matters arising

'Spatial oscillations' in the Zhabotinskii reaction

SIR,—In a recent study of temperature effects and the Zhabotinskii reaction, Thoenes¹ measured the speed of the reaction wave fronts and related it to the temperature distribution in the sample. A temperature gradient was artificially imposed from outside the system.

Thoenes' interpretation of the data is, however, either unclear or misleading on some points.

In the first paragraph Thoenes indicates that the theoretical analysis which he uses was suggested by Beck and Váradí². It seems more probable, however, that the reference should be to Zaikin and Zhabotinskii³. These authors refer to the work of Prigogine and Nicolis⁴, among others, as providing the theoretical foundation for their simplified analyses. Thoenes' implication that his theoretical analysis is independent of the work of Prigogine and coworkers is therefore misleading.

This analysis rests on the assumption that the frequency of the oscillations, ω , can be described as a function of the position, x :

$$\omega(x) = \omega^0 F(x) \quad (1)$$

This is Thoenes' equation (1). He later identifies $F(x)$ with

$$\exp(-E/RT(x)) \quad (2)$$

where E is an energy and $T(x)$ is the position dependent temperature. This is Thoenes' equation (5). Thoenes states that this treatment explains all the phenomena reported by Zaikin and Zhabotinskii³. This is not surprising as they had already shown this to be true. (In this context, recent work by Winfree⁵ is also interesting.)

But equation (1) can also be misleading in the context in which it is given. The oscillatory behaviour which it implies is rather rare in chemical reactions and the Zhabotinskii reaction is a very special case. Several authors have discussed the requirements for, and the characteristics of, such chemical reactions⁶⁻⁸. These works point out that equation (1) can only describe very special types of chemical reactions.

The interpretation of equation (2) may not be as simple as Thoenes suggests. The heat output and the redox potential step during the oscillations change according to the number of oscillations which have occurred⁹. Equation (2)

would not therefore be expected to give a single datum, as Thoenes apparently assumes. Some of the effects of heat production in the Zhabotinskii reaction have already been noted by Busse¹⁰, although his interpretations of some other points were incorrect¹¹. The chemistry of the Zhabotinskii reaction has been discussed extensively^{12,13}, and there has been a theoretical study¹⁴ of an ideal system of the type studied by Prigogine and coworkers but with heat production included. Beck and Váradí² also explicitly mention the effects of the container walls on the reaction characteristics.

Thoenes' statement "I conclude that spatial patterns in the Zhabotinskii reaction are not examples of dissipative structures as described by the theory of Prigogine" does not therefore seem to be correct. Thoenes' analysis is in fact based on Prigogine's work.

I conclude that Thoenes has reported very interesting experimental results on the effect of temperature on the Zhabotinskii reaction, and that in order to interpret this data he has also reformulated and enlarged upon a previous mathematical description by Zaikin and Zhabotinskii³ which was in turn based on the theories of Prigogine and coworkers⁴.

Yours faithfully,

DOUGLAS H. MCQUEEN

Organic Electron Physics Group,
Chalmers University of Technology,
Göteborg, Sweden

¹ Thoenes, D., *Nature phys. Sci.*, **243**, 18 (1973).

² Beck, M. T., and Váradí, Z. B., *Nature phys. Sci.*, **235**, 15 (1972).

³ Zaikin, A. N., and Zhabotinskii, A. M., *Nature*, **225**, 535 (1970).

⁴ Prigogine, I., and Nicolis, G., *J. chem. Phys.*, **46**, 3542 (1967).

⁵ Winfree, A. T., *Science*, **175**, 634 (1972).

⁶ Glansdorff, P., and Prigogine, I., *Thermodynamic Theory of Structure, Stability, and Fluctuations* (Wiley, London, 1971).

⁷ Prigogine, I., and Nicolis, G., *Q. Rev. Biophys.*, **4**, 107 (1971).

⁸ Prigogine, I., Nicolis, G., and Babloyantz, A., *Physics Today*, **23-28** November, (1972) 38-44 (December, 1972).

⁹ Körös, E., Orbán, M., and Nagy, Zs., *Nature phys. Sci.*, **242**, 30 (1973).

¹⁰ Busse, H. G., *J. phys. Chem.*, **73**, 750 (1969).

¹¹ Gray, B. F., *Nature*, **242**, 257 (1973).

¹² Field, R. J., and Noyes, R. M., *Nature*, **237**, 390 (1972).

¹³ Noyes, R. M., Field, R. J., and Körös, E., *J. Am. chem. Soc.*, **94**, 1394 (1972).

¹⁴ Rosen, G., *Phys. Lett.*, **43A**, 349 (1973).

Structure of water in porous glass

SIR,—In an attempt to measure proton mobility, Roberts and Northey, used signal line broadening from steady state nuclear magnetic resonance (NMR) to study slices of sintered glass with a pore size of $\sim 15 \mu\text{m}$ (ref. 1). They infer "long range modification of the water structure by sintered glass". Their conclusions do not necessarily indicate an ordering effect, and new evidence for the water-glass system casts doubt on their results^{2,3}.

Signal line broadening from steady state NMR has been used as an indicator of orientation effects for adsorbed systems. Interpretation of the data is, however, often ambiguous⁴. Pulse or spin echo techniques are considered more promising and have recently been applied to many systems⁵, including water on porous glass^{2,3}.

Our results, using pulse NMR, indicate that for a specially prepared porous powdered glass at 100% relative humidity, with an average pore size of $\sim 24 \text{ \AA}$, about 80% (v/v) of the adsorbed water is motionally restricted, and the remaining 20% (v/v) is most probably bulk water³. As the average pore radius approaches 100 $\text{ \AA}$, the amount of motionally restricted water in the Vycor glass is reduced to below 10% (v/v), which is approximately one layer of surface-bound water about 3 $\text{ \AA}$ thick (ref. 2). Thus, for very large average pore diameters, such as the 15 μm used by Roberts and Northey, with relatively small surface areas, it is probable that far less than 10% (v/v) of the occluded water is bound. In addition, because of the notoriously low sensitivity of NMR, detection of small percentages of bound water within very large percentages of bulk water is unlikely.

For the steady state NMR experiment, broadening which results from field inhomogeneities produced by the glass matrix would occur even if 100% (v/v) of the occluded water was free. Interpretation of the NMR data for adsorbed systems is far more complicated than the observation of the broadening effect⁵. For example, relaxation rates within, and exchange rates between, various environmental states (phases) critically affect the estimation