



Modified Rate Law for Bimolecular Reactions: Applicable to Surface as well as Non-surface Reactions

GAMI GIRISHKUMAR BHAGAVANBHAI¹ and RAWESH KUMAR^{2*}

¹Department of Chemistry, Sankalchand Patel University, Gujarat, India.

²Department of Chemistry, Indus University, Ahmedabad, India.

*Corresponding author E-mail: kr.rawesh@gmail.com

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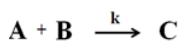
ABSTRACT

The rate equations in kinematics are expressed through basic laws under surface reaction as well as non-surface reaction. Rate law is center theme of non-surface reaction whereas Langmuir adsorption isotherms are basis of surface reaction rate expressions. A modified rate equation for bimolecular reaction is presented which considers both catalyst surface affairs as well as fraction of successful collision of different reactant for cracking and forming bonds. The modified rate law for bimolecular reaction for surface as well as non-surface reaction is stated as "Rate of a reaction is directly proportional to concentration as well as catalyst surface affair of each reactant" as $r = k \Omega_A [A] \Omega_B [B]$ where catalyst surface affair of i^{th} species is defined as $\Omega_i = K_i / (1 + K_i [i] + K_j [j] + \dots)$. Here, K_i is the equilibrium constant of " i " species for adsorption-desorption processes over catalyst. i, j, \dots indicates the different adsorbed chemical species at uniform catalyst sites and the same $[i], [j], \dots$ indicates the concentration of different adsorbed chemical species at uniform catalyst sites.

Keyword: Surface Reaction, Non-surface reaction, Modified Rate law, Bimolecular reaction, Catalyst surface affair.

INTRODUCTION

The rate law is the center of all rate expressions for non-surface reactions. The core of the rate law is embedded in kinetic theory of collisions with the assumption that fraction of collisions having enough energy leads molecular vibration and thereafter breaking/forming of new bonds¹. Simply for a second order reaction, rate is directly proportional to different concentration of reactants.



$$r = k [A] [B]$$

(1)

If surface reactions are included, the rate of reaction can be broadly assigned as interaction between two adsorbed chemical species (on catalyst surface) or interaction between adsorbed species (on catalyst) and non-adsorbed species (expressed in term of concentration/pressure) or interaction between non-adsorbed species in the reaction mixture. For the first case, interaction between the two adsorbed species can be shown by product of surface coverage of both different species over the catalyst surface as shown in Scheme 1(1). For second case, interaction between one adsorbed and one non-adsorbed species can be shown by product of



$$\Omega_i = K_i / (1 + K_i [i] + K_j [j] + \dots) \quad (11)$$

Where K_i is the equilibrium constant of “i” species for adsorption-desorption processes over catalyst. i, j, k, ... indicates the different adsorbed chemical species at uniform catalyst sites and the same [i], [j], [k], ... indicates the concentration of different adsorbed chemical species at uniform

catalyst sites. So in the catalyst surface affairs of one species, there will be contributions of another species also which are adsorbed on uniform catalyst sites (as “i” and “j” species are adsorbed on metal atom sites of catalyst).

The equation (11) can be presented as described below.

$$\Omega_{\text{particular species}} = \frac{\text{Equilibrium constant of the particular species}}{1 + (\text{Sum of products of Equilibrium constant and concentration of each adsorbed species at uniform catalyst sites})}$$

So, for a reaction pattern where reactants A and B are adsorbed on uniform catalyst surface (Langmuir-Hinshelwood uniform surface,) and then adsorbed species undergo for a reaction and liberates product C as presented below.

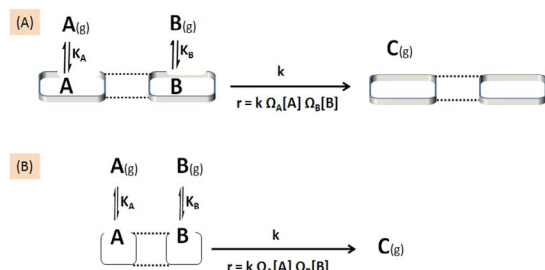


Fig. 1. (A) Scheme of reaction: A and B in gas phase interact with the surface and then undergoes a reaction which yields in product C. (B) Quick presentation of Scheme of reaction

Then catalyst surface affairs of A and B species are defined as

$$\Omega_A = K_A / (1 + K_A [A] + K_B [B]) \quad (12)$$

$$\Omega_B = K_B / (1 + K_A [A] + K_B [B]) \quad (13)$$

So, rate of surface reaction can be found by putting equation 12 and 13 in modified rate equation, $r = k \Omega_A [A] \Omega_B [B]$

$$r = k \left(\frac{K_A}{(1 + K_A [A] + K_B [B])} \right) [A] \left(\frac{K_B}{(1 + K_A [A] + K_B [B])} \right) [B] \quad (14)$$

$$r = k K_A [A] K_B [B] / (1 + K_A [A] + K_B [B])^2 \quad (15)$$

Synthesis of ammonia by N_2 and H_2 over Fe_2O_3 catalyst is the simplest example of Langmuir-Hinshelwood uniform surface reaction. H_2 and N_2 are adsorbed dissociately over catalyst surface and then adsorbed atomic species “H” and “N” undergo reaction and liberate ammonia.

Case I. If product (C) will form and subsequently C interacts with the catalyst surface having adsorption phenomena. Then catalyst surface affair of reactant A and B are modified as below.

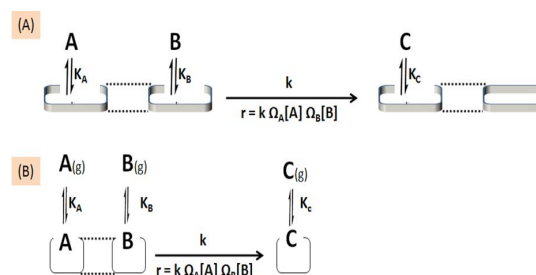


Fig. 2. (A) Scheme of reaction: A and B in gas phase interact with the surface and then undergoes a reaction which yields in product C. C again undergoes adsorption-desorption interaction with catalyst surface (B) Quick presentation of Scheme of reaction

$$\Omega_A = K_A / (1 + K_A [A] + K_B [B] + K_C [C]) \quad (16)$$

$$\Omega_B = K_B / (1 + K_A [A] + K_B [B] + K_C [C]) \quad (17)$$

So, rate of surface reaction can be finding by putting equation 15 and 16 modified rate equation,

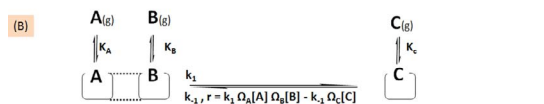
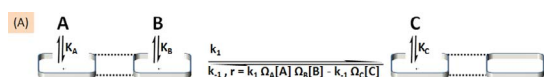
$$r = k \Omega_A [A] \Omega_B [B]$$

$$r = k \left(\frac{K_A}{(1 + K_A [A] + K_B [B] + K_C [C])} \right) [A] \left(\frac{K_B}{(1 + K_A [A] + K_B [B] + K_C [C])} \right) [B] \quad (18)$$

$$r = k K_A [A] K_B [B] / (1 + K_A [A] + K_B [B] + K_C [C])^2 \quad (19)$$

Case II. If product (C) will be adsorbed on uniform catalyst sites and further involve in reverse reaction. This time not only catalyst surface affairs of reactant A and B will be modified but also new affairs of C with catalyst surface should also be considered. The rate of reaction can be expressed as below:

$$r = k_1 \Omega_A [A] \Omega_B [B] - k_{-1} \Omega_C [C] \quad (18)$$



$$\Omega_A = K_A / (1 + K_A [A] + K_B [B] + K_C [C]) \quad (19)$$

$$\Omega_B = K_B / (1 + K_A [A] + K_B [B] + K_C [C]) \quad (20)$$

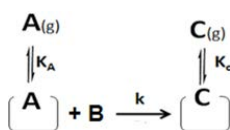
$$\Omega_C = K_C / (1 + K_A [A] + K_B [B] + K_C [C]) \quad (21)$$

So, rate of surface reaction can be found by putting equation 19-21 into equation 18.

$$r = \{k_1 K_A [A] K_B [B] / (1 + K_A [A] + K_B [B] + K_C [C])^2\} - \{k_{-1} K_C [C] / (1 + K_A [A] + K_B [B] + K_C [C])^2\} \quad (22)$$

Case III. If a reactant (say B) from the gas/solution reacts with an adsorbed reactant (say A) without adsorbing itself on the surface as in Eley-Rideal process⁶. This time non-adsorbed reactant (B) had no surface affairs on catalyst surface and so catalyst surface affairs of non-adsorbed reactant (B) should be removed from equation 10. Then the new rate expression will be as below:

$$r = k \Omega_A [A] [B] \quad (23)$$



$$\Omega_A = K_A / (1 + K_A [A] + K_C [C]) \quad (24)$$

So, rate of surface reaction can be found by putting eq (24) into eq. (23).

$$r = k K_A [A] [B] / (1 + K_A [A] + K_C [C]) \quad (25)$$

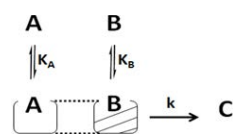
Hydrogenation of gaseous ethylene molecule by adsorbed hydrogen over Ni surface⁷, The esterification of "chemisorbed 1-hexene" with "heptanoic acid in bulk" over Amberlyst catalyst⁸ and the dimerization of chemisorbed alkene C8 and C24 linear alkenes in liquid phase over Amberlyst catalyst follow Eley-Rideal kinetics⁹.

Case IV. Another possibility may be that reactants (A and B) adsorbed on non-uniform surfaces of the catalyst (respect to each other

catalyst sites) or adsorbed at different sites of catalyst in close proximity (Langmuir-Hinshelwood non-uniform surface). Here, at one uniform catalyst surface only one species is adsorbed. So, in the catalyst surface affairs of one species, there will be no participation of another species which is adsorbed on different sites/non-uniform sites. The parts of catalyst which adsorb "i" species are different from those which adsorb "j" species.

The rate of reaction can be expressed as below:

$$r = k \Omega_A [A] \Omega_B [B] \quad (26)$$



$$\Omega_A = K_A / (1 + K_A [A]) \quad (27)$$

$$\Omega_B = K_B / (1 + K_B [B]) \quad (28)$$

So, rate of surface reaction can be found by putting eq (27 & 28) into eq. (26)

$$r = k K_A K_B [A] [B] / ((1 + K_A [A]) (1 + K_B [B])) \quad (29)$$

The reaction between hydrogen and nitrous oxide on gold¹⁰ and reaction between hydrogen and carbon dioxide on tungsten¹¹ are examples of such kinetics. Two gases H₂ and N₂O are adsorbed independently over gold, they react and form H₂O and N₂. In the same way, two gases H₂ and CO₂ are adsorbed independently over tungsten, they react and form H₂O and CO.

Case V. If neither's of reactants have catalyst surface affair or both reactants are simply interacting and finally gives the product C. Then, catalyst surface affairs of reactants A and B should be removed from equation 10. This time, the rate of reaction is same as rate law for second order reaction as equation (1).

$$A + B \xrightarrow{k} C$$

$$r = k [A] [B] \quad (30)$$

CONCLUSION

It can be concluded that the modified rate law for bimolecular reaction is easier and equally applicable to both surface reaction and non-surface reaction. Along with normal non-surface reaction,

all the case of surface reaction based on Langmuir-Hinshelwood uniform surface treatment, Eley-Rideal and Langmuir-Hinshelwood non-uniform surface treatment can be derived easily within couple of steps.

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Conflict of Interest

The authors declare that they have no known financial interests with the work reported in this paper.

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