity (SV)} = V_o/V_c(\text{time}^{-1}) \quad (2.15)$$

In designing reactors, the reactor volume, V_r , which is required to hold a given mass or volume of catalyst, is routinely used:

$$SV = V_o/V_r(\text{time}^{-1}) \quad (2.16)$$

thus V_r depends on the packing density of the catalyst particles. This quantity of SV is typically expressed in reciprocal hours, h^{-1} , and is frequently near unity in commercial processes. The inverse of the space velocity is the space time, τ

$$\tau = 1/SV = V_r/V_o \text{ (time)} \quad (2.17)$$

and it gives the time required to process one reactor volume of feed. The space time yield refers to the quantity of product produced per quantity of catalyst per unit time. It should be emphasized that the space time, τ , is equal to the average residence time, \bar{t} , only if all the following conditions are met: 1) P and T are constant throughout the reactor, 2) the density of the reacting mixture is independent of ξ , and 3) V_o is the reference volumetric flow rate [6].

2.12 Metal Dispersion (Fraction Exposed)

The dispersion, D_M , or fraction exposed of a metal catalyst is the ratio of the number of surface metal atoms to the total number of metal atoms:

$$D_M = N_{M_s}/N_{M_t} \quad (2.18)$$

i.e., the fraction of metal atoms at the surface, where N_{M_s} and N_{M_t} are typically reported per g catalyst.

2.13 Metal-Support Interactions (MSI)

A variety of metal-support effects can occur to alter the adsorptive and/or catalytic behavior of a metal surface, and these include: 1) Incomplete reduction of the metal; 2) Support-induced cluster size; 3) Epitaxial growth; 4) Particle morphology; 5) Contamination by the support; 6) Bifunctional catalysis; 7) Spillover and porthole phenomena; and 8) Charge transfer between a metal and a semiconductor [2]. In addition, one might cite the stabilization of extremely small (1-3 atom) metal clusters on a support [7].

Also, there is one additional type of metal-support effect that was originally termed SMSI (Strong Metal-Support Interactions) by the researchers at Exxon, where it was discovered [8], and its presence using a reducible oxide support was demonstrated by a marked decrease in H_2 and CO chemisorption capacity, especially the former, with no increase in metal crystallite size, i.e., no decrease in dispersion [8]. This was subsequently shown to be primarily due to reduction of the support accompanied by its migration or the migration of one of its suboxides onto the metal surface, thus causing decreased chemisorption capacity due to physical blockage of

surface sites, rather than due to any significant electronic interaction [9,10]. However, this “SMSI” state, which is typically induced by a high-temperature reduction in H₂, was found to have a major synergistic effect on certain types of hydrogenation reactions, particularly those involving hydrogenation of a carbonyl bond [11–14], and this is attributed to the creation of new active sites at the metal-support interface due to the removal of oxygen atoms from the surface of the oxide lattice structure [13–16]. This latter situation is the one which is most appropriately designated as an MSI (Metal-Support Interaction) effect.

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Vannice, M.A.

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