REFERENCES

[1] Haynes W M, Hiza M J and Frederick N V, *Rev Sci Instrum* 1976 **47** 1237
[2] Haynes W M and Hiza, M J, *J Chem Thermodyn* 1977 **9** 1979
[3] Hiza M J, Haynes W M and Parrish W R, *J Chem Thermodyn* 1977 **9** 873
[4] Miller R C and Hiza M J, *Fluid Phase Equil* 1978 **2** 49
[5] Haynes W M, Hiza M J and McCarty R D, *Proc 6th Int Conf on LNG*, Paper III-11, Vol 2 Institute of Gas Technology, Chicago 1977
[6] Mollerup J and Rowlinson J S, *Chem Engng Sci* 1974 **29** 1373
[7] Teja A S and Rowlinson J S, *Chem Engng Sci* 1973 **28** 529
[8] Teja A S, *A I Ch E J* 1980 **26** (in press)
[9] Hiza M J, *Fluid Phase Equil* 1978 **2** 27
[10] Rodosevich J B and Miller R C, *Advan Cryogenic Engng* 1974 **19** 339
[11] Teja A S, *Chem Engng Sci* 1978 **33** 609

Chemical Engineering Science Vol 35 pp 2351–2352
Pergamon Press Ltd, 1980 Printed in Great Britain

Macroscopic clusters induced by diffusion in catalytic oxidation reactions

(*Received* 20 *December* 1979, *accepted* 4 *February* 1980)

Ordered state of catalysts surface layers has been recently proposed for various oxidation reactions[1, 2] It is known that simultaneous occurence of a non-linear chemical reacton and diffusion may produce periodic structures ("dissipative structures" by Prigozhin[3]) These phenomena have been analyzed in more detail by Barelko *et al* (see, e g [4]) The objective of this study is to explain the appearance of these structures for the catalytic reaction oxidation of CO on Pt

MODEL

We consider the following reaction mechanism (see, e g [5]):

$$O_2 + 2Pt \rightleftharpoons 2PtO, \quad (1)$$
$$CO + Pt \rightleftharpoons PtCO, \quad (2)$$
$$PtO + PtCO \rightarrow 2Pt + CO_2, \quad (3)$$
$$CO + PtO \rightarrow Pt + CO_2 \quad (4)$$

Assume that (i) diffusion of adsorbed CO molecules on the surface is due to "jumps" onto the neighbouring vacancies, (ii) the temperature interval is such that oxygen adsorption is localized and oxygen diffusion on Pt surface may be neglected

Then the model which describes the process in the chemisorbed layer will be as follows

$$\begin{aligned} x &= 2k_1 p_{O_2} z^2 - 2k_{-1}x^2 - k_3 xy - k_4 p_{CO} x, \\ y &= k_2 p_{CO} z - k_{-2} y - k_3 xy + D(z\Delta y - y\Delta z), \end{aligned} \quad (1)$$

where

$$x = [PtO],\ y = [PtCO],$$

$$z = 1 - x - y = [Pt]$$

Using the balance considerations we can easily receive eqn (1) The diffusion term in eqn (1) is not generally accepted The details will be presented in our next article

Consider now one-dimensional stationary problem

$$\Delta = \frac{\partial^2}{\partial \xi^2},\ x = y = 0,$$

i e

$$2k_1 p_{O_2}(1 - x - y)^2 - 2k_{-1}x^2 - k_3 xy - k_4 p_{CO} x = 0, \quad (2)$$

$$D\left((1 - x)\frac{d^2 y}{d\xi^2} + y\frac{d^2 x}{d\xi^2}\right) + k_2 p_{CO}(1 - x - y) - k_{-2} y - k_3 xy = 0 \quad (3)$$

Main properties of the system

(1) Equation (2) determines a single-valued dependence (provided that $x \geq 0$, $y \geq 0$, $x + y \leq 1$)

$$x(y) = \frac{b - \sqrt{(b^2 - 4ac)}}{2a},$$

where

$$\begin{aligned} a &= 2k_1 p_{O_2} - 2k_{-1}, \\ b &= 4k_1 p_{O_2}(1 - y) + k_3 y + k_4 p_{CO}, \\ c &= 2k_1 p_{O_2}(1 - y)^2 \end{aligned}$$

$x(y)$ is differentiable function, therefore, eqn (3) may be reduced to

$$a_2(y)\frac{d^2 y}{d\xi^2} + a_1(y)\left(\frac{dy}{d\xi}\right)^2 + a_0(y) = 0, \quad (4)$$

where

$$\begin{aligned} a_2(y) &= D\left(1 - x(y) + y\frac{dx}{dy}\right), \\ a_1(y) &= Dy\frac{d^2 x}{dy^2}, \\ a_0(y) &= k_2 p_{CO}(1 - x(y) - y) - k_{-2} - k_3 x(y) y \end{aligned}$$

(2) At higher derivative the coefficients in eqn (4) are not equal to zero where the function $x(y)$ is determined It holds true for such y that $x(y) \leq 1$ Equation (4) may be integrated in the explicit form By substituting

$$\rho(y) = \frac{dy}{d\xi}$$

we arrive at

$$\rho^2(y) = \left(2A - 2\int_0^y f(u)\exp\left(2\int_0^u r(v)\,dv\right)du\right)\exp\left(-\int_0^y r(u)\,du\right), \quad (5)$$

where A is an arbitrary constant,

$$f(y) = \frac{a_0(y)}{a_2(y)},$$

$$r(y) = \frac{a_1(y)}{a_2(y)}$$

An inspection of (5) indicates that $\sqrt{(\rho(y))}$ (accurate to within

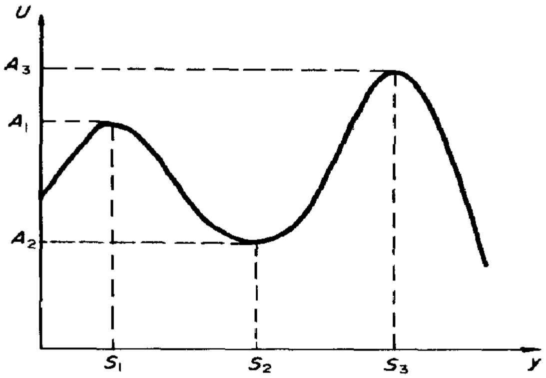

Fig 1

non-zero multiplier) is coincident with the rate of motion of the unit body with energy A in the field of potential energy

$$U(y) = \int_0^y f(u) \exp\left(2\int_0^u r(v)\,dv\right) du$$

(3) If a lumped system described in terms of mechanism (1)–(4) has three steady states (which are possible in a wide range of temperatures and pressures[6, 7]), then the shape of the function $U(y)$ is similar to that shown in Fig 1 Here S_1, S_3 stand for stable steady states, S_2 is an unstable steady state If in (5)

$$A_2 < A < \min\{A_1, A_3\}$$

then we obtain a periodic solution of eqn (4) which represents the searched "dissipative structure" Even more interesting case is observed when

$$A = \min\{A_1, A_3\}$$

We deal with the object well-known in the theory of non-linear waves, namely, so called solitary wave (soliton)[8, 9] This solution corresponds to the case when at $\xi \to \pm\infty$ one of the stable steady states exists on the surface and in a certain region the state approaches another steady state (not reaching it) (Fig 2)

CONCLUSION

Existence of the above properties of system (2), (3) indicates that at simultaneous occurence of a complex catalytic reaction and surface diffusion the appearance of ordered structures, spots, clusters, etc is possible They may be of pure macroscopic origin The problem of stability of these formations is beyond the scope of this study

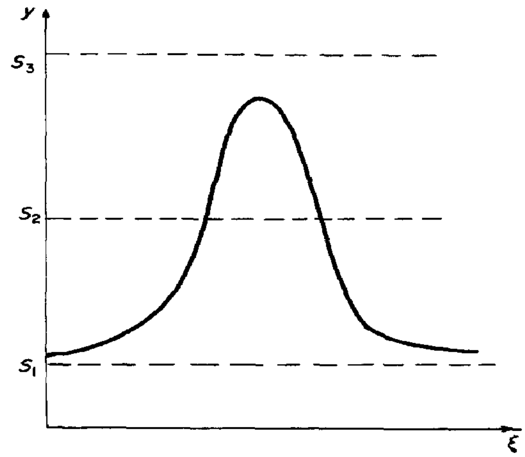

Fig 2

Computing Center, Siberian Branch
U S S R. Academy of Sciences
Krasnoyarsk 660049, U S S R

A N GORBAN
V I BYKOV

Institute of Catalysis
Siberian Branch
U S S R Academy of Sciences
Novosibirsk 630090, U S S R

G S YABLONSKII

REFERENCES

[1] May J A, *Advan Catal* 1970 **21** 151
[2] Berman A D and Krylov O V, *Nestatsionarnye i neravnovesnye processy v geterogennom katalize*, pp 102–115 Nauka, Moscow 1978
[3] Glensdorf P and Prigozhin I, *Termodinamicheskaya teoriya struktury, ustoichivosti i fluktuatsii* Mir, Moscow 1973
[4] Barelko V V, Kurochka I I, Merzhanov A G and Shkadinskii K G, *Chem Engng Sci* 1979 **33** 805
[5] Kuchaev V L and Nikitushina L M, *All-Union Conference on the Mechanism of Heterogeneous-catalytic reactions*, preprint 59 Moscow 1974
[6] Yablonskii G S, Bykov V I, Slinko M G and Kuznetsov Yu I, *Dokl AN SSSR* 1976 **229** 917
[7] Bykov V I, Yablonskii G S and Slinko M G, *Dokl AN SSSR* 1976 **229** 1356
[8] Whithem G B, *Linear and Nonlinear Waves* Wiley, New York 1974
[9] Pismen L M, *J Chem Phys* 1978 **69** 4149

Chemical Engineering Science Vol 35, pp 2352–2356
Pergamon Press Ltd 1980 Printed in Great Britain

Bubble growth in a viscous Newtonian liquid

(*Accepted 5 March* 1980)

The problem of diffusion-fed gas bubble growth in a liquid is of interest in many areas of engineering The particular case of such growth in a highly viscous fluid has application in polymer foam formation One method of foam formation involves growth of bubbles by diffusion of blowing agent from an oversaturated solution of the blowing agent in the liquid surrounding the bubbles The oversaturation may be achieved by a lowering of the system pressure, or by some other means

A large body of literature exists on the subject of phase growth Detailed bibliographies may be found in the works of Scriven[1], Street *et al* [2] and Rosner and Epstein[3] Diffusion-fed phase growth in viscous liquids has been treated by Barlow and Langlois[4], Street *et al* [2] and Szekely and Martins[5] Barlow and Langlois and Szekely and Martins treated phase growth in Newtonian liquids while Street *et al* considered growth in an Ostwald–de-Waele power law liquid The analysis of Street *et al* is further complicated by considering the liquid surrounding the bubble to be finite, the liquid viscosity to vary