APPENDIX-1
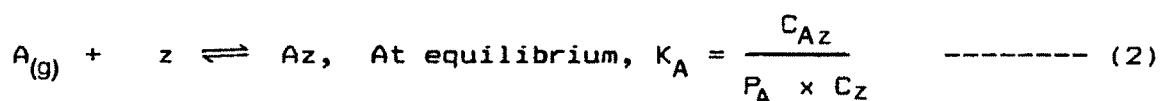
Derivation of Langmuir-Hinshelwood Type Models

The dehydrogenation of n-dodecane falls in the general class of reactions,
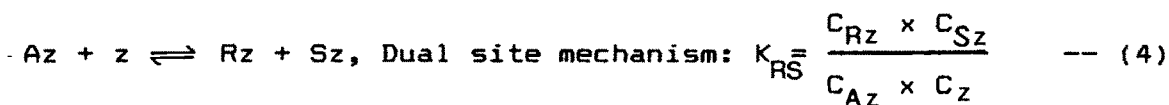
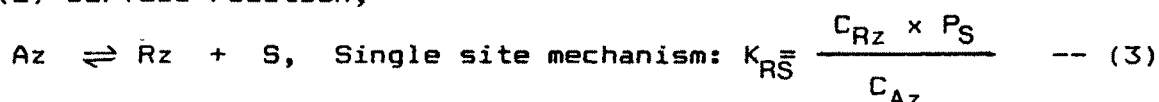$$A \rightleftharpoons R + S \tag{1}$$

The following three steps can be assumed to occur during the course of conversion of "A" to "R" and "S".

(1) Adsorption of reactant on to active site,
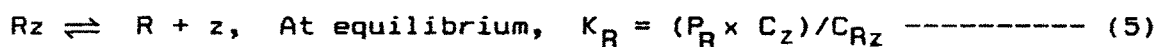
$$A_{(g)} + z \rightleftharpoons Az, \quad \text{At equilibrium,} \quad K_A = \frac{C_{Az}}{P_A \times C_z} \tag{2}$$

(2) Surface reaction,

$$Az \rightleftharpoons Rz + S, \quad \text{Single site mechanism:} \quad K_{RS} = \frac{C_{Rz} \times P_S}{C_{Az}} \tag{3}$$

$$Az + z \rightleftharpoons Rz + Sz, \quad \text{Dual site mechanism:} \quad K_{RS} = \frac{C_{Rz} \times C_{Sz}}{C_{Az} \times C_z} \tag{4}$$

(3) Desorption of products from the active sites,

$$Rz \rightleftharpoons R + z, \quad \text{At equilibrium,} \quad K_R = (P_R \times C_z)/C_{Rz} \tag{5}$$

$$Sz \rightleftharpoons S + z, \quad \text{At equilibrium,} \quad K_S = (P_S \times C_z)/C_{Sz} \tag{6}$$
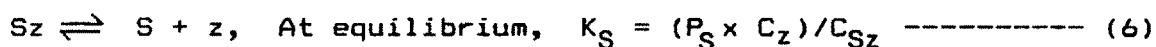
For further simplification it is assumed that only one of these steps is rate controlling. Thus, it is implicit that the other steps are at chemical equilibrium. Assuming that the dual site surface reaction step is rate controlling, the rate equation can be written as follows,

$$r_{SR} = k_{SR} \times C_{Az} \times C_z - k_{SR}^{-1} \times C_{Rz} \times C_{Sz} \tag{7}$$

Since all the other steps are assumed to be at equilibrium, the unknown surface concentration of adsorbed species A, R and S can be eliminated by means of the equilibrium relationships for these equations.

Therefore,

From equation (2) $C_{Az} = K_A P_A C_z$ ————————— (8)

From equation (5) $C_{Rz} = \dfrac{P_R C_z}{K_R}$ ————————— (9)

From equation (6) $C_{Sz} = \dfrac{P_S C_z}{K_S}$ ————————— (10)

Substituting into equation (7)

$$r_{SR} = k_{SR} K_A P_A C_z^2 - k_{SR}^{-1} \frac{P_R C_z}{K_R} \times \frac{P_S C_z}{K_S}$$

$$= k_{SR} K_A P_A C_z^2 - \frac{k_{SR}^{-1}}{K_R K_S} \times P_R P_S C_z^2$$

$$= k_{SR} K_A \left[P_A C_z^2 - \frac{P_R P_S}{K_{eq}} \times C_z^2 \right] \quad ————————————— (11)$$

The concentration of active sites is determined as follows:

Total number of sites, $Z = C_z + C_{Az} + C_{Rz} + C_{Sz}$ ————————— (12)

Again using the equilibrium relationships of eq. (2), (5) & (6)

$$Z = C_z + K_A P_A C_z + \frac{P_R C_z}{K_R} + \frac{P_S C_z}{K_S}$$

$$Z = C_z \left(1 + K_A P_A + K_R P_R + K_S P_S \right)$$

K_R & K_S now represent adsorption equilibrium constants.

Therefore, $C_z = Z / (1 + K_A P_A + K_R P_R + K_S P_S)$ —————————— (13)

Substituting in equation (11),

$$r_{SR} = \frac{k_{SR} K_A Z^2 (P_A - P_R P_S / K_{eq})}{(1 + K_A P_A + K_R P_R + K_S P_S)^2}$$

$$r_{SR} = \frac{k_{SR} K_A (P_A - P_R P_S / K_{eq})}{(1 + K_A P_A + K_R P_R + K_S P_S)^2} \quad ———————————— (14)$$

where $k_{SR} = k_{SR} \times Z^2$

Thus, equation (14) represents the rate equation for the reaction,

$$A \rightleftharpoons R + S,$$

with dual site surface reaction as the rate controlling step. Similarly, rate equations with the other three steps as rate controlling can be derived. The final forms of the equations are given below.

Model/Rate controlling step	Rate equation
Dual site adsorption of reactant	$r = \dfrac{k(P_A - P_R P_S / K_{eq})}{(1 + K_P P_R P_S / K_{eq} + K_R P_R + K_S P_S)}$
Dual site surface reaction	$r = \dfrac{k K_A (P_A - P_R P_S / K_{eq})}{(1 + K_A P_A + K_R P_R + K_S P_S)^2}$
Dual site desorption of product "R"	$r = \dfrac{k K_{eq} K_A (P_A / P_S - P_R / K_{eq})}{(1 + K_A P_A + K_{eq} K_R P_A / P_S + K_S P_S)}$
Dual site desorption of product "S"	$r = \dfrac{k K_{eq} K_A (P_A / P_R - P_S / K_{eq})}{(1 + K_A P_A + K_{eq} K_S P_A / P_R + K_R P_R)}$
Single site adsorption of reactant	$r = \dfrac{k(P_A - P_R P_S / K_{eq})}{(1 + K_P P_R P_S / K_{eq} + K_R P_R)}$
Single site surface reaction	$r = \dfrac{k K_A (P_A - P_R P_S / K_{eq})}{(1 + K_A P_A + K_R P_R)}$
Single site desorption of product "R"	$r = \dfrac{k K_{eq} K_A (P_A - P_R P_S / K_{eq})}{P_S + K_A P_A P_S + K_{eq} K_A P_A}$