A CNDO/2 study carried out on this system also predicted that the SiH radical was stable by 3.6 eV relative to SiH₄ + H. Of all the configurations considered, the lowest energy was found for the Cᵥ geometry.

The SCF calculation reported here was carried out primarily to study the importance of d functions on silicon, especially for SiH₄ where the coordination number of silicon is five. In addition the stability of SiH₄ relative to SiH + H is also examined.

The geometry of SiH₄ was taken from ref. 13. The present calculations indicate the importance of including polarization functions especially for SiR, with possible participation of 3d functions on silicon.

The geometry of SiH₄ was taken from ref. 13. The present calculations indicate the importance of including polarization functions especially for SiR, with possible participation of 3d functions on silicon.

The results of these calculations are given in Table 3. Both the calculations predict no stability for the SiH₄ radical relative to SiH + H. Although in the second calculation the difference is reduced, the effect of including 3d functions on silicon is appreciable for SiH₄, there being a decrease of 0.0565 a.u.

The present calculations indicate the importance of including polarization functions especially 3d functions for molecules containing second row atoms. The decrease in energy by the inclusion of d functions is much more for molecules containing second row atoms, with possible participation of d functions in bonding.

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References


Network Thermodynamic Modelling of Enzyme-catalysed Reactions

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The methods of linear network theory have been utilised to derive expressions for the steady state reaction velocity and the relaxation time for an enzyme catalysed reaction.

MEIXNER’s pioneering ideas on the relation between non-equilibrium transport processes and network theory have recently been extended to include the description and treatment of biological systems. The network approach is quite general and with modifications it can be applied widely to thermodynamic systems. This approach, indeed has several advantages. Not only does it provide an alternative formalism but it brings thermodynamics of irreversible processes within the framework of dynamical systems theory.

An attempt has been made to utilise the formalism of network thermodynamics to calculate the steady state reaction velocity and the relaxation time for an enzyme catalysed reaction, and the results are reported in this note.

Let us consider the well known enzyme catalysed reaction (1) involving two steps:

$$(1) \quad E + S = ES \quad k_1$$

$$(2) \quad ES \rightarrow E + P \quad k_2$$

where E, S, ES and P represent respectively enzyme, substrate, enzyme-substrate complex and product. If $J_1$ and $J_2$, respectively, represent the reaction rates of the steps (1) and (2), one can write

$$\frac{d[E]}{dt} = J_2 - J_1 \quad \ldots (2)$$

$$\frac{d[ES]}{dt} = J_1 - J_2 \quad \ldots (3)$$

$J_1$ and $J_2$ can be written in terms of the affinities $A_1$ and $A_2$ of the steps (1) and (2), i.e.

$$J_1 = k_1[E][S] \left\{ 1 - \exp \left( -\frac{A_1}{RT} \right) \right\} \quad \ldots (4)$$

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When the reaction is close to equilibrium Eqs (4) and (5) reduce to
\[
J_1 = k_1 [E] [S] \left( \frac{A_1}{RT} \right) \quad \text{and} \quad J_2 = k_2 [ES] \left\{ 1 - \exp \left( -\frac{A_2}{RT} \right) \right\} \quad \text{(5)}
\]

where \( R \) is the gas constant and the affinities \( A_1 \) and \( A_2 \) are defined as:
\[
A_1 = \mu_B + \mu_S - \mu_{ES}; \quad \text{and} \quad A_2 = \mu_{ES} - \mu_B - \mu_P, \quad \mu \text{ being the chemical potential of the species denoted by the subscripts.}
\]

Following the network thermodynamic considerations\(^{58}\) the chemical reaction system \( (1) \) can be represented by a two-port network shown in Fig. 1(a). The bond graph representation\(^{78}\) of the two-port network (Fig. 1(a)) has been shown in Fig. 1(b) where \((-\!-\!-\!-\!-)\) represents a parallel or a zero junction and \((-\!-\!-\!\!-\!-\!-)\) represents a series or a one junction. Applying Kirchoff’s voltage and current laws to the network shown in Fig. 1, we can write
\[
J_1 = \frac{\mu_S + \mu_B - \mu_{ES}}{R_1} \quad \text{and} \quad J_2 = \frac{\mu_{ES} - \mu_B - \mu_P}{R_2} \quad \text{(8)}
\]

where \( R_1 \) and \( R_2 \) are the resistive elements (Fig. 1). For the flow through the capacitors representing enzyme-substrate complex and enzyme, one can write
\[
J_1 = C_{ES} \frac{d[ES]}{dt} \quad \text{and} \quad J_2 = C_1 \frac{d[E]}{dt} \quad \text{(9)}
\]

Using Eq. (12), Eq (13) can be further transformed into Eq. (14).
\[
\mu_{ES} = \frac{R_2 [\mu_B + R_1 [\mu_P + R_2 [\frac{C_{ES}}{C_E + C_{ES}}] + \mu^* - \frac{C_{ES}}{C_E + C_{ES}}]}{R_1 + R_2} \quad \text{(14)}
\]

Equation (14) gives the value of \( \mu_{ES} \) at the steady state. Similarly for the value of \( \mu_B \) at the steady state we can write
\[
\mu_B = \frac{R_2 [\mu_B + R_1 [\mu_P + R_2 [\frac{C_E}{C_E + C_{ES}}] + \mu^* - \frac{C_E}{C_E + C_{ES}}]}{R_1 + R_2} \quad \text{(15)}
\]

Now substituting the steady state values of \( \mu_{ES} \) and \( \mu_B \) from Eqs (14) and (15) into Eq. (8) we get
\[
J = \frac{\mu_{ES} - \mu_P}{R_1 + R_2} \quad \text{(16)}
\]

Comparing Eqs (6) and (7) with Eqs (8) and (9) one can write
\[
R_1 = \frac{RT}{k_1 [E] [S]} \quad \text{and} \quad R_2 = \frac{RT}{k_2 [ES]} \quad \text{(17)}
\]

Substituting the values of \( R_1 \) and \( R_2 \) in Eq. (16) we get
\[
J = \left( \frac{A_1 + A_2}{RT} \right) \left( \frac{k_1 k_2 [E] [S]}{k_1 + k_2 [E] [S]} \right) \quad \text{(18)}
\]

Since at the steady state \([ES]/[E][S] = k/k'\), Eq. (18) can be rewritten in the form
\[
J = \left( \frac{A_1 + A_2}{RT} \right) \frac{k_1 [E] [S]}{K_m} \quad \text{(19)}
\]

where \( K_m \) is the well known Michaelis-Menten constant and is given by \( K_m = (k_e + k_i)/k_i \). Equation (19) arrived at from network consideration is an expression for the reaction velocity at the steady state.

When the concentration of the substrate greatly exceeds that of the enzyme and the enzyme-substrate complex, a steady state is reached. In the steady state flow through the enzyme-substrate capacitor and the enzyme capacitor ceases (Eq 10 and 11). For calculating the relaxation time for the chemical reaction system \( (1) \) one has to calculate the \( RC \) time for the network shown in Fig. 1. Making use of the Laplace transform method\(^8\) the \( RC \) time which
equals the relaxation time (τ) for the chemical reaction system (1) can be shown to be given by

$$\frac{1}{\tau} = \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \frac{1}{C_{ES}}$$ ...

Now making use of the definition of the generalised capacitance, i.e. \( C_{ES} = [ES]/[E][S] \), and substituting the values of \( R_1 \) and \( R_2 \) from Eq. (17) in Eq. (21) we can write

$$\frac{1}{\tau} = k_1 \frac{[E][S]}{[ES]} + k_2$$ ...

Since the equilibrium between enzyme, substrate and enzyme-substrate complex is reached very fast, the relation \( [ES]/[E][S] = k_1/k'_1 \) can be utilised to transform Eq. (22) into

$$\frac{1}{\tau} = k'_1 + k_2$$ ...

which gives an expression for the relaxation time in terms of the velocity constants.

The surface species formed during the oxidation of CO on ferrites of Co, Ni and Zn have been identified by IR spectroscopy to be various types of carbonate species.

It is known that on metal oxides the interaction of adsorbed CO either with lattice oxygen or with adsorbed oxygen does not result in the formation of CO₂ directly; most often it leads to the formation of a variety of intermediate carbonate type species. A variety of experimental techniques especially IR spectroscopy have been employed to confirm the formation and existence of such species originally proposed by Garner and coworkers on the surfaces of oxidation catalysts. Infrared spectroscopy (800-2400 cm⁻¹) has been employed in the present study to monitor and characterise the nature of the various types of species formed by the oxidation of CO on the surfaces of ferrites of Co, Ni and Zn.

Self-supporting discs of the catalyst prepared by pressing ∼ 80 mg of the material in a die at about 8 tons/cm² were kept in a cell attached to the adsorption apparatus and were treated in various ambient atmospheres at the selected temperatures. The cell was evacuated after quenching the disc to room temperature and the spectra recorded in a Beckmann IR 12 spectrometer. Details regarding the preparation of the catalysts and the apparatus used could be found in an earlier communication.

Adsorption of CO alone on fresh catalysts at room temperature did not give rise to any absorption bands. The catalysts were conditioned at 230°C with 1 torr of oxygen and the systems cooled to room temperature and evacuated. CO at 5 torr pressure was allowed to come in contact with these pretreated catalysts at room temperature. These catalysts were then evacuated after 5 hr to 10⁻⁸ torr and the spectra recorded. A number of new absorption bands in addition to the background absorption bands at 1050 and 1210 cm⁻¹ in the case of ZnFe₂O₄ in the region 1300-1700 cm⁻¹ attributable to various kinds of carbonate species have been recorded. In Table 1 the positions of the observed IR absorption bands under various experimental conditions employed are given together with the proposed assignments. For comparison the characteristic absorption frequencies reported in literature for the various types of species relevant to CO oxidation are recorded in Table 2. The analysis of the spectra obtained in the case of ZnFe₂O₄ and CoFe₂O₄ reveals that the interaction of CO with the surface leads to the formation of monodentate and bidentate (species A, B and C) carbonate species in addition to uncoordinated CO₃ (species D) and adsorbed CO. The observation that the conductivity of n-type ferrites increases with the adsorption of CO shows that it is probable that M-CO₂⁺ species is formed rather than neutral adsorbed species.