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# An analysis of the Mars–van Krevelen rate expression

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## Abstract

An analysis of the ''mechanism'' and the assumptions incorporated into the derivation of the Mars–van Krevelen rate expression for heterogeneously catalyzed oxidation reactions reveals a number of inconsistencies. The expression as derived is properly applicable only for a reaction involving molecular oxygen adsorbed on a single site; however, the model assumes that lattice O ions (or atoms) react with the substrate being oxidized. Furthermore, the steps describing the model are not elementary steps and, in addition, the competitive adsorption of intermediates and products is not considered. Consequently, the original derivation is incorrect and this rate expression must be viewed only as a mathematical data-fitting function. Alternative Langmuir–Hinshelwood, Hougen–Watson-type catalytic sequences can typically provide similar, and sometimes identical, rate equations which can fit rate data better than, or at least as well as, the Mars–van Krevelen expression. These latter models also provide rate parameters that can be evaluated for thermodynamic consistency.

*Keywords:* Kinetics; Mars–van Krevelen rate expression; Langmuir–Hinshelwood; Hougen–Watson rate expressions; Oxidation; O atoms

Researchers in catalysis, or in any other field for that matter, should be thorough in their awareness, review, and citation of previous relevant work, not only to avoid ''rediscovering the wheel'', but also to assess the validity and completeness of these earlier studies. For instance, during the learning process, it is important to understand the rationale and any assumptions that are incorporated into the derivation of a particular rate expression. An appropriate example of this is the Mars–van Krevelen rate expression, which invokes a surface redox mechanism and has been used to describe rates of oxidation reactions on heterogeneous oxide catalysts for over 50 years [1]. Although their rate expression has been frequently cited and utilized, I cannot find any paper that has analyzed and assessed the kinetic steps comprising their ''mechanism'' for this general reaction and has evaluated the assumptions resulting in the final rate equation. This paper, therefore, constitutes such an effort. It will show that the derivation is erroneous and that the rate expression reported in their paper (the subscript R refers to the reactant being oxidized):

$$r_R = \frac{1}{1/k_1 P_R + \beta/k_2 P_{O_2}^n} = \frac{k_1 k_2 P_R P_{O_2}^n}{k_1 P_R + k_2 P_{O_2}^n} \quad (1)$$

is inapplicable for any value of $n$ other than unity, and even then the equation is inconsistent with the assumptions made in the model.

In their study utilizing vanadium oxide catalysts, Mars and van Krevelen investigated the oxidation of benzene to benzoquinone, maleic anhydride, $CO_2$, CO and $H_2O$, toluene to benzaldehyde and benzoic acid, naphthalene to naphthoquinone and phthalic anhydride, and anthracene to anthraquinone and phthalic anhydride. They also applied their rate equation to data reported in the literature for $SO_2$ oxidation to $SO_3$ over various vanadium oxide-based catalysts (1). Their reaction ''mechanism'' was written as follows:

I. aromatic compound + oxidized catalyst $\xrightarrow{k_1}$ oxidation products + reduced catalyst
II. reduced catalyst + oxygen $\xrightarrow{k_2}$ oxidized catalyst

The following assumptions were then made:

(1) the reaction in step I is first order with respect to the reactant and the fraction of sites covered by oxygen, $\theta$;
(2) certain lattice O ions at the surface are involved in the oxidation reaction in step I;
(3) only O ions (atoms) are assumed to exist on these sites (no reactant or products);

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(4) the rate of surface reoxidation (step II), i.e., $O_2$ adsorption, is proportional to $P_{O_2}^n$ and to the concentration of active sites not covered by oxygen, i.e., $1-\theta$.

Based on these assumptions, these two steps above can be more correctly represented by the following two equations:

$$R + x\,O - S \xrightarrow{k_1} \text{Products} + x\,S \tag{2}$$

$$\left(\frac{x}{2}\right)[2S + O_2 \xrightarrow{k_2} 2O - S] \tag{3}$$

where S represents an active site (a lattice surface vacancy). Their derivation is as follows [1]. From step I:

$$r_R = k_1 P_R \theta \tag{4}$$

and from step II:

$$r_{O_2} = k_2 P_{O_2}^n (1-\theta) \tag{5}$$

If the oxidation of one aromatic molecule requires β molecules of $O_2$, then

$$r_R = \frac{r_{O_2}}{\beta} \tag{6}$$

and at steady state:

$$\beta k_1 P_R \theta = k_2 P_{O_2}^n (1-\theta) \tag{7}$$

Consequently,

$$\theta = \frac{k_2 P_{O_2}^n}{\beta k_1 P_R + k_2 P_{O_2}^n} \tag{8}$$

and from Eqs. (4) and (8) the final rate expression is that given by Eq. (1).

Let us now examine the problems associated with this particular model:

(A) First and foremost, from the kinetic theory of gases, the rate of adsorption of a molecule on vacant sites is always directly proportional to its pressure [2]; therefore, step II is valid only when $n = 1$. Furthermore, Eq. (5) represents only single-site adsorption because if two sites were required, $(1-\theta)^2$ would be used, thus molecular $O_2$ adsorption on a single site is indicated. However, the oxidation of the reactant is assumed to involve O lattice ions, which necessitates $O_2$ dissociation into atoms or ions prior to reaction. This omitted step constitutes a major inconsistency in the model.

(B) Step I is clearly not an elementary step and the probability of a single multi-body interaction between an aromatic molecule and surface oxygen atoms to produce all the products is clearly essentially zero. Thus a sequence of elementary steps constituting the surface oxidation process is a much more correct way to represent the chemistry associated with step I. Note that the simplest reaction studied, toluene oxidation to benzaldehyde:

$$C_6H_5CH_3 + O_2 \rightarrow C_6H_5CHO + H_2O \tag{9}$$

requires two O atoms if it occurs with 100% selectivity, which is highly unlikely, and if this occurs as a single elementary step it still requires, as a minimum, the breaking of three bonds and the formation of three bonds simultaneously, which is highly improbable. An even more extreme case is the oxidation of naphthalene to phthalic anhydride, which requires a minimum of nine O atoms:

$$C_{10}H_8 + \tfrac{9}{2}O_2 \rightarrow C_6H_4(CO)_2O + 2CO_2 + 2H_2O \tag{10}$$

The obvious requirement of multiple bond breaking and bond making clearly eliminates the possibility of the Rideal–Eley reaction represented by step I.

(C) Finally, an additional limitation exists because no intermediate species or final products (or reactant other than oxygen) are included in the site balance—only O ions (atoms) are considered even though only nondissociative $O_2$ adsorption is represented by step 2, as written.

As a result of this analysis, one concludes that, although a surface redox mechanism may properly describe the oxidation process, the rate expression derived by Mars and van Krevelen is inconsistent and incorrect, and it must be viewed only as a mathematical data-fitting function with no physical relevance.

Having said this, it is fair to ask if other surface redox rate expressions, based on valid kinetic steps, can be derived which provide rate equations identical or similar to Eq. (1). First, in a catalytic sequence of irreversible steps, if the surface intermediate involved in the last step is the most abundant reactive intermediate (*mari*), then the only two kinetically significant steps are the first one and the last one [3]. Consequently, steps I and II can be more properly represented as a series of irreversible elementary steps, if desired, without complicating the kinetic rate expression significantly because oxidation reactions are quite irreversible in nature and adsorbed oxygen in some form is very possibly the *mari.* Second, the possibility of an activated $O_2$ molecule adsorbed on a lattice vacancy (an active site) can be considered. Now, if the very simplest oxidation reactions are examined, i.e., the addition of either an $O_2$ molecule or an O atom to the reactant with no by-products, they can be respectively represented as

$$R + O_2 - S \xrightarrow{k_1} RO_2 - S \tag{11}$$

$$RO_2 - S \xrightarrow{k_2} RO_2 + S \tag{12}$$

$$\underline{O_2 + S \xrightarrow{k_3} O_2 - S} \tag{13}$$

$$R + O_2 \rightarrow RO_2 \tag{14}$$

and

$$R + O_2 - S \xrightarrow{k_1} RO + O - S \tag{15}$$

$$R + O - S \xrightarrow{k_2} RO + S \tag{16}$$

$$\underline{O_2 + S \xrightarrow{k_3} O_2 - S} \tag{17}$$

$$2R + O_2 \rightarrow 2RO \tag{18}$$

even though whether all steps can be considered to be elementary is questionable. Regardless, one sees in either case that $r_1 = r_2 = r_3$ at steady state, and $r_R = 2r_1$ in the latter sequence. If the adsorbed oxygen is molecular and $O_2$–S is the *mari*, then a site balance gives:

$$\theta_{O_2} = \frac{k_3 P_{O_2}}{k_1 P_R + k_3 P_{O_2}} \quad (19)$$

and the final rate equation is identical to the Mars–van Krevelen expression with $n = 1$:

$$r_R = \frac{k_1 k_3 P_R P_{O_2}}{k_1 P_R + k_3 P_{O_2}} \quad (20)$$

or, in the latter sequence:

$$r_R = \frac{2 k_1 k_3 P_R P_{O_2}}{k_1 P_R + k_3 P_{O_2}} \quad (21)$$

Alternatively, if one considers a Hougen–Watson (H–W) model assuming desorption of the product, either $RO_2$ or RO, is the rate determining step (rds) with all previous elementary steps quasi-equilibrated, for example:

$$\mathrm{R + S} \underset{\ominus}{\overset{K_R}{\rightleftharpoons}} \mathrm{R{-}S} \quad (22)$$

$$\mathrm{O_2 + S} \underset{\ominus}{\overset{K_{O_2}}{\rightleftharpoons}} \mathrm{O_2{-}S} \quad (23)$$

$$\mathrm{R{-}S + O_2{-}S} \underset{\ominus}{\overset{K_3}{\rightleftharpoons}} \mathrm{RO_2{-}S + S} \quad (24)$$

$$\mathrm{RO_2 - S} \xrightarrow{k_4} \mathrm{RO_2 + S} \quad (25)$$

and then assumes that the active sites are nearly saturated with adsorbed R and adsorbed oxygen so that the vacant site concentration is extremely low [4], then the H–W rate expression involving nondissociative $O_2$ adsorption is

$$r_R = \frac{k_{O_2} P_R P_{O_2}}{K_R P_R + K_{O_2} P_{O_2}} \quad (26)$$

and for a similar sequence involving dissociative $O_2$ adsorption it is

$$r_R = \frac{k_O P_R P_{O_2}^{1/2}}{K_R P_R + K_{O_2}^{1/2} P_{O_2}^{1/2}} \quad (27)$$

These two equations are identical to the Mars–van Krevelen rate expression for $n = 1$ and 1/2, respectively; however, it can be readily argued that product desorption in an oxidation reaction is unlikely to be a rds. Regardless, the $K_R$ and $K_{O_2}$ parameters represent adsorption equilibrium constants which can be evaluated for their validity [3,4].

If the Mars–van Krevelen assumption that lattice O ions are involved in the reaction is enforced, then, from steps 4 and 5, the simplest reaction sequence is

$$\mathrm{O_2 + 2S} \xrightarrow{k_1} \mathrm{2O - S} \quad (28)$$

$$\underline{2[\mathrm{R + O - S} \xrightarrow{k_2} \mathrm{RO + S}]} \quad (29)$$

$$\mathrm{2R + O_2 \rightarrow 2RO} \quad (30)$$

The rate is $r_R = k_2 P_R \theta_O$ and at steady state:

$$\frac{d[O - S]}{dt} = 2k_1 P_{O_2} \theta_v^2 - k_2 P_R \theta_O = 0 \quad (31)$$

where $\theta_v$ is the fraction of empty sites and the overall site density, $L$, is incorporated into $k_1$ and $k_2$. If only O atoms (ions) are included in the site balance, then

$$1 = \theta_O + \theta_v \quad (32)$$

and

$$\theta_O = \frac{2k_1 P_{O_2} (1 - \theta_O)^2}{k_2 P_R} \quad (33)$$

thus the rate contains a quadratic solution for the surface coverage of oxygen ions and a Mars–van Krevelen expression is not obtained. If a much less likely, but possible, sequence involving a three-body interaction resulting in the simultaneous addition of two O atoms is considered, steps 4 and 5 give:

$$\mathrm{O_2 + 2S} \xrightarrow{k_1} \mathrm{2O - S} \quad (34)$$

$$\mathrm{R + 2O - S} \xrightarrow{k_2} \mathrm{RO_2 - 2S} \quad (35)$$

$$\mathrm{R + O_2 \rightarrow RO_2} \quad (36)$$

The rate is now $r_R = k_2 P_R \theta_O^2$ and at steady state:

$$\frac{d[O - S]}{dt} = 2k_1 P_{O_2} \theta_v^2 - 2k_2 P_R \theta_O^2 = 0 \quad (37)$$

If only O atoms are included in the site balance, the final rate is

$$r_R = \frac{k_1 k_2 P_R P_{O_2}}{\left(k_2^{1/2} P_R^{1/2} + k_1^{1/2} P_{O_2}^{1/2}\right)^2} \quad (38)$$

which again does not conform to the Mars–van Krevelen rate expression given by Eq. (1).

It is now worthwhile to consider some Langmuir–Hinshelwood (L–H) rate expressions that could easily represent more realistic reaction models, i.e., the rds is an elementary step occurring on the surface and all other steps are quasi-equilibrated. One reaction model that results in an equation similar to Eq. (1) is a bimolecular surface reaction between R adsorbed on one type of site ($S_1$) and oxygen adsorbed on another, such as a lattice vacancy ($S_2$). Considering the different size and chemistry of the R molecule, this may well be a very reasonable assumption. If an irreversible reaction with an adsorbed activated $O_2$ species to form $RO_2$ is chosen, then, if only adsorbed R and $O_2$ are the dominant surface species, the rate expression is [4]:

$$r_R = \frac{k' P_R P_{O_2}}{(1 + K_R P_R)(1 + K_{O_2} P_{O_2})} \tag{39}$$

which has similarities to Eq. (1) with $n = 1$ if the pressure terms are large relative to unity, but $K_R$ and $K_{O_2}$ again represent adsorption equilibrium constants, which can be evaluated to determine if the model is physically and thermodynamically consistent [3,4]. Alternatively, if only a single O atom is added to produce RO, then the rate expression is [4]:

$$r_R = \frac{k' P_R P_{O_2}^{1/2}}{(1 + K_R P_R)(1 + K_{O_2}^{1/2} P_{O_2}^{1/2})} \tag{40}$$

which has similarities to Eq. (1) with $n = 1/2$. Over a limited range of pressures, these latter two expressions will have the capability to fit data as well as, or better than, Eq. (1), because of an additional fitting parameter.

If adsorption of R and oxygen on the same type of site (lattice vacancies) is assumed, then the denominator in the rate expression, which reflects the site balance, will be squared and, if addition of the first O atom is the rds, it has for an irreversible reaction the form [4]:

$$r_R = \frac{k' P_R P_{O_2}^{1/2}}{(1 + K_R P_R + K_{O_2}^{1/2} P_{O_2}^{1/2})^2} \tag{41}$$

if only adsorbed R and oxygen are included in the site balance. If the rds involves an $O_2$ molecule to form $RO_2$ as a product and again the site balance includes only adsorbed R and oxygen, the rate expression is

$$r_R = \frac{k' P_R P_{O_2}}{(1 + K_R P_R + K_{O_2} P_{O_2})^2} \tag{42}$$

Alternatively, if addition of two O ions (atoms) occurs sequentially to form $RO_2$ as a product, with addition of the second O atom being the rds, all other steps quasi-equilibrated, and only R and O atoms included in the site balance, the final rate expression is

$$r_R = \frac{k' P_R P_{O_2}}{(1 + K_R P_R + K_{O_2}^{1/2} P_{O_2}^{1/2})^2} \tag{43}$$

It is again highly likely that, with three fitting parameters, these latter two expressions can provide fits to kinetic data better than Eq. (1). Finally, it is very likely that sequences of irreversible elementary steps, more complicated than those shown in Eqs. (11)–(18) and possibly involving only lattice O ions, can be proposed which result in rate expressions similar to Eq. (1) which can fit rate data equally well after reasonable, appropriate and consistent assumptions are made to eliminate the contradictions contained in the Mars–van Krevelen model.

Finally, as a test of their model, the above authors applied it to rate data available for $SO_2$ oxidation to $SO_3$ over vanadia-based catalysts [1], the sequence of which was represented as

$$SO_2 + \text{Cat} - O \xrightarrow{k_1} SO_3 + \text{Cat} \tag{44}$$

$$\text{Cat} + O_2 \xrightarrow{k_2} \text{Cat}{-}O \tag{45}$$

where Cat–O and Cat correspond to the oxidized and reduced catalyst, respectively. Note that this does not represent a balanced sequence. Regardless, they cited reports that $SO_3$ strongly reduced the rate of $SO_2$ formation and assumed that a third reaction:

$$SO_3 + \text{Cat} \xrightarrow{k_3} SO_2 + \text{Cat}{-}O \tag{46}$$

was equilibrated and controlled the concentration of vacant sites (oxygen was not included). As a consequence, the derived rate expression had the form:

$$r_{SO_2} = \frac{k P_{SO_2} P_{SO_2}^n}{K P_{SO_2} + P_{SO_3}} \tag{47}$$

which they stated provided satisfactory fits to data from several studies, with $n = 1/2$ in one particular case. Now, one recognizes that a bimolecular reaction between $SO_2$ and O atoms in a rds assuming that two types of sites exist gives the following expression for a reversible reaction [4]:

$$r_{SO_2} = \frac{k_1 P_{SO_2} P_{O_2}^{1/2} - k_2 P_{SO_3}}{(1 + K_{SO_2} P_{SO_2} + K_{SO_3} P_{SO_3})(1 + K_{O_2}^{1/2} P_{O_2}^{1/2})} \tag{48}$$

which allows for a negative effect of $SO_3$ on the rate. However, even for an irreversible reaction, if $\theta_{SO_3}, \theta_{SO_2} \gg \theta_v$ on $S_1$ sites and $\theta_O \ll \theta_v$ on $S_2$ sites, the rate becomes:

$$r_{SO_2} = \frac{k P_{SO_2} P_{O_2}^{1/2}}{K_{SO_2} P_{SO_2} + K_{SO_3} P_{SO_3}} \tag{49}$$

which is identical to Eq. (47) with $n = 1/2$. Furthermore, if $\theta_O$ is not assumed to be very small, then $n$ can vary between 0 and 1/2. A similar sequence involving adsorbed $O_2$ molecules can give [4]:

$$\frac{k P_{SO_2} P_{O_2}}{(K_{SO_2} P_{SO_2} + K_{SO_3} P_{SO_3})(1 + P_{O_2})} \tag{50}$$

which is similar to Eq. (47) with $n = 1$ and now allows values of $n$ from zero to unity.

In summary, the Mars–van Krevelen kinetic model for redox oxidation reactions on solid catalysts, as originally stated, is inconsistent and incorrect. Consequently, the rate expression derived from this model is inapplicable except for one particular situation involving the adsorption of $O_2$ molecules on a single site; however, in this instance the model is still inconsistent because O ions (or atoms) are proposed as the reactive oxygen species rather than adsorbed $O_2$ molecules. As a result, the form of the rate expression in Eq. (1) has no physical relevance and must be viewed only as a mathematical fitting function. Alternate kinetic models, such as Langmuir–Hinshelwood and Hougen–Watson-type catalytic sequences can typically provide similar, if not identical, rate equations which can fit rate data better than, or at least as well as, the Mars–van Krevelen rate expression.

## References

[1] P. Mars, D.W. van Krevelen, Chem. Eng. Sci. 3 (Special Suppl.) (1954) 41.
[2] D.O. Hayward, B.M.W. Trapnell, Chemisorption, Buttersworth, London, 1964.
[3] M. Boudart, AIChE J. 18 (1972) 465.
[4] M.A. Vannice, Kinetics of Catalytic Reactions, Springer, 2005.