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EFFECT OF INTERACTION AND MOBILITY ON FIXED-BED REACTOR PERFORMANCE

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The roles of interaction and mobility in determining surface rates and hence reactor performance, as reflected in the space time values required for achieving a desired conversion or selectivity, are demonstrated. It is shown that localized adsorption models predict larger space times in comparison to the mobile models. Further, repulsive forces lead to higher space times in comparison to attractive forces, and the divergence between models is most marked for localized adsorption.
KEYWORDS Adsorption Surface heterogeneity Adsorbate interactions Selectivity Catalytic reactions Surface nonideality

INTRODUCTION

Rapid progress in surface science has revealed a rich variety of phenomena, such as phase transitions among adsorbed species, adsorbate restructuring and island formation (Ertl, 1983; Woodruff *et al.*, 1983; Madix, 1983; Somorjai, 1978), but these have not influenced reactor design concepts in any significant way. A wealth of new phenomena including the role of surface phase transformations in causing dynamic instability like oscillating rates have been uncovered (Ertl, 1985). Equally intriguing is the observation of island formation among adsorbed species (oxygen atoms in particular) as a prelude to catalytic reaction proper, observed in many oxidation reactions (Barteau *et al.* 1981; Gland *et al.*, 1982). Computer simulations (Silverberg *et al.*, 1985) as well as direct experimental observations (Gland and Kollin, 1983; Shigeishi and King, 1978) have unequivocally demonstrated that non-classical rate behaviour will be exhibited by these systems, primarily as a result of interactions between adsorbed molecules.

While it is impossible to model all these effects in their totality, some attempts have been made in the past to account for the role of interactions in determining activity and selectivity (Benziger and Madix, 1979; Zhadnov, 1981; Bhat *et al.*, 1984). The first paper (Benziger and Madix, 1979) analyzed the rate behavior using a first-order interaction model like the Fowler–Guggenheim model, the second dealt with a more refined quasi-chemical approximation model (Zhadnov, 1981), and in the third paper the important problem of selectivity patterns was analyzed by employing both these models (Bhat *et al.*, 1984).

A natural engineering consequence of these previous studies is the need to address the questions: How significant are these effects in determining reactor performance? Do the gross rates (which are obtained by averaging the point rates over the entire reactor length) still reflect the subtleties of interaction or are they masked? Does refinement in accounting for interaction effects change the picture dramatically? The last question is of particular importance as the computational effort increases substantially with refinement to account for interactions.

A closely related problem is that in many experimental systems the adsorbate phase becomes mobile at temperatures close to those at which catalysis occurs. Thus conventional engineering models (in which molecules are assumed to be nailed to the surface sites) would become unrealistic and it would be necessary in such cases to consider adsorbate mobility superimposed on interaction effects.

The main objectives of the work are:

(1) By using accurate numerical methods, to demonstrate the significant role of interactions (attractive and repulsive) in determining the reactor performance, as indicated by the space time needed for achieving a desired conversion.

(2) To assess the necessity for refinements in accounting for interactions between adsorbed molecules and the consequent effects on reactor performance.

Throughout the paper, the analysis will be confined to the simplest possible model—the plug flow reactor—so as to focus attention on the main theme of the work. Further, to make the analysis tractable only simple reaction schemes are used.

FORMULATION

In the presentation that follows, single step control (i.e. surface reaction control) will be assumed. It will also be assumed that the adsorption-desorption steps are so fast compared to surface reaction that adsorption equilibrium prevails between the gas and surface phases at all pressures. Thus the surface and gas concentration can be related through adsorption isotherms, and expressions can be readily written for the surface rates. All the products of reaction are assumed to be weakly bound, so that they are readily desorbed under conditions of reaction.

The reaction schemes chosen are presented in Table I. All the reaction schemes are important in analyzing hydrocarbon conversions (Davis and Somorjai, 1983). Reaction schemes I and II are first- and second-order, respectively, but occur without a net change in the overall number of molecules. In schemes III and IV, respectively, volume expansion and contraction occur. Hypothetical schemes I, III, IV idealize key steps in metal catalyzed isomerization and acid catalyzed isomerization in reforming. In contrast to this, scheme II represents an acid catalyzed disproportionation reaction. In scheme III a net volume expansion occurs. This could correspond to a metal catalyzed dehydrogenation step.

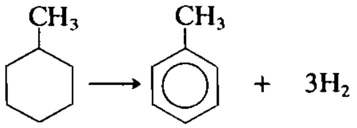

TABLE I

Reaction schemes studied in the present work

$$A_g \underset{k_d}{\overset{k_a}{\rightleftarrows}} A_s$$

$$A_s \xrightarrow{k_1} B_g$$

Scheme I, $\varepsilon = 0$

$$A_g \underset{k_d}{\overset{k_a}{\rightleftarrows}} A_s$$

$$2A_s \xrightarrow{k_2} C_g + D_g$$

Scheme II, $\varepsilon = 0$

$$A_g \underset{k_d}{\overset{k_a}{\rightleftarrows}} A_s$$

$$A_s \xrightarrow{k_1} E_g + F_g$$

Scheme III, $\varepsilon = 1$

$$A_g \underset{k_d}{\overset{k_a}{\rightleftarrows}} A_s$$

$$2A_s \xrightarrow{k_2} P_g$$

Scheme IV, $\varepsilon = -1/2$

$$A_g \underset{k_d}{\overset{k_a}{\rightleftarrows}} A_s$$

$$A_s \xrightarrow{k_1} B_g$$

$$2A_s \xrightarrow{k_2} C_g + D_g$$

Scheme V, $\varepsilon = 0$

The volume change factor ε is defined as the ratio the net number of molecules produced to the number of reactant molecules. Thus for the reaction by stochiometry ε is 3. Now if the mole fraction of the reactant is f, the actual volume change factor would be $f\varepsilon$. Thus with $(f = 1/3)$ the actual volume change factor is unity. A choice of unity for ε is thus not unreasonable for real applications. However, for the reaction scheme III, A_S would represent an adsorbed cyclohexane molecule, E_g, F_g denote desorbed cyclohexene and hydrogen respectively. For this reaction, the stochiometric ε is unity, and the pure feed $(f = 1)$ is assumed for the computations. Scheme IV could, in a sense, represent a dimerization step through a carbonium ion mechanism. There is a net decrease in the volume in this case. Thus it will be an ideal counterpart to reaction scheme III.

Reaction scheme V is the simplest one can construct by combining the schemes mentioned above and wherein the question of selectivity figures. Thus in this scheme we look for divergence in the selectivity behavior of the various models in addition to that in the rate behavior. This is the simplest reaction scheme which is describable in terms of one-component adsorption theory and which in a transparent way demonstrates the novel features of reactor selectivity as a consequence of the nonidealities.

THE ADSORPTION MODELS

The adsorption models chosen in the present work can be classified roughly into two types, viz. localized and mobile. It is to be noted that virtually all the formulations of heterogeneous kinetics assume the molecules to be nailed to the surface (the classical checker board picture suggested originally by Langmuir). Although the possibility exists that in many realistic adsorption systems the adsorbate phase may be partially mobile, the theoretical treatment of such a situation is beyond the scope of the present work. All the models of isotherms studied are presented in Table II.

For the localized adsorbate the simplest model accounting for interactions is the Fowler–Guggenheim (FG) model (Fowler and Guggenheim, 1939), considering only nearest neighbour interactions derived on the basis of what is called the bond-approximation (Honig, 1967). In contrast to this, a more refined approximation is the so-called quasi-chemical (QC) approximation which considers pairs of molecules adsorbed on adjoining sites that are considered to be independent (Hill, 1956; Bhat *et al.*, 1984; Zhadnov, 1981; Fowler and Guggenheim, 1939).

The principal parameter ω (interaction energy between adsorbed molecules) which appears in the localized models is usually evaluated by LEED measurements through the construction of an adsorbate phase digram. A thorough scan of the literature failed to provide independent estimates of the interaction parameters for molecules in a reforming network (similar to that involving xylene, toluene, etc.). However, the correct magnitude of the interaction parameter is between 0.5 and 1.5 kcal/mole (Silverberg *et al.*, 1985) and our choice conforms to this. z denotes the coordination number of the lattice which is 4 in our work (i.e. a square lattice).

The FG and QC models can be formulated for multicomponent adsorption as

TABLE II

Isotherms and Adsorption parameters

Localized	Mobile
Fowler–Guggenheim (FG)	Hill-de Boer (HD)
$p = b_0 \exp(-Q/RT)(\theta/1-\theta)\exp(A\theta/RT)$	$p = b_0 \exp(-Q/RT)(\theta/1-\theta)\exp(A_1\theta)\exp(\theta/1-\theta)$
Quasi-Chemical (QC)	Simple Free Volume (SFV)
$p = b_0 \exp(-Q/RT)(\theta/1-\theta)$ $\times [(2-2\theta)/(\beta+1-2\theta)]^z$ $\beta = [1-4\theta(1-\theta)(1-\exp(-\omega_1))]^{0.5}$	$p = (b_0/4)[\theta/(1-\theta^{0.5})^2]\exp(\theta^{0.5}/1-\theta^{0.5}$ $+A_1\theta - Q/RT)$

b_0(localized) = IE 8 Torr, b_0(mobile) = IE 5 Torr, $Q = 17$ Kcal/mole, $A = z\omega$, $z = 4$(square lattice), $A_1 = \alpha\omega/RT$, $\omega_1 = \omega/RT$, ω(repulsive) = 1.25 Kcal/mole, ω(attractive) = -0.75 Kcal/mole, α(mobile) = 4.

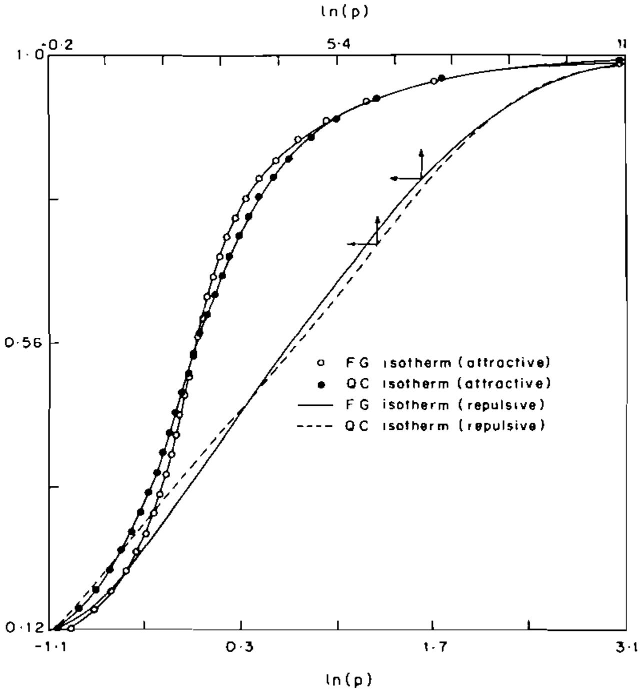

FIGURE 1 Comparison of Fowler Guggenheim and Quasichemical isotherms. $b_0 = 1E8$ Torr, $Q = 17$ Kcal/mole. ω(repulsive) = 1.25 Kcal/mole, ω(attractive) = −0.75 Kcal/mole.

well. This would involve solving two simultaneous nonlinear equations for the FG model (two surface coverages). But the QC method is much more complex to apply, and involves solving 9 highly nonlinear simultaneous equations (six pair probabilities of all the possible molecular pairs and three surface coverages, i.e. of the two components and the vacant site). However, this has been done (to be published) but it is too complex a topic to be dealt with here.

For the mobile model an equation analogous to the two-dimensional van der Waals equation† (otherwise known as the Hill–de Boer equation) (Hill, 1956; de Boer, 1953) will be considered for describing equilibrium adsorption. Further, as a first order refinement, the model derived on the basis of a simple free volume approach (SFV) (van Dongen, 1970) will also be used to see how far the predictions based on this model would be different from those based on the simpler Hill–de Boer model. The mobile model also can be extended to deal with multicomponent adsorption but we do not discuss this problem here.

All the isotherms reduce to Henry's law isotherms at low pressure, i.e. $\theta \rightarrow 0$.

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† By statistical mechanics we can derive an equation analogous to the two-dimensional van der Waals equation for mobile chemisorption. However the constants appearing in such an equation (for mobile chemisorption) have no simple interpretation in terms of two-dimensional critical constants for the physisorbed state.

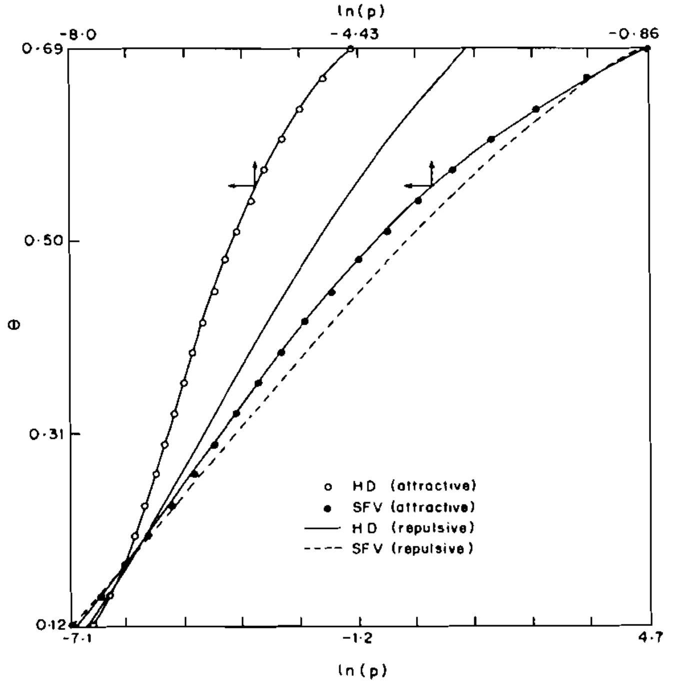

FIGURE 2 Comparison of Hill–de Boer and simple Free Volume approach isotherms. $b_0 = \text{IE}\,5$ Torr, $Q = 17$ Kcal/mole. Interaction parameter for repulsive and attractive cases are 1.25 Kcal/mole and −0.75 Kcal/mole respectively.

The parameters b_0 and Q which appear in the models denote the entropy change factor ($e^{\Delta S/R}$) and heat of adsorption. Values of $b_0 = \text{IE}\,8$ ($\Delta S \cong -37$ e.u) and $b_0 = \text{IE}\,5$ ($\Delta S \cong -23$ e.u) are employed for the localized and mobile models respectively. The initial heat of adsorption is 17 kcal/mole for all the models which is a representative value in accordance with the literature value.

Figures 1 and 2 illustrate the differences between the localized and mobile models and also between the operation of diametrically opposite type of forces namely, repulsive and attractive types. Notice the large variation of surface coverage with pressure in a narrow range of pressure for the localized model, both for the FG and QC models for the attractive interaction model. Also notice the appreciable differences for the same coverage between the pressure values for the repulsive and attractive type models especially in the high coverage region.

Figure 2 deals with the Hill-de Boer (HD) and the Simple Free Volume (SFV) models. In the HD model the adsorbate phase is assumed to be mobile (in the sense of a two dimensional gas) while in SFV model the molecule is allowed to translate freely in a cage bounded by the neighbouring molecules. The divergence between the SFV and HD models is much more than the corresponding localized models.

THE BASIC EQUATIONS AND NUMERICAL METHODS TO CALCULATE SPACE TIME

Since in all the reaction schemes presented in Table I, surface reactions are controlling and adsorption-desorption steps are so fast that adsorption equilibrium is rapidly established, one can easily write expressions for surface rates directly as functions of adsorption isotherms $\theta(T, p)$. Thus for an nth order surface reaction:

$$r_n = k_n\theta^n(T, p) \tag{1}$$

the space time τ can be easily related to the inlet partial pressure p_0, molar feed rate F and exit conversion level x_e as

$$\tau = (W/F) = \int_0^{x_e} \frac{dx}{r_n(x, T, p_0)} = \int_0^{x_e} \frac{dx}{k_n\theta^n(x, T, p_0)} \tag{2}$$

The surface coverage was calculated as a function of pressure using a chord (regula falsi) method. 8 point Gaussian quadrature was used with the following substitutions

$$x = \tfrac{1}{2}(x_e + x_i) + \tfrac{1}{2}(x_e - x_i)y \tag{3}$$

where x_i, x_e denote the inlet and exit conversions, respectively. In order to ensure high accuracy the basic interval $(0, 1)$ has been split into subintervals $(0, 0.1)$, $(0.1, 0.2)$ etc. and the quadrature formulae given below applied for each of the subintervals.

$$\tau = W/F = (x_e - x_i)/2 \int_{-1}^{1} \frac{dy}{r_n'(y, p_0)} \tag{4}$$

$$\tau = (x_e - x_i)/2 \sum_{K=1}^{K=8} A_k/r_n'(y_k, p_0) \tag{5}$$

where A_k are the quadrature weights, y_k are the roots of the kth order Legendre polynomial (Van der Graft, 1978), and $r_n'(y, p_0)$ is the transformed rate in terms of y, p_0.

LOCALIZED ADSORPTION WITH INTERACTIONS

First-order reactions

The role of interactions can be demonstrated by calculating the space time needed for achieving a desired conversion using the FG model with repulsive interactions. Table III presents the values of space time for both FG and QC models as a function of the interaction parameter ω at sufficiently high value of inlet pressure and a high exit conversion level. Notice the strong influence of the interaction parameter on the space time values and the ratio of space times can be

TABLE III

Space time variation with interaction energy ω for first, and second order reactions: FG and QC models $p_0 = 10\,\text{Torr}$, $x_e = 0.9$

	FG Model		QC Model	
ω Kcal/mole	τ First	τ Second	τ First	τ Second
−1.25	—	—	0.90726	0.91461
−1.0	0.920142	1.05212	0.92256	0.94625
−0.75	0.969543	1.01108	0.97965	1.07816
−0.50	1.142808	1.568908	1.148298	1.574871
−0.25	1.45335	2.676868	1.453805	2.66868
0	1.85322	4.348157	1.85322	4.348157
0.25	2.273073	6.438212	2.266057	5.568910
0.5	2.680975	8.829367	2.637835	8.498596
0.75	3.071456	11.46276	2.951252	10.49956
1.0	3.445823	14.30756	3.207217	12.28536
1.25	3.806352	17.34477	3.412781	13.81957

as large as 14 if we consider attractive and repulsive models especially for second order reactions. Notice that for the value of interaction parameter lower than −1, the FG isotherm predicts a loop (corresponding to a phase transition) in the $\theta - p$ plane. Hence we have not studied influence of the interaction parameter for lower values of ω for the FG model. The QC isotherm predicts a phase transition only if the value of the interaction parameter is greater than 1.36 in absolute magnitude. The interaction parameter is chosen (especially for attractive case) such that the phase transition region is excluded.

Figure 3 shows a plot of space time as a function of conversion and inlet concentration for a first-order reaction. As is obvious, at low inlet partial pressures the space time values (for various conversion levels) are considerably larger. Besides, the spread of space times is much greater at low inlet partial pressures. The calculations were performed for an adsorption heat $Q = 17\,\text{kcal/mole}$, which is a representative value in agreement with previous studies (Bhat *et al.*, 1985; Prasad and Doraiswamy, 1983).

In Figure 4 the corresponding values of space time for the QC model for a square lattice are plotted. Clearly, the refinements in accounting for interactions have a larger effect at higher inlet partial pressures (and consequently at higher surface coverages), and do not manifest themselves at low pressures. Also, at higher pressures, say at $p_0 = 10\,\text{Torr}$, the maximum deviation was found to be 10% at the highest conversion level of 90%.

From Figures 3 and 4 it is obvious that qualitatively the behavior of the QC and FG isotherms is the same except for some minor variations at high inlet partial pressures and conversions. Thus it is as if the refinements in accounting for the interactions are smoothened out by the process of integration. But the divergence between the FG and QC models is appreciable for second order reactions (see

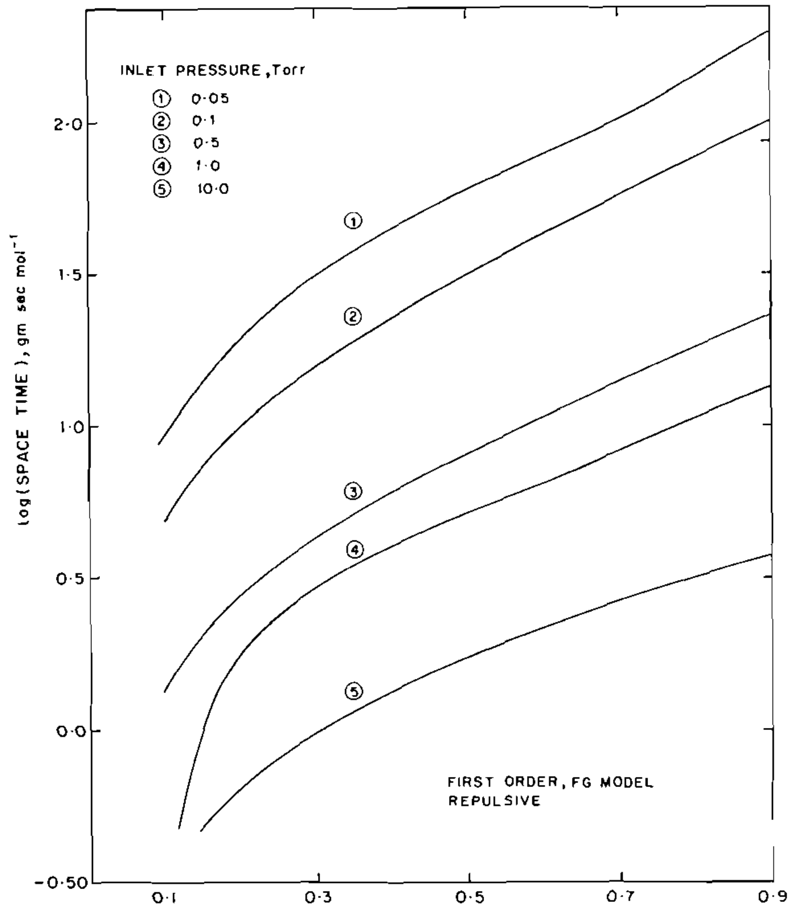

FIGURE 3 Plot of space time as a function of exit conversion for the Fowler–Guggenheim (FG) isotherm with repulsive interactions at various inlet partial pressures p_0. First order reaction.

Table III). Since the QC model is more accurate from a theoretical viewpoint, this model will be employed here for dealing with localized adsorption.†

Next, the effects of volume change are considered in Figure 5 (scheme III) for the QC model with repulsive interactions. As expected, since the concentration at any point in the reactor decreases due to volume expansion, the space time is correspondingly larger. The increase in space time is most apparent at low inlet partial pressures and high conversions. The maximum deviation in space time (≅50%) compared to the case of no volume change occurs at an inlet pressure of

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† The quasichemical approximation predicts different values of space time for $z = 6$ and $z = 4$. These are usually comparable except at high inlet partial pressures. Hence in subsequent work it will be assumed that $z = 4$ (a square lattice).

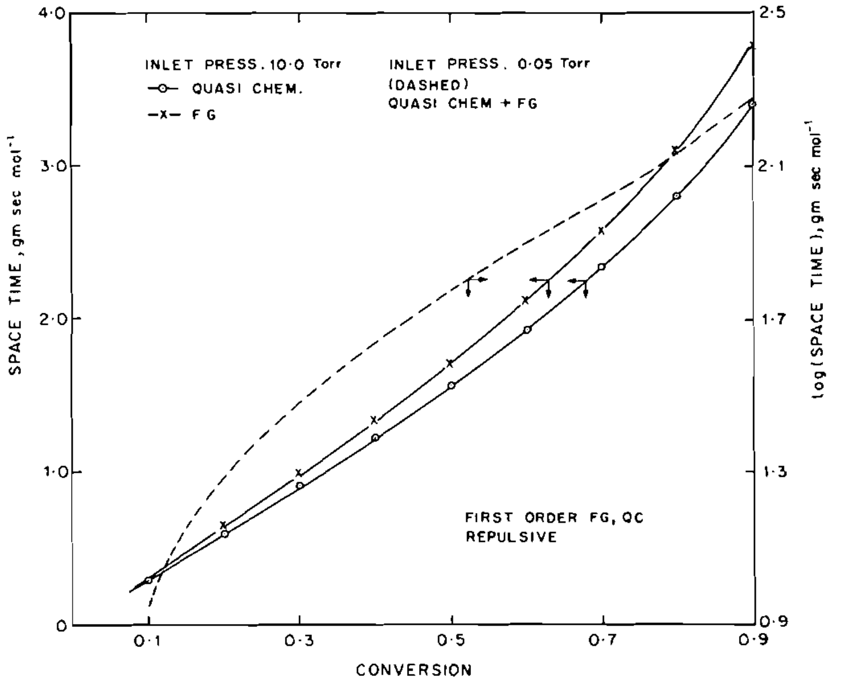

FIGURE 4 Comparison of space times for the FG and quasi-chemical isotherms (QC) with repulsive interactions as a function of exit conversion for two inlet partial pressures, $p_0 = 0.05$ Torr, and $p_0 = 10$ Torr. First order reaction.

0.05 Torr, i.e. $p_0 = 10$ Torr, by those of interaction and this falls to about 8% in the high pressure region, where the effects due to volume change are nullified.

Further we consider the qualitatively different effects when the type of interaction changes from repulsive to attractive. The nature of interaction energies and their magnitudes have been considered in detail elsewhere (Bhat *et al.*, 1984). At sufficiently high values of the interaction parameter there is a possibility of phase transitions (and phase separations) existing in the adsorbed phase. However, for the interaction parameter value chosen, this is not observed in the present study. In Figure 6 the space time-conversion behavior is illustrated for the case of attractive interactions between adsorbed molecules. At low inlet partial pressures, since the surface coverage is generally small on all the patches, the contribution of interaction energy to the adsorption heat is not appreciable. Thus the QC model with attractive and repulsive interactions predicts nearly identical space times at very low inlet partial pressures. Since the rates are higher in the attractive case, the attractive model predicts lower space times in the entire range of partial pressures. However the most dramatic difference can be illustrated at 10 Torr inlet pressure. While the attractive interaction model predicts nearly zero-order behavior with space time numerically equal to the conversion, the repulsive interaction model predicts space time values which can be four-fold higher, especially at the highest conversion level $x_e = 0.9$.

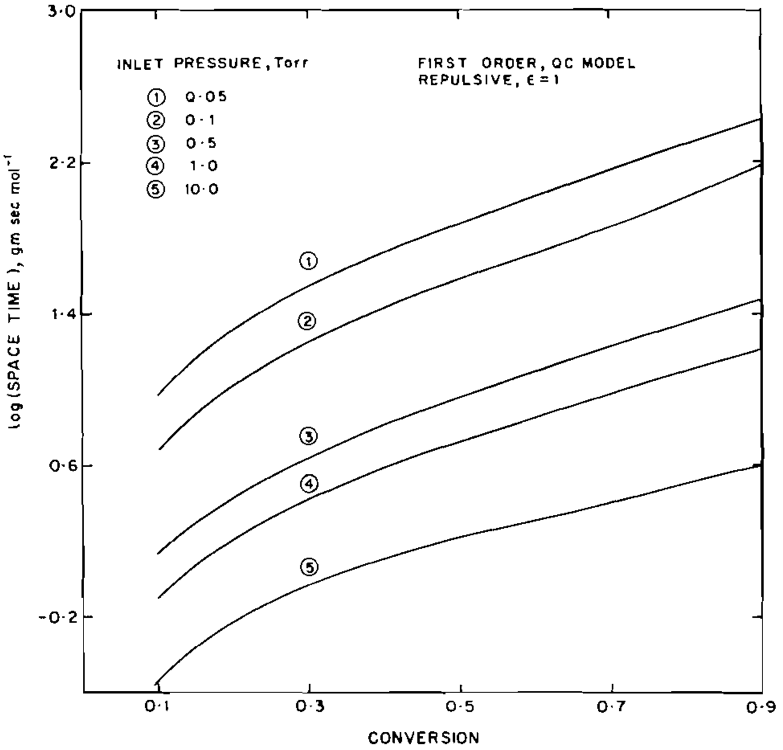

FIGURE 5 Space time conversion plots for the QC isotherm (repulsive) with volume expansion, $\varepsilon = 1$. First order reaction.

In Figure 7 we consider again the attractive QC model with volume expansion. If we compare Figures 5 and 7 the maximum difference in space times is again manifested at 10 Torr inlet partial pressure, which once again corresponds roughly to 400%. Thus we see that in a suitable concentration range (inlet partial pressure) discrimination between attractive and repulsive models can be achieved. More importantly, qualitative differences between the attractive and repulsive models are reflected in the values of space time needed for achieving a desired conversion even in the presence of volume expansion.

Second-order reactions

The analysis can be readily extended to second-order surface reactions to see whether the qualitative differences between attractive and repulsive models are present or magnified for second-order surface reactions. As before, in Figures 8 and 9 the space time is plotted as a function of conversion and inlet partial pressure for the repulsive and attractive QC models. Since the surface coverage and rates are very small at low inlet partial pressures, the space time values are unusually large and for representative purposes are shown on the logarithmic scale. As in the case of a first-order reaction, maximum divergence between the

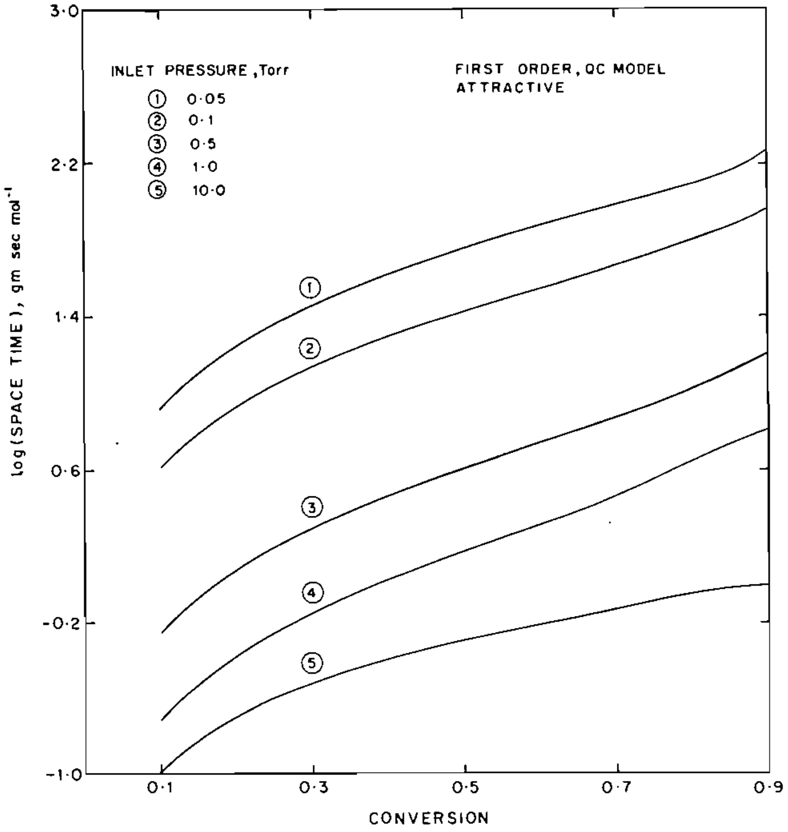

FIGURE 6 Space time conversion plots for the QC isotherm (attractive). First order reaction.

space times is observed at 10 Torr inlet partial pressure (a factor of 13). Thus we see that in the case of a second-order reaction the space time values show larger divergence than for the first-order case, illustrating a greater role of interaction effects in determining reactor performance.

Next the effects of a reduction in volume (see reaction scheme IV) are considered. Since the effect of volume contraction is to increase the gas and surface concentrations, the space times are smaller compared to the case of no volume change. In Figure 10 the ratio of space times is shown for the attractive and repulsive models at two inlet partial pressures and 10 Torr. Even though the ratio of space times is smaller in comparison to the case of no volume change, one can easily notice a variation by a factor of 10.6 in this ratio. *It may therefore be concluded that volume expansion or contraction does not mask the effects due to attractive or repulsive interactions, as clearly reflected in the respective space time values needed for achieving a desired conversion.*

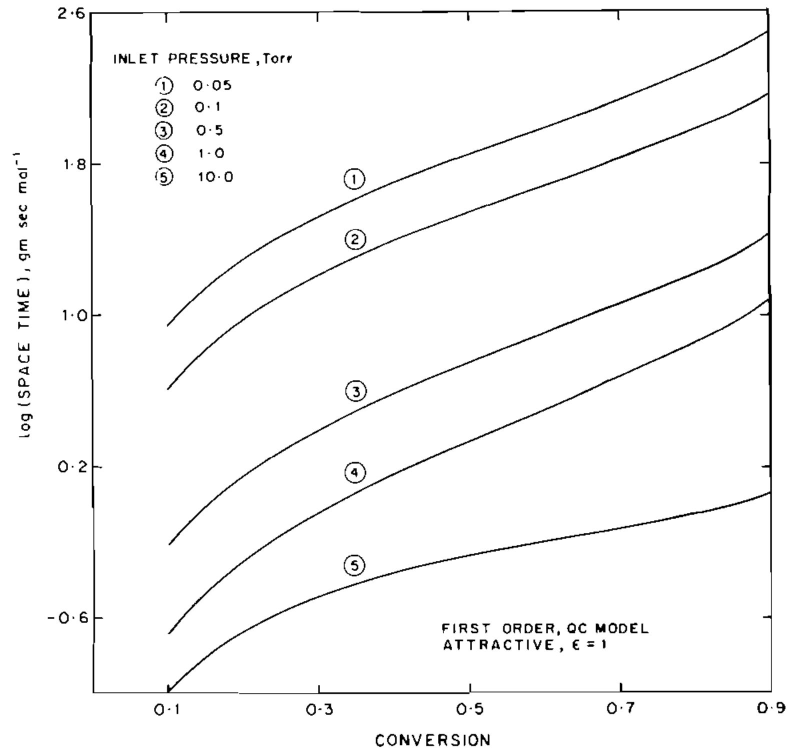

FIGURE 7 Space time conversion plots for the QC isotherm (attractive) with volume expansion, $\varepsilon = 1$. First order reaction.

MOBILE ADSORPTION

First-order reactions

For the case of mobile adsorption we consider the simple mobile model of Hill-de Boer (HD) and the refined model derived on the basis of the simple free volume approach (SFV). The difference between the two models, though not appreciable, is nevertheless higher than that observed between the QC and FG models. SFV predicts space time values which show a maximum variation of 30% compared to HD. Further, SFV predicts much smaller space times than HD.

Since the mobile adsorbed phase has two additional degrees of freedom, the entropy change factor of the mobile model is assumed to be much smaller (IE 5 in contrast to IE 8) than that of the localized models. As a consequence, the surface coverage values are higher than for the localized models at a given pressure. Since the rates are determined by surface coverage it is obvious that the space time values will be correspondingly smaller. In the present work attention is restricted to mobile adsorption using SFV.

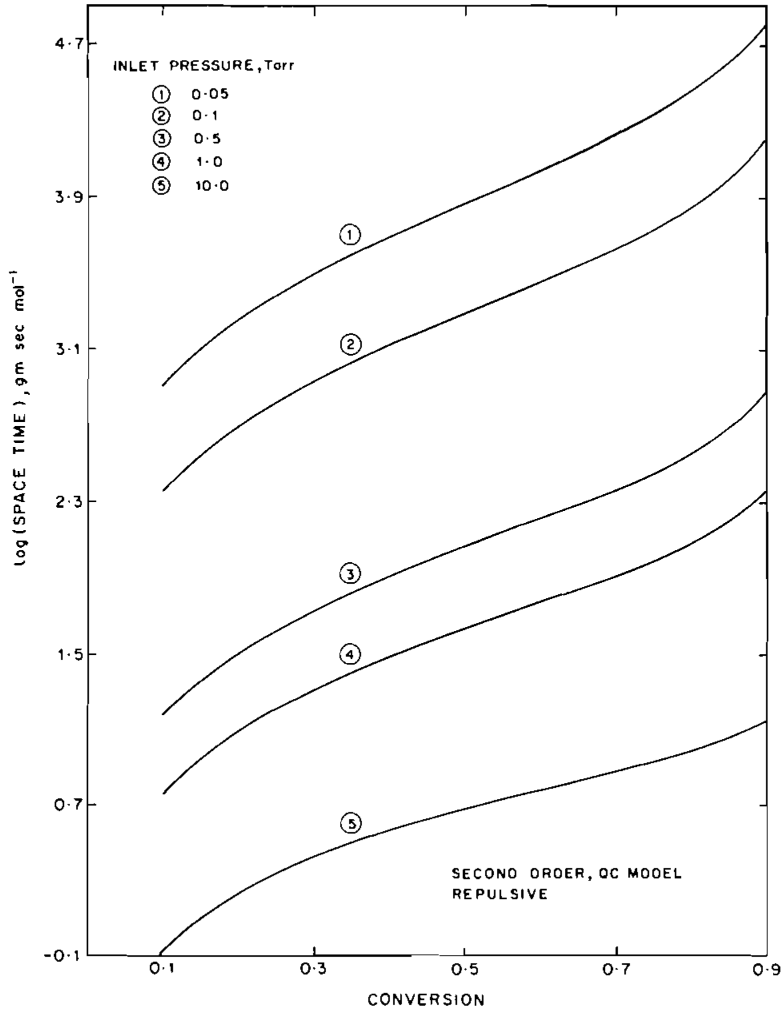

FIGURE 8 Space time conversion plots for the QC isotherm (repulsive). Second order reaction.

In Figures 11 and 12 the space time is plotted as a function of conversion and inlet concentration for the case of no volume change, for the repulsive and attractive models, respectively. In contrast to the localized adsorption models, we investigate the space time behavior in a lower range of inlet partial pressures. For such a range the difference between attractive and repulsive interaction models amounts to a factor ≃1.8, almost half of what is observed for the case of the localized models.

In the region of inlet partial pressures studied in the present work, volume change ($\varepsilon = 1$, corresponding to expansion) has negligible effect on the values of space time (maximum deviation of 10%) unlike in the case of localized models where the space times could be different by as much as 50%.

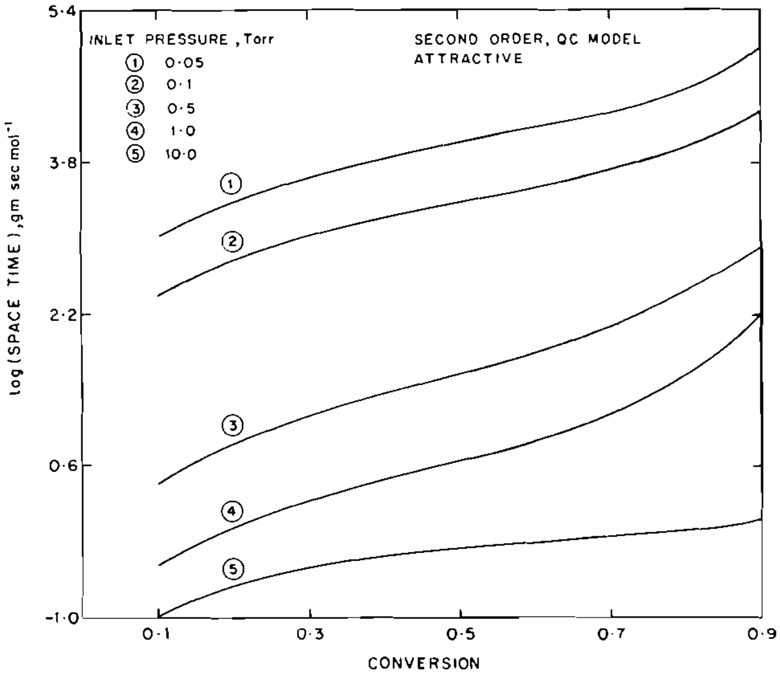

FIGURE 9 Space time conversion plots for the QC isotherm (attractive). Second order reaction.

Second-order reaction

It remains to be seen whether a significant difference in space time values between the attractive and repulsive models is shown for SFV in the case of second-order reactions. The difference is of a lower order of magnitude for the mobile models than for the localized models, nevertheless significant as illustrated in Figure 13. Also, it may be noticed that since the surface coverage and rates are appreciable for the mobile model even at the low inlet partial pressures used in the present study, the space time value required for achieving a desired conversion is much lower for the mobile model in comparison to the localized models for comparable values of inlet partial pressure and exit conversion.

INFLUENCE OF INTERACTIONS ON SELECTIVITY: LOCALIZED ADSORPTION

Since in many industrial reactions, the question of selectivity figures more prominently than that of activity, it would be desirable to investigate the influence of interactions and mobility on the selectivity of reaction scheme V. This scheme could be synthesized from a right combination of reaction schemes I and II. Therefore the analysis developed in previous sections could be very easily

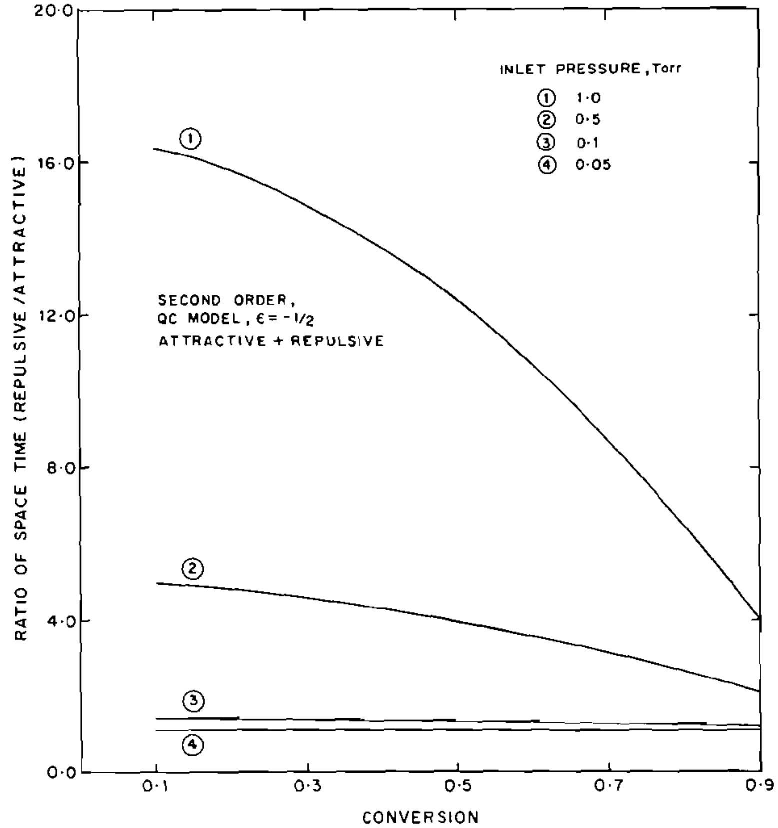

FIGURE 10 Comparison of space times of the QC isotherm for both repulsive and attractive forces as a function of exit conversion with volume contraction, $\varepsilon = -1/2$. Second order reaction.

adapted to deal with such a situation. Although this reaction scheme is hypothetical, it could form one of the subschemes of the more complex reforming network.

Since selectivity behavior is considered, the problem may be posed as follows: for a given inlet pressure and ratio of intrinsic kinetic constants, what is the conversion level at which a desired average selectivity is achieved? This definition of average selectivity is essential since the selectivity at every point of the reactor varies with the distance.

Let the selectivities with respect to first- and second-order reactions be denoted by S_1 and S_2 (see scheme V).† Then

$$S_1 = \frac{k_1\theta_A}{1 + k_1\theta_A + k_2\theta_A^2} = \frac{1}{1 + \dfrac{k_2}{k_1}\theta_A} \tag{6}$$

$$S_2 = 1 - S_1 \tag{7}$$

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† Conventionally selectivity is defined as the ratio of the rate of specific reaction (summed from the inlet to the outlet) to the overall rate. However in actual practice the computed values of selectivities using this approach and our approach yielded almost identical results.

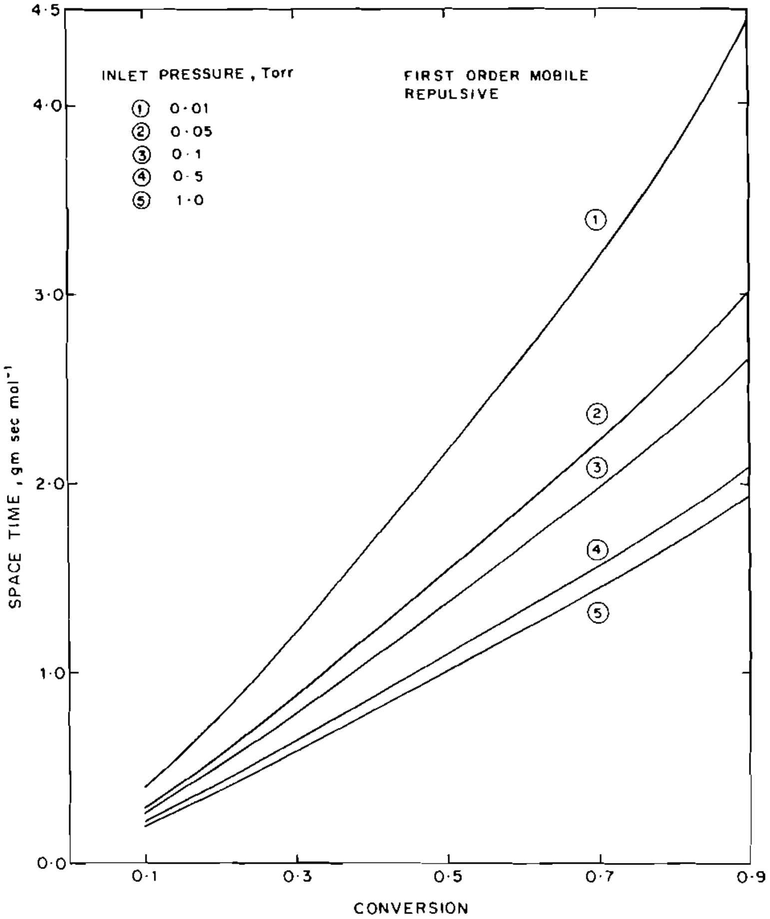

FIGURE 11 Space time consersion plots for the refined mobile model based on a simple free volume approach (SFV). The repulsive interactions are studied. First order reaction.

Since in a PFR the selectivity is a function of the conversion x_e, we define an average selectivity as

$$\bar{S}_1 = \int_0^{x_e} S_1(x)\, dx/x_e \tag{8}$$

$$\bar{S}_2 = \int_0^{x_e} (1 - S_1(x))\, dx/x_e = 1 - \bar{S}_1 \tag{9}$$

Using these definitions and Eq. (2) one can easily calculate $\bar{S}_1$, $\bar{S}_2$. Note that the integrals in Eqs. (8) and (9) can be evaluated using a quadrature formula similar to Eq. (5).

In practice, we would like to calculate the conversion x_e at which $\bar{S}_1/\bar{S}_2$ has the desired value after fixing the inlet concentration p_0. If we denote this ratio by λ

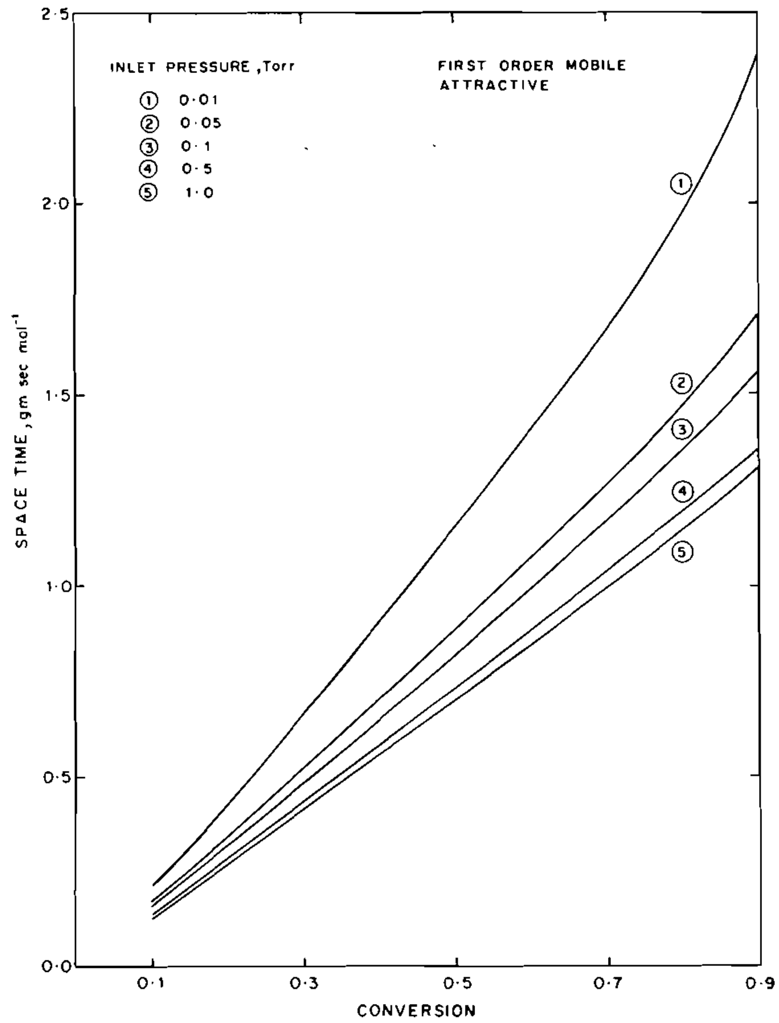

FIGURE 12 Space time conversion plots for the mobile SFV isotherm (attractive). First order reaction.

then,

$$\lambda = \frac{\bar{S}_1}{\bar{S}_2} = \frac{\bar{S}_1}{1 - \bar{S}_1} \tag{10}$$

and we have

$$\bar{S}_1 = \lambda/(1+\lambda) \tag{11}$$

Using a quadrature formula for $\bar{S}_1$ we get a nonlinear equation involving 8 terms for x_e in Eq. (9). x_e can be solved for by using a variant of the chord method.

Once the desired selectivity $\bar{S}_1$ (corresponding to a given ratio) is achieved, it is

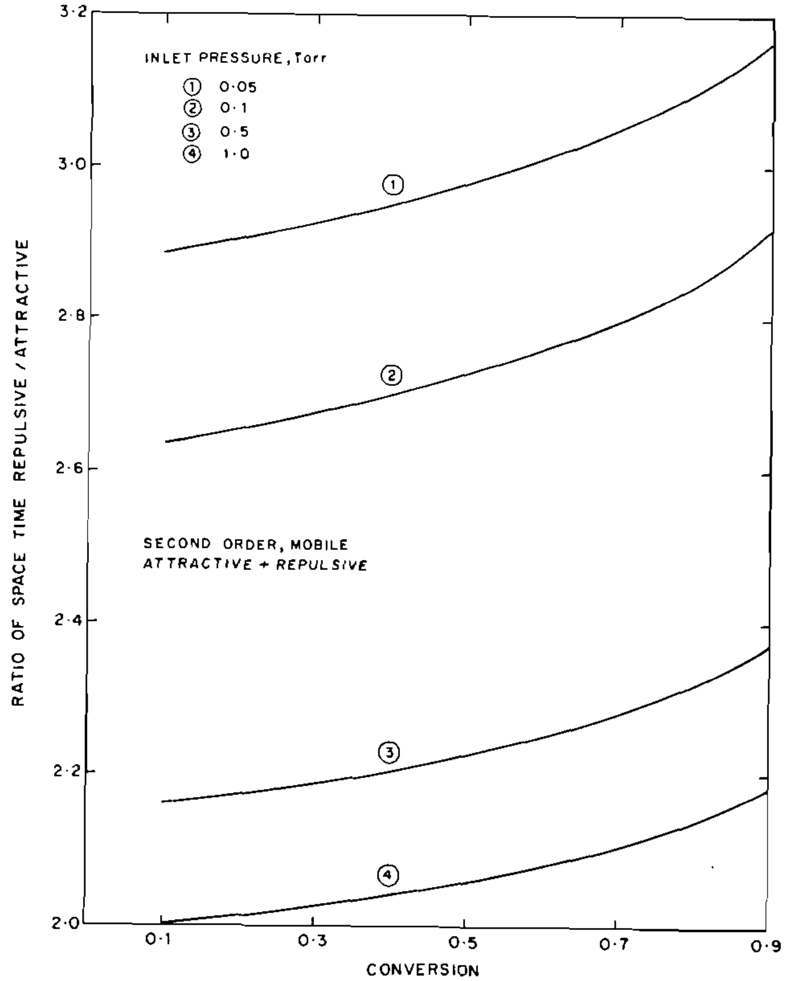

FIGURE 13 Comparison of space times of the SFV isotherm for both repulsive and attractive models as a function of exit conversion.

a straight forward matter to compute the space time needed for achieving the conversion (for a fixed value of p_0). But the space time will have to be computed by considering the overall rate of conversion of A as the sum of first- and second-order steps, i.e.

$$\tau_{1+2} = (W/F) = \int_0^{x_e} \frac{dx}{r_1(x, T, p_0) + r_2(x, T, p_0)} \tag{12}$$

Once again the 8-point quadrature formula is used to compute τ_{1+2} which denotes the space time needed for achieving the desired conversion when both first- and second-order surface reactions are simultaneously occurring.

A few facts are immediately apparent when we consider Eq. (8) for the mean selectivity. At very high inlet pressures, since θ approaches unity, θ_A is independent of pressure. Therefore we have

$$\bar{S}_1{}_{p\to\infty} = 1/[1 + (k_2/k_1)] \tag{13}$$

which forms the lower bound. The upper bound can similarly be calculated as follows: For $p \to 0$ the FG or QC model reduces to Henry's law behavior

$$\bar{S}_1{}_{p\to 0} = \frac{1}{x_e}\int_0^{x_e} \frac{dx}{[1 + (k_2/k_1)C_1 p_0(1-x)]} \tag{14a}$$

$$\bar{S}_1{}_{p\to 0} = \frac{-1}{(1+\mu_1)x_e}\ln\left[1 - \left(\frac{\mu_1}{\mu_1 + 1}\right)x_e\right] \tag{14b}$$

with

$$\mu_1 = (k_2/k_1)\exp(Q/RT)(p_0/b_0) \tag{14c}$$

where C_1 is a Henry's law constant given by

$$C_1 = \exp(Q/RT)/b_0 \tag{15}$$

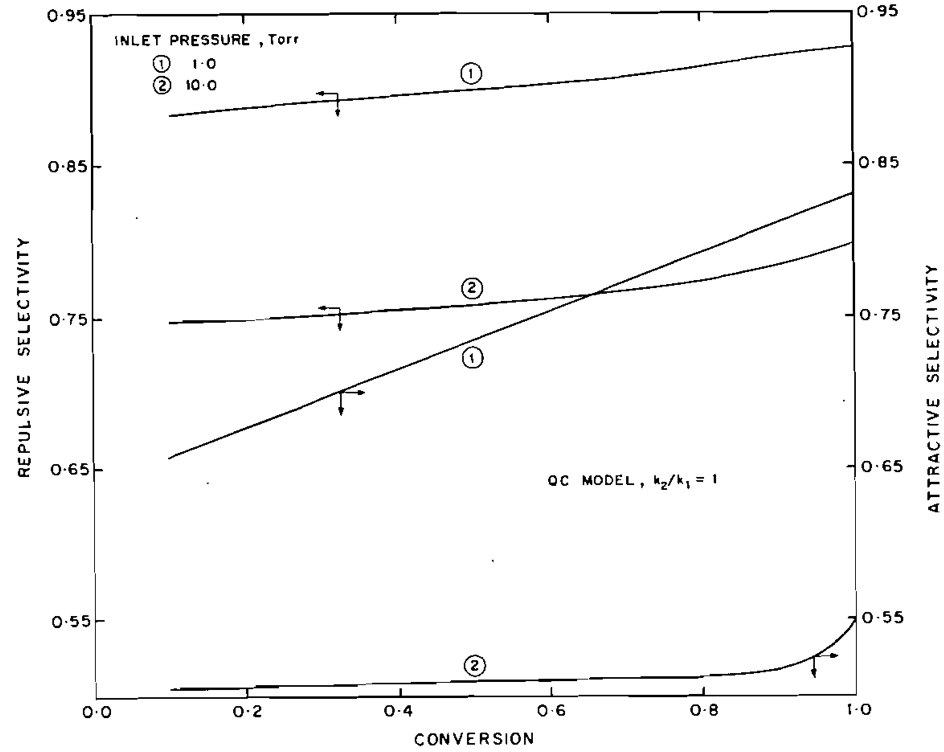

FIGURE 14 Comparison of selectivity conversion plots for the repulsive and attractive QC models with $k_2/k_1 = 1$.

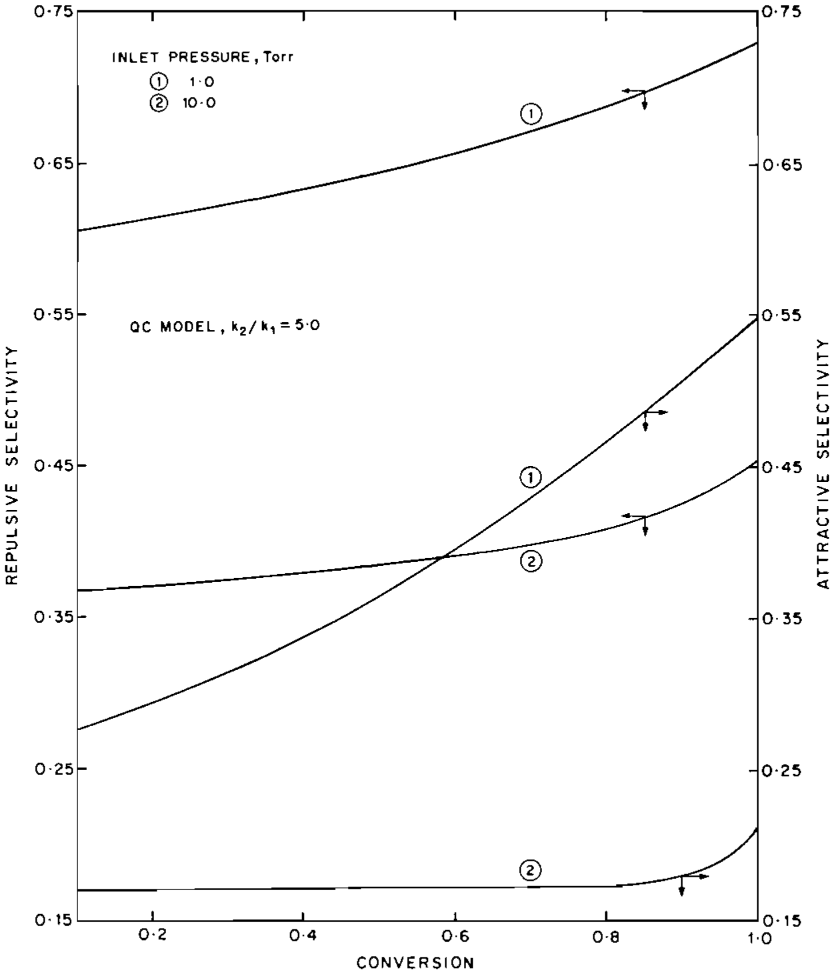

FIGURE 15 Comparison of selectivity conversion plots for the repulsive and attractive QC models with $k_2/k_1 = 5$.

Q denotes the heat of adsorption and b_0 the entropy change factor, if an ideal Henry's law model were applicable.

In general, for the attractive model the surface coverage is higher than for the repulsive model, and as a consequence of Eq. (6) the selectivity progressively decreases with increasing coverage. The *repulsive FG model predicts a higher mean selectivity* $\bar{S}_1$ *for the first-order reaction product* F_g *(see scheme V) in comparison to the attractive model.*

The difference in selectivity behavior between the attractive and repulsive models can be further demonstrated for the case of $k_2/k_1 = 1$. Thus, for an inlet partial pressure $p_0 = 1$ Torr and a conversion level of 100%,† we have for the

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† it can be easily demonstrated that the maximum selectivity for $\bar{S}_1$ occurs for the case of Scheme V at 100% conversion for a given p_0.

repulsive case $\lambda = 12.852$, $\bar{S}_1 = 0.928$. The corresponding values for the attractive model are $\lambda = 4.89$, $\bar{S}_1 = 0.830$. At $p_0 = 10$ Torr, we have $\lambda = 3.89$, $\bar{S}_1 = 0.798$ and $\lambda = 1.222$, $\bar{S}_1 = 0.55$, respectively, for the two models illustrating the drastic role of attractive and repulsive interactions.

We can plot the characteristic inlet partial pressure needed to achieve the desired selectivity ratio ($\bar{S}_1$ or λ) as a function of the kinetic constants ratio k_2/k_1 for a fixed x_e. Also, if the inlet pressure is fixed, one can look for the conversion difference between the attractive and repulsive models.

To illustrate the latter point, at $(k_2/k_1) = 5$ and $p_0 = 0.5$ Torr for the repulsive model we have $x_e = 0.4$ and $\bar{S}_1 = 0.737$. To achieve a comparable selectivity $\bar{S}_1 \cong 0.735$, we have $x_e = 1$ for the attractive model, illustrating once again the significant role of interactions.

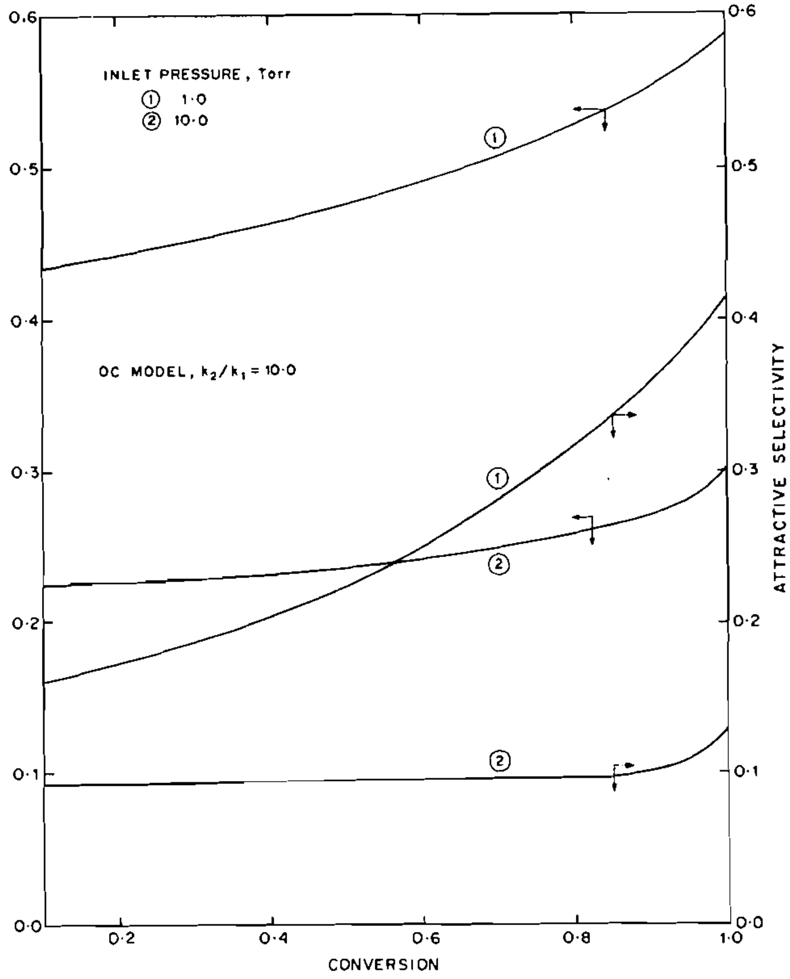

FIGURE 16 comparison of selectivity conversion plots for the repulsive and attractive QC models with $k_2/k_1 = 10$.

The influence of the kinetic constant on selectivity behavior is illustrated in Figures 14, 15 and 16 where $\bar{S}_1$ is plotted for two inlet partial pressures (the variation of $\bar{S}_1$ as a function of conversion being appreciable). From these figures it is obvious that $\bar{S}_1$ falls drastically as (k_2/k_1) is increased. The qualitative difference between the attractive and repulsive models is once again obvious even for a high value of $(k_2/k_1) = 10$. For an ideal inlet pressure of 1 Torr, is less than unity for the attractive model ($\lambda = 0.704855$, $\bar{S}_1 = 0.4134$), in contrast to the repulsive case ($\lambda = 1.4260$, $\bar{S}_1 = 0.5878$).

CONCLUSIONS

The significant roles of interactions and mobility of the adsorbed molecules in determining activity and selectivity are illustrated. How localized molecules differ in their qualitative behavior from mobile molecules is the central theme of the present work. Also the drastic difference in activity and selectivity due to the operation of different interaction forces, viz. attractive and repulsive, is highlighted.

For analyzing localized adsorption, the Fowler–Guggenheim (FG) model and the refined quasi-chemical (QC) model are employed. Mobility is investigated by using the simple Hill-de Boer (HD) model and the more refined model derived on the basis of a simple free volume approach (SFV). Both attractive and repulsive interactions are studied by changing the sign of the interaction parameter. The value of the interaction parameter chosen in the present work is such that the phase transition region is excluded.

The nonidealities due to interaction and mobility are reflected in the space time needed for achieving a desired conversion or selectivity. A very accurate numerical method involving 8-point Gauss-Legendre quadrature is used to calculate the space time as a function of the equilibrium partial pressure. The point rates in the reactor are expressed as a function of surface coverage which in turn is calculated as a function of pressure using a regula falsi method.

Five representative reaction schemes are analyzed. These schemes are complimentary in idealizing the key steps involved in more complex processes.

For a first-order reaction the space time needed for achieving a desired conversion is analyzed assuming localized adsorption. When we compare the predictions of the simple FG and QC models we find that the divergence is not much, except at high inlet partial pressures. Even at the highest inlet partial pressure of 10 Torr employed in the present work, the divergence accounts for a maximum of 10%. It appears that the refinements in treating localized adsorption have been obscured by the process of integration. However, since the QC isotherm is more fundamental we restrict our attention to this model for analyzing localized adsorption.

The attractive QC model predicts considerably lower space times in comparison to the repulsive model, which can be several-fold different (the maximum ratio of space times can be four-fold). Besides, the attractive interaction model predicts nearly zero-order behavior at this inlet partial pressure of 10 Torr.

The difference between the attractive and repulsive models is further magnified when we analyze second-order reactions. As before, the highest variation is observed at 10 Torr inlet pressure. The space time required for the repulsive interaction model can be 13-fold higher in comparison to the attractive case.

Volume change effects do not mask the qualitative difference in reactor performance due to the operation of these two types of forces.

When we compare localized and mobile models, since the latter predicts higher surface rates, the space time values needed to achieve a desired conversion are smaller for the latter. For a first-order reaction the ratio of space time values for the repulsive and attractive models is 1.8 for the mobile model, almost half of what is observed for the case of the localized models. Similarly, for the second-order reaction, even though this ratio is much smaller in comparison to localized adsorption, nevertheless it is significant.

Volume change effects have a smaller influence on the overall values of space time for the mobile model when a second-order surface reaction is occurring.

The selectivity problem is studied for a simple parallel reaction scheme involving first- and second-order steps. The role of interaction forces is more pronounced for the localized model in comparison to the mobile model and hence we restrict our attention to the localized model. Since the repulsive model predicts lower second-order surface rates in comparison to the attractive model, the selectivity with respect to component 1 (product of the first-order step) is higher for the former. The ratio of second-order to first-order kinetic constants has a marked influence on selectivity. The inlet partial pressure also has a significant effect; nevertheless the qualitative difference between repulsive and attractive models remain unaffected.

NOMENCLATURE

b_0	entropy change factor in the ideal Henry's law isotherm, Torr
F	feed rate of reactant, mol/sec
k_1	kinetic constant for first order surface reaction, mol gm^{-1} sec^{-1}
k_2	kinetic constant for second order surface reaction, mol gm^{-1} sec^{-1}
p_0	inlet partial pressure, Torr
p	pressure, Torr
Q	heat of adsorption for the Henry's law isotherm, Kcal/mol
r_n	nth order surface rate, mol gm^{-1} sec^{-1}
S_1	point selectivity with respect to component 1
S_2	point selectivity with respect to component 2
$\bar{S}_1$	conversion averaged selectivity with respect to component 1
$\bar{S}_2$	conversion averaged selectivity with respect to component 2
W	weight of the catalyst, gms

T	temperature, °K
x	conversion level at any point inside the reactor
x_i, x_e	inlet and exit conversion level of the reactor
z	cordination number of the lattice

Greek Letters

$\theta(T, p)$	adsorption isotherm as a function of temperature and pressure
ε	volume change factor
θ	surface coverage
λ	ratio of mean selectivities, $\bar{S}_1/\bar{S}_2$
τ	space time, gm sec mol^{-1}
τ_{1+2}	space time required for overall conversion of A when reactions 1, 2 occur in parallel, gm sec mol^{-1}
ω	interaction energy, Kcal/mol

Subscripts

g	gas phase
s	adsorbed phase

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