Temperature Variations in an Oscillating Chemical Reaction

Most chemical reactions in homogeneous mixtures are characterized by monotonic changes in the concentrations of the reactants. But the kinetic rate law also predicts oscillating chemical reactions[1] and such chemical systems have recently been discovered[2–6]. These systems are especially useful in the study of phenomena which are far from thermodynamic equilibrium.

In such reactions measurements of the temperature can provide information about some features of the oscillating process. The behaviour of the temperature as a function of time in a chemical system containing $H_2C(COOH)_2$, $KBrO_3$, $Ce_2(SO_4)_3$ and H_2SO_4 was investigated with a thermistor covered with a thin silicon rubber film and is shown in Fig. 1. (The initial concentrations are given in the legend.) At first, the temperature increased with an approximate coefficient of 0.14 calorie cm^{-3} min^{-1}. As soon as the oscillating state was reached the temperature also began to oscillate about an almost constant value. The change of Ce^{3+} to Ce^{4+} was accompanied by an increase in temperature and the opposite change was accompanied by a decrease. The surroundings of the reaction vessel were not kept at constant temperature. During one particular period, approximately 0.025 calorie cm^{-3} of heat was produced and absorbed.

The temperature oscillation can be considered in the following way. The entropy, S, of the system can be regarded as a Liapunov function[7], which is always definite in the mathematical sense; the same holds for dS/dt. As well as the equilibrium states (given by $dS/dt=0$) there may be other states for which $dS/dt \sim 0$ holds and in which the system might stay for a longer time. This time is probably given by a quality factor (a measure of the proximity dS/dt is to zero). If the oscillating state is of the second type, it would, in the limits of extrapolation, show reversibility during oscillation.

The oscillation of the temperature around a nearly constant value means that there is almost no overall heat production. Therefore the converted chemical energy within one cycle might be expected to appear, for example, as mechanical energy associated with the formation of gaseous CO_2 (ref. 8). The rate of production of CO_2 in the oscillating state (Fig. 1) is roughly 10^{-7} m cm^{-3} min^{-1} and is about two to six times higher in the preceding lag phase. This could, in a sense, be considered as an efficient conversion of chemical to mechanical energy. Conversely, one might expect an oscillatory state (and correspondingly a spatial state[9,10], e.g. perhaps a membrane) in a system which far from thermodynamic equilibrium converts energy very efficiently[11].

HEINRICH G. BUSSE*

Molekularbiologische Forschungsgesellschaft,
Stöckheim/Braunschweig,
Mascheroder Weg 1

Received April 13, 1971.

*Present address: Max-Planck-Institut für Ernährungsphysiologie, Dortmund (D-46), Rheinlanddamm 201.

[1] Lotka, A., *J. Phys. Chem.*, 14, 271 (1910).
[2] Bray, W. C., *J. Amer. Chem. Soc.*, 43, 1962 (1921).
[3] Chance, B., Hess, B., and Betz, A., *Biochem. Biophys. Res. Commun.*, 16, 182 (1964).
[4] Belousov, B. P., *Sborn. Referat. Radiat. Med. Za. 1958, Medg.* (Moscow, 1959).
[5] Zhabotinskii, A. M., *Dokl. Akad. Nauk SSSR*, 157, 392 (1964).
[6] Zhabotinskii, A. M., Babiliu, B. A., Iagnzhinskii, L. C., and Krupianko, B. I., in *Oscillatory Processes in Biological and Chemical Systems* (Nauka Publ., Moscow, 1967).
[7] Hahn, R., in *Mathematical Tools for Engineers* (Springer, Berlin, 1970).
[8] Degn, H., *Nature*, 213, 589 (1967).
[9] Zaikin, A. N., and Zhabotinskii, A. M., *Nature*, 225, 535 (1970).
[10] Herschkowitz-Kaufman, M., *CR Acad. Sci.*, 270, 1049 (1970).
[11] Boiteux, A., and Chance, B., *Biochim. Biophys. Acta* (in the press).

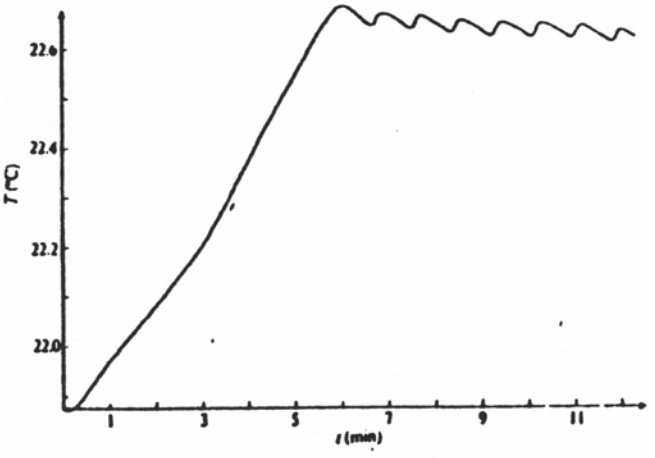

Fig. 1 Temperature T as a function of time in the chemical system containing $H_2C(COOH)_2$ (0.2 M); $KBrO_3$ (0.06 M); $Ce_2(SO_4)_3$ (0.002 M); H_2SO_4 (solvent 2 N).