

# **FRONTIERS IN CHEMICAL REACTION ENGINEERING**

**Edited by  
L K DORAISWAMY  
R A MASHELKAR**



**VOLUME II**

**A HALSTED PRESS BOOK**

# Frontiers in Chemical Reaction Engineering

VOLUME II

EDITORS

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## PREFACE

The foundations of modern chemical reaction engineering can be traced to the publication 1947 of Part III, **Kinetics and Catalysis of Chemical Process Principles** by Professors O.A. Hougen and K.M. Watson. True, modern mathematical methods of analysis were absent in this book, and a solitary procedure of designing a fixed-bed reactor was all that it contained by way of design and analysis as we understand it today. This book, however, inspired many other attempts in the general area of chemical reactor design which was subsequently (perhaps about ten years later) christened, by nobody in particular, as chemical reaction engineering and popularised through the book **Chemical Reaction Engineering** by Professor Octave Levenspiel. Chemical reactions are ubiquitous, and cannot be restrained by any boundaries. What started out principally as analysis and design of catalytic and gas-liquid reactors today encompasses a variety of reacting systems such as polymeric, biochemical, electrochemical, nuclear, environmental, etc.

There is considerable interest among the international community of chemical engineers to periodically meet and exchange views and results of research in this constantly widening field. As a natural consequence of this interest, the European Federation of Chemical Engineering has undertaken to organize at intervals of two years International Symposia on Chemical Reaction Engineering (ISCRE). Seven such symposia have so far been organized, alternately in Europe and USA, and the eighth symposium is scheduled to be held in Edinburgh later in 1984. The Poona symposium **International Chemical Reaction Engineering Conference (ICREC)** may be regarded as a complementary effort, with the primary objective of assembling at the National Chemical Laboratory renowned researchers in chemical reaction engineering and organizing plenary lectures as well as lectures outlining the results of research in specific areas. Another objective of this conference is to focus attention of the world community of chemical engineers on the fact that chemical reaction engineering occupies a preeminent position not only in Europe and USA, but in many Asian and other countries as well, particularly in India. As will be seen from the list of plenary lectures and papers presented, there are authors from China, Japan, India and Australia.

Coincidental but important is the remarkable fact that a number of events pertaining to chemical engineering have been taking place at the National Chemical Laboratory during the last year or two. A book titled **Three-Phase Catalytic Reactors** by P.A. Ramachandran and R.V. Chaudhari (Gordon and Breach) was published a few months ago. The first three volumes of the series **Advances in Transport Processes** (Wiley Eastern) jointly edited by A. Mujumdar of McGill University and R.A. Mashelkar of National Chemical Laboratory have already appeared (there are in these issues several articles pertaining to chemical reaction engineering). A two-volume treatise titled **Heterogeneous Reactions: Analysis, Examples and Reactor Design** by M.M. Sharma of the University of Bombay and L.K. Doraiswamy of the National Chemical Laboratory (Wiley Interscience) is expected to be published in January 1984. Additionally, one of the editors of the present volume (L.K.D.) has also edited another book titled **Recent Advances in the Engineering Analysis of Chemically Reacting Systems**. This book, which is a **Special Number** of the Indian Chemical Engineer (the official journal of the Indian Institute of Chemical Engineers) is also expected to be published around the same time as the present volumes. These facts are being mentioned, not to specifically bring out the contributions of this laboratory in chemical reaction engineering, but rather to emphasize the fact that the organization of this conference at this laboratory has been a natural consequence of the spurt of activity in this country in general and in this laboratory in particular.

A total of 81 articles consisting of 14 plenary lectures and 67 research papers will be presented at the conference. Since these constitute approximately 1200 pages it was decided to publish them in two volumes. Thus the proceedings of this conference which covers gas-solid catalytic and noncatalytic reactors, multiphase reactors, fluid bed reactors, steady state and dynamic behavior, biochemical engineering, polymeric reacting systems, and general articles, will appear in two volumes organized as follows:

### Volume I

- Plenary lectures
- Multiphase reactors
- Biochemical reactors
- Polymerization reactors
- General

### Volume II

- Gas-solid catalytic and noncatalytic reactors
- Dynamics and stability
- Fluidized bed reactors

Although the coverage of chemical reaction engineering in these volumes is by no means complete, one cannot fail to see that many important aspects of the subject have been included. The plenary

lectures provide a fascinating mix of theory, experiment and practice. The research papers tend to continue this trend. A feature of the conference, which unfortunately cannot be covered in these volumes, is a panel discussion on **Frontiers in Chemical Reaction Engineering** with experts drawn from the academia and industry. This promises to be a very exciting discussion.

Editing such a heterogeneous mix of articles from different countries is indeed a mammoth task. One of the thrusts of our editorial policy was to retain the authenticity of the original articles to the fullest extent possible. As a result some nonuniformities in the papers may be noticed, such as: retention of American and English spellings, variations in the style of referencing both in the body of the text and under references, and in the placement of figures.

In organizing a symposium of this magnitude, considerable assistance is necessary not only from different agencies in terms of financial support but also from colleagues and coworkers in matters of correspondence, assembling of papers, making editorial corrections, organizing the material, and in a number of other ways which cannot be recorded. The financial support received by the organizers from a number of agencies is acknowledged separately in each of these volumes. We would also like to take this opportunity of expressing our deep sense of gratitude to those organizations without whose enthusiastic support this conference would not have been possible. In particular we would like to mention the Council of Scientific and Industrial Research (of which this laboratory is a constituent), Indian Oil Corporation, Indian Petrochemicals Corporation Ltd, Tata Chemicals Ltd, Hindustan Organic Chemicals Ltd, Alchemie Research Centre, Hico Products Ltd, and Hindustan Lever Ltd.

In the scientific organization of the programme we have received assistance from a number of our colleagues and students. In particular we would like to place on record our deep sense of gratitude to Dr. B.D. Kulkarni for the invaluable help rendered by him. He has helped both as joint secretary of this conference and as a chemical engineer gifted with an incisive mind and originality. We are also grateful to Dr. Ravi Kumar, Mr. S.S. Tambe, and Mr. N.S. Dabke. A major event such as ICREC cannot be successful without the enthusiastic support of a large number of persons. We wish to place on record our sincere appreciation of the untiring efforts of numerous individuals from NCL, who gave of their best. Indeed, the dedicated effort of the entire infrastructure of NCL has been responsible for this success. The cheerful support received from the secretarial staff and the draughtsmen is particularly appreciated. The assistance of Dr. S.H. Iqbal, Head of the Division of Technical Services of NCL, and Mr. M.M. Sharma, Administrative Officer of NCL, has been most invaluable. The organization of this symposium started out with a great deal of enthusiasm in 1981. The National Organising Committee has been of great help, in particular Professor M.M. Sharma to whom we have often turned for help and advice.

Among the galaxy of internationally renowned scientists who have contributed to this conference, one unique personality we have sadly missed is Professor Neal Amundson. He was to have presented a keynote lecture entitled 'Early Developments in Chemical Reaction Engineering', but had to withdraw due to ill-health. This was most unfortunate since modern chemical engineering owes much to Professor Amundson, and his views and reflections on the developments would have been of immense value.

The quality of a conference of this type is judged largely by the quality of the individual contributions. We wish to record our sincere thanks to the plenary lecturers and panelists who readily responded to our invitation: G. Allen, R. Aris, G. Astarita, K.B. Bischoff, G. Boreskov, J.B. Butt, J.B. Cropley, J.F. Davidson, G. Froment, V. Hlavacek, H. Hofmann, D. Luss, O.E. Potter, D. Ramkrishna, W.H. Ray, M.M. Sharma, Y.T. Shah, W.E. Stewart, A. Varma, J. Villadsen, V. Weekman and J. Wei. We wish to thank Dr. Haldar Topsoe for agreeing to give the inaugural address and Prof. M.G.K. Menon, Member, Planning Commission, and one of the foremost scientists of this country, for having agreed to give the valedictory address.

It is pleasant to record that the enthusiasm with which we launched this effort did not show any abatement as the months passed, and the response from the international community of chemical engineers was uniformly spontaneous and encouraging. At the time of writing this preface the conference has not yet taken place, and we hope we shall have the good fortune to say that all those who accepted our invitation have indeed attended and that the conference has been a uniquely successful one.

Carried away by the overwhelming response we received and our own waxing enthusiasm, we had visions during the last two years of making this conference a periodic event at this laboratory. The effort, expense and local persuasions involved are so heavy and taxing that we are not sure at this time whether we would not be content to leave this as a one-time effort. If we may end on a personal note, the encouragement and cooperation we have received and the friendships we have cultivated from chemical engineers through out the world have been the most rewarding and lasting experience of this fascinating endeavour.

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**GAS-SOLID CATALYTIC AND NON-CATALYTIC REACTORS**



# Kinetics of Catalysis on Heterogeneous Surfaces: Some Unusual Pressure Relationships

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## SUMMARY

The kinetic consequences of the Polanyi-Brønsted relationship between the activation energy and enthalpy change for an elementary step and its implications in catalysis are analyzed in the present work. It is becoming increasingly popular to measure adsorption isotherms at conditions close to or approximating real catalysis and seek agreement with the values deduced from kinetic analysis. The present analysis highlights the pitfalls involved in this procedure and clearly demonstrates that the pressure exponents measured in pure adsorption experiments and those measured along with reaction could be very much different.

For quantitative formulations three well known site energy distributions are used. Depending on the values of the heterogeneity parameter and the Polanyi-Brønsted parameter the positive exponential, negative exponential and constant distributions are shown to display identical selectivity patterns. Further, it is shown that the nature of the site-energy distribution can be completely disguised as a result of the Polanyi-Brønsted relationship. This is in sharp contrast to the case when statistical independence is assumed between the activation energy of the surface reaction and the heat of adsorption, when all the three distributions display unique pressure dependencies in their selectivity behavior.

A characteristic pressure is defined in the present work, and a formalism involving a Mellin transform is used to relate it to the parameters defining the site-energy distribution and the equilibrium pressure. The significance of the characteristic pressure is that by operating at the pressure we realize a desired selectivity pattern.

It is shown that the inclusion of an Eley-Rideal step shifts the characteristic pressure to lower values.

Finally it is concluded that even for the case of the interactive adsorption (when the analysis is carried out within the framework of the condensation approximation), the pressure exponents are different in the presence and absence of chemical reaction.

## INTRODUCTION

Interpretation of the experimentally observed catalytic rate laws is often beset with numerous difficulties (Refs. 1-4). The genesis of many nonideal rate expressions has

been the subject of many works (Refs. 5-8); still an unambiguous interpretation in terms of effects due to surface heterogeneity (Refs. 2-11) or interactions among adsorbed molecules or a combination of both is often not possible (Refs. 8 and 12).

The random patch model (Refs. 5-13) of the heterogeneous surface has found wide spread acceptance among workers in the field of catalysis (Ref. 2). This model retains the essential features of the real surface, and is readily applicable in the quantitative treatment of catalytic kinetics.

There are two principal approaches to the determination of the site-energy distribution, which forms the basis of all deductions. In one approach, the site-energy distribution is found by the solution of the adsorption integral equation with finite or infinite limits - (Refs. 14-18). In the second approach, the functional forms of the site-energy distributions are assumed a priori and the theoretically deduced rate expressions are compared with the experimental predictions so as to validate the particular choice of the distribution - (Refs. 2,6,7 and 13). In the present work the second method is adopted.

Often for mathematical convenience the assumption  $(0, \infty)$  as limits for the heats of adsorption is made (Refs. 2,15-16). If we keep in mind the Balandin volcano principle (Ref. 1), then the assumption of an infinite upper limit becomes superfluous. Besides, the predicted differential heat at zero coverage tends to infinity in sharp contrast to the experimental findings. In the present analysis such a restrictive assumption is avoided.

While the Polanyi-Brønsted relationship between the activation energy and enthalpy change for an elementary step has been used extensively in interpreting gas-phase kinetics, only very few reported studies have dealt with its application to catalytic kinetics (Refs. 19-20). In the present work we explore the functional dependence of activation energy for surface reaction on the heat of adsorption bearing in mind this particular relationship. The resulting unusual pressure relationships of the gross catalytic rates are then explored.

It is becoming increasingly popular to carry out equilibrium adsorption measurements (adsorption isotherms) at conditions close to and approximating real catalysis, but taking special care that no reaction occurs. It is one of the purposes of the paper to show that when the Polanyi-Brønsted relationship is valid the predictions of the pressure dependent part of the rates may be subject to considerable errors.

For many catalytic reactions, determining the conditions under which a desired selectivity pattern is realized is of paramount importance (Refs. 12,21). We propose methods to find a characteristic pressure (by operating at this pressure we get the desired selectivity) and relate it to the kinetic parameters as well as those characterizing the site-energy distributions. The analysis is carried out both when the Polanyi-Brønsted relationship is valid and when it is not.

At high surface coverages the role of interactions in changing adsorbate structure and hence catalytic rates can be significant (Ref. 22). The superimposed effects due to the Polanyi-Brønsted relationship have been unexplored so far. We pursue the question whether the Polanyi-Brønsted relationship still causes artifacts in the observed kinetics and an answer is sought.

A simple hypothetical reaction scheme is used throughout the analysis so as not to obscure the effects of surface heterogeneity and those resulting as a consequence of the Polanyi-Brønsted relationship.

Three functional forms of the site-energy distribution are used in the present work, viz. (1) the positive exponential distribution (Refs. 5-7), (2) the negative exponential distribution (Refs. 6-7,13), and (3) the constant distribution (Refs. 13,24). These distributions have been chosen because they explain the differential heat variation well and also the pressure dependence of many catalytic rate laws applicable to a heterogeneous surface (Ref. 2).

The study was undertaken with several well defined objectives: (1) to derive exact relationships for the gross rates and selectivity as functions of the equilibrium gas pressure and the parameters characterizing the site-energy distribution, using a Mellin transform

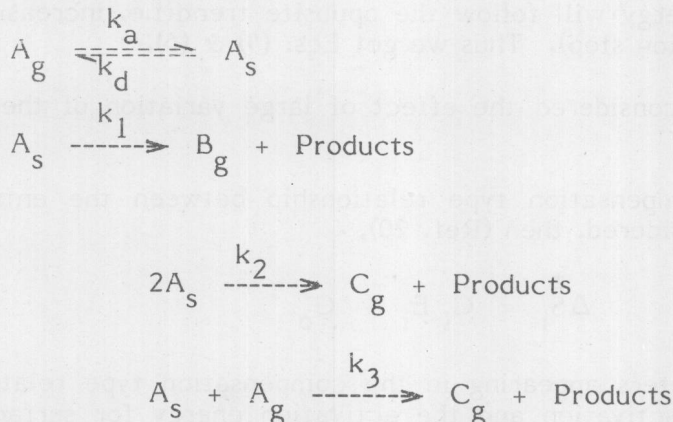
method with realistic limits of the heats of adsorption; (2) to highlight some of the artifacts involved in the interpretation of catalytic kinetics of processes occurring on heterogeneous surfaces: (a) nonuniqueness of the site-energy distribution in giving rise to a specific rate form, (b) pitfalls in predicting pressure dependencies of catalytic rates on the basis of the measurements of adsorption isotherms carried out under conditions of no reaction; (3) to deduce methods to determine a characteristic pressure at which a desired selectivity is achieved and to see whether discrimination between the site-energy distributions is possible on the basis of their characteristic pressure values; (4) to obtain limiting forms of the expressions for selectivity and rates in various ranges of pressure and thus explain the genesis of nonideal expressions, and the novel features arising as a consequence of the Polanyi-Brønsted relationship; and (5) to determine the possible role of interactions (within the framework of the lattice gas model) in shifting the characteristic pressure values when the Polanyi-Brønsted relationship is valid.

## FORMULATION

### 1. Polanyi-Brønsted relationship with compensation

As mentioned in the introduction, the analysis will be carried out within the framework of the random patch model. In this model the surface is visualized as a collection of miniature uniform surfaces (Refs. 5-13) randomly distributed. Adsorption equilibrium is assumed to prevail between gas and surface phases on each of the patches and a local isotherm (denoted by  $\theta_{ii}(T,p)$ ) describes the surface coverage on each patch as a function of equilibrium gas pressure and temperature (Refs. 6,13).

The following hypothetical reaction scheme is chosen for the purpose of analysis (Ref. 12):



This reaction scheme is analogous to the reaction sequence in alcohol dehydration. Also some of the key steps involved in cracking and disproportionation reactions taking place on zeolite catalysts can be idealized by this scheme. First, for simplifying the analysis, we set  $k_3 = 0$ , i.e. the contribution of the Eley-Rideal mechanism in producing  $C_g$  is ignored. The adsorption-desorption rate constants are supposed to be large in magnitude compared to the surface reaction rate constants. So surface reactions (both first and second order) are assumed to be controlling on each of the patches. If now we assume the site-energy distribution  $\delta(Q)$  to be temperature independent, all statistical averages of interest (mean surface rates) can be computed by integration over  $\delta(Q)$ .

To proceed further, we need to explore the relationship between activation energy of the surface reaction and heat of adsorption on each of the patches. Rather than employing ad hoc relationships we first recall the Polanyi-Brønsted relationship between the activation energy and enthalpy change for an elementary step, i.e. (Ref. 19):

$$E_I = E_O + a \Delta H_{SA} \quad (1)$$

where  $a$  denotes the Polanyi-Bronsted constant,  $\Delta H_{SA}$  denotes the enthalpy change for surface reaction, i.e. the more exothermic the heat of surface reaction the less the activation energy. If we now write the overall enthalpy balance for  $A_g \rightarrow B_g$ ,  $A_g \rightarrow 1/2 C_g$  (assumed to be exothermic) we have

$$\Delta H_{aA} + \Delta H_{SA}^1 + \Delta H_{dB} = \Delta H_{ov}^1 \quad (2)$$

$$\Delta H_{aA} + \Delta H_{SA}^2 + \Delta H_{dC} = \Delta H_{ov}^2 \quad (3)$$

First we consider the case when all the quantities  $\Delta H_{ov}^1, \Delta H_{ov}^2, \Delta H_{aA}, \Delta H_{SA}^1, \Delta H_{SA}^2$  are negative.  $\Delta H_{ov}^1, \Delta H_{ov}^2, \Delta H_{aA}, \Delta H_{SA}^1, \Delta H_{SA}^2$  represent the enthalpy change for the overall reactions 1 and 2, heat of adsorption of A, heats of surface reactions resulting in B and C, respectively. Invoking the Polanyi-Bronsted relation enables us to write finally

$$E_i^1 = E_o^1 + a_1 (Q_i - Q_o^1) \quad (4)$$

$$E_i^2 = E_o^2 + a_2 (Q_i - Q_o^2) \quad (5)$$

$E_o^1, E_o^2, Q_o^1, Q_o^2, a_1, a_2$  represent the activation energies of the surface reactions for the lowest energy adsorption sites, lumped constants containing enthalpy change for the overall reaction and desorption of products, and Polanyi-Bronsted parameters for the surface reactions 1,2 respectively. The superfix  $i$  denotes the values for the  $i$ th patch. Notice that in our notation  $[-\Delta H_{aA} = Q]$ , i.e. the  $Q$  is positive for exothermic reactions.

A simple physical interpretation can be given to Eqs. (4) & (5). The higher the exothermicity of adsorption, lower the exothermicity of the surface reaction. As a consequence of Eq. (1) the activation energy will follow the opposite trend (i.e. increasing with increasing exothermicity of the adsorption step). Thus we get Eqs. (4) & (5).

So far we have not considered the effect of large variation of the activation energy on the entropy of activation.

In addition, if a compensation type relationship between the entropy of activation and activation energy is considered, then (Ref. 20),

$$\Delta S_i^\ddagger = C_1 E_i + C_o \quad (6)$$

where  $C_1, C_o$  are parameters appearing in the compensation type relationship and  $\Delta S_i^\ddagger, E_i$  denote the entropy of activation and the activation energy for surface reaction on the  $i$ th patch, respectively. The net result will be that when we write expressions for mean surface rates, the rate terms on the  $i$ th patch get multiplied by  $\exp(C_1 a_1 Q - a_1 Q/RT)$  and  $\exp(C_2 a_2 Q - a_2 Q/RT)$ , apart from some temperature dependent multiplicative constants depending on  $E_o^1, E_o^2, a_1 Q_o^1, a_2 Q_o^2$  which will be denoted by  $\lambda_1, \lambda_2$  in the text. For the three distributions a Mellin transform method is proposed to get closed analytical expressions for the statistical rates.\*

In order to minimize empiricism in the rate expressions, the lower heat of adsorption is chosen as equal to the heat of adsorption on the first BET layer: a representative value for  $Q_1$  will be 7 kcal/mol. For  $Q_2$ , 21 kcal/mole is a plausible value. For the quantitative treatment, the experimental value observed for the differential heat extrapolated to zero coverage may be used for the upper limit if it is available.

\* When no Polanyi-Bronsted relationship and or compensation effects are operative, we get well known expressions for the statistical rates which are well documented (Refs. 6,21). However, the mathematical techniques used for the above case has a close parallel to that employed in the present work. Hence the details of the derivation may be found in (Refs. 6,21) and are omitted in the text.

Thus we write for  $\bar{r}_1, \bar{r}_2$

$$\bar{r}_1 = \int_{Q_1}^{Q_2} \delta'(Q) \theta_{1i}(T,p) dQ \quad (7)$$

$$\bar{r}_2 = \int_{Q_1}^{Q_2} \delta''(Q) \theta_{2i}^2(T,p) dQ \quad (8)$$

where  $\delta(Q), \delta''(Q)$  are defined as

$$\delta'(Q) = \exp(C_1 a_1 Q - a_1 Q/RT) \delta(Q) \lambda_1 \quad (9)$$

$$\delta''(Q) = \exp(C_2 a_2 Q - a_2 Q/RT) \delta(Q) \lambda_2 \quad (10)$$

$\bar{r}_1, \bar{r}_2$  denote the mean surface rates,  $\lambda_1$  and  $\lambda_2$  the temperature dependent constants,  $Q_1, Q_2$  the limits of the heats of adsorption, and  $\delta(Q)$  the site-energy distribution. The analytical expression for  $\bar{r}_1, \bar{r}_2$  valid for the three possible pressure ranges are presented in Table 1.

The local isotherm used in the present work is

$$\theta_{1i}(T,p) = 1/[1 + b_0/p) \exp(-Q/RT)] \quad (11)$$

where  $Q$  denotes the heat of adsorption and  $b_0$  the entropy change factor (the standard state of the adsorbed molecules is that of half coverage). The variation of  $b_0$  with the heat of adsorption is neglected (Refs. 13-14,23). At this stage, the role of interactions has been neglected. In a concluding section this will also be considered.

Using Eqs. (7) and (8) one can easily derive expressions for the selectivities with respect to components 1 and 2:

$$S_1 = \bar{r}_1/(\bar{r}_1 + \bar{r}_2) \quad (12)$$

$$S_2 = \bar{r}_2/(\bar{r}_1 + \bar{r}_2) = 1 - S_1 \quad (13)$$

Often  $S_1 = \sigma S_2$  is the one sought for in practice where  $0 < \sigma < 1$ . Equating  $S_1 = \sigma S_2$  and keeping in mind that  $\bar{r}_1, \bar{r}_2$  are functions of the gas pressure we solve for the characteristic pressure. The characteristic pressure is a property of the site-energy distribution, when the kinetic constants are held constant.

Three distributions have been employed in the present work, viz. (1) the positive exponential distribution, (2) the negative exponential distribution, (3) the constant distribution. The functional forms are given as under:

1. Positive exponential distribution (Refs. 5-7)

$$\delta(Q) = \exp(Q/Q_M) C_P \quad (14)$$

2. Negative exponential distribution (Refs. 6-7,13)

$$\delta(Q) = \exp(-Q/Q_M) C_N \quad (15)$$

3. Constant distribution (Refs. 13,24)

$$\delta(Q) = 1/(Q_2 - Q_1) \quad (16)$$



$C_p, C_N$  denote respectively, the normalization constants. The  $Q_M$  parameters in these distributions are chosen such that the differential heat at zero coverage tends to the upper limit of the heat of adsorption, and the slope and shape of the  $Q, \theta$  curves are in agreement with experiments. In all these studies the one assumption employed is that a large class of experimental data can be adequately represented by one of the three distributions.

## EXPRESSIONS FOR RATES AND SELECTIVITY

### 1. Nonuniqueness of the site-energy distribution

A brief examination of Table I shows that the expressions for selectivity and rates in the various pressure ranges are quite complex. Further the functional forms for  $\bar{r}_1, \bar{r}_2$  are similar in their analytical dependence on the equilibrium pressure. A few interesting features of these expressions are considered in the following paragraphs.

The expressions for the rates and selectivity are similar for the positive exponential given by Eq. (14) for most values of the heterogeneity parameter. We define three parameters as follows ( $RT = 1$  kcal/mole)  $RT/Q_M = \mu$ ;  $-\eta_1 = a_1 (C_1 - 1)$ ;  $-\eta_2 = a_2 (C_2 - 1)$ . Three possibilities exist for the positive exponential distribution, especially for the first order rate.

(1)  $\mu > |\eta_1|$ . The resulting expressions are similar to that derived for a positive exponential distribution with an effective  $\mu_1 = \mu - \eta_1$ , but as though no Polanyi-Brønsted relationship were operative.

(2)  $\mu = |\eta_1|$ . The expressions for  $\bar{r}_1$  are similar to those derived for the constant distribution case, in absence of the Polanyi-Brønsted relationship, i.e. a logarithmic relationship results.

(3)  $|\eta_1| > \mu$ . The resulting expressions for  $\bar{r}_1$  are similar to those derived for the negative exponential distribution with an effective  $\mu_1 = |\mu - \eta_1|$  (but as if no Polanyi-Brønsted relationship is operative).

Similar criteria can also be derived for the second order rate  $\bar{r}_2$ , by appropriately defining an effective  $\mu_2 = \mu - \eta_2$ . The positive exponential distribution behaves as though it is a negative exponential distribution.

For the negative exponential distribution defined by Eq. (15) we likewise define  $\mu_1 = \mu + \eta_1$ ;  $\mu_2 = \mu + \eta_2$ . In sharp contrast to the positive exponential distribution, expressions for  $\bar{r}_1, \bar{r}_2$  are unchanged in functional form but similar to that derived for the negative exponential distribution with effective  $\mu = \mu_1, \mu = \mu_2$  for the situation when no Polanyi-Brønsted relationship is operative.

For the constant distribution defined by Eq. (16), on the contrary, the expressions for  $\bar{r}_1, \bar{r}_2$  derived in the presence of a Polanyi-Brønsted effect are similar to that derived for a negative distribution with effective  $\mu = \eta_1, \mu = \eta_2$ . Thus the constant distribution can display selectivity behavior of the negative exponential distribution.

The above discussion clearly highlights the pitfalls involved in interpreting the experimental data on selectivity in terms of a unique site-energy distribution. In particular the nature of the site-energy distribution can be disguised by the effects due to Polanyi-Brønsted relation. Thus under certain conditions the positive exponential, negative exponential and constant distributions can show identical selectivity behavior (that of a negative exponential distribution with appropriately redefined  $\mu$  parameters). Similarly, a constant distribution in the absence of Polanyi-Brønsted relationship can show logarithmic dependence on pressure for  $\bar{r}_1$ , surprisingly identical to the positive exponential distribution for the condition  $\mu = |\eta_1|$  or  $\mu = |\eta_2|$ .

When the Polanyi-Brønsted relationship is no longer valid or statistical independence is assumed between the distributions characterising activation energy and heat of adsorption,