

we find particle *b* moving in the retarded and attenuated field of particle *a*, and particle *a* moving in the full advanced and attenuated field of particle *b*. The use of the full advanced field rather than half the advanced tends to double the radiation reaction. The attenuation tends to cut it down—as it turns out—exactly in half.

The reason for the last point is that the response field from a layer of optical thickness $d\tau$ turns out to be proportional to $e^{-\tau d\tau}$ (ref. 2). The factor $e^{-\tau}$ is due to the attenuation of the field of *a* at *b*. When the reaction is also attenuated, an extra factor $e^{-\tau}$ is required, and the contribution becomes proportional to $e^{-2\tau d\tau}$. In the final result for the response field, the inclusion of attenuation has the effect of replacing $\int_0^\infty e^{-\tau} d\tau = 1$ by $\int_0^\infty e^{-2\tau} d\tau = \frac{1}{2}$.

Whether the effects of doubling the response field and of attenuating it cancel also outside the classical limit should be made clear.

AMNON KATZ
EZUZ ORNAN
MOSHE SCHWARTZ

Department of Physics,
Weizmann Institute,
Rehovoth, Israel.

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Microbarograph Observation of Acoustic Gravity Waves

MAY I comment on the recent letter in *Nature* by Murty and Curry¹ on microbarographic observation of acoustic gravity waves.

Events such as these authors describe are rather commonplace in Victoria, Australia, and one such occurrence has been recorded² at some length, while Potheary³ has noted an English case. Although it would be rash to claim that the processes responsible for exciting gravity waves in the atmosphere are fully understood, it is recognized here that pronounced and sustained pressure oscillations, of amplitude of the order of a millibar, are almost invariably associated with a shallow layer (1–2 km) of cold air, underlying much warmer air. This commonly occurs when a shallow but intense cold front moves north or north-eastward over Melbourne and becomes almost stationary. In most cases it is also possible to find evidence of precipitation, which may be associated with thunder, originating in the warmer air and penetrating the inversion, somewhere within, say, a hundred miles. The conclusion has been drawn that excitation by precipitation, or its concomitant downdraughts, of gravity waves on a marked low level inversion is responsible for the observed oscillations of surface pressure. Ramm and Warren⁴ have given a quantitative treatment of the processes involved.

It is suggested that your correspondents should pay some attention to the vertical and horizontal density and wind distribution at the time of the phenomenon they describe.

R. H. CLARKE

CSIRO,
Division of Meteorological Physics,
Aspendale, Victoria 3195,
Australia.

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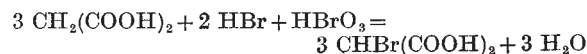
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Concentration Wave Propagation in Two-dimensional Liquid-phase Self-oscillating System

OSCILLATING chemical reactions are interesting, not only in themselves but as models of a number of important biological processes^{1–5}. Oscillating reactions have been described in which cerium (or manganese) ions catalyse the oxidation of analogues of malonic acid by bromate^{6–8}. Oscillations in the concentrations of oxidized and reduced forms of the catalyst cause oscillations in the solution colour, while stirring leads to forced synchronization of oscillations throughout the whole volume. In the absence of stirring, periodic propagation of concentration waves occurs in certain conditions, and such a phenomenon in a one-dimensional system (a long tube) has been described^{9,10}. Our work deals with patterns in a thin layer of solution (two-dimensional system).

Fe(1,10-phenanthroline)₃ is a convenient indicator for observation of spatial effects in our system. Ferriin and Fe(2,2'-dipyridyl)₃ could also be used, not only as indicators but also as catalysts, and it seems that a number of variable valence ions with one-electron transition and standard potential between 0.9 and 1.6 V may be used as catalysts in the system. In the present work, the system bromate, bromomalonic acid (BMA), ferriin was used. BMA was prepared by bromination of malonic acid by bromate-bromide mixture in acidic aqueous solution.



Similar results are obtained with BMA prepared by the method described by Conrade¹¹. The reaction was performed at room temperature (about 20°C) in Petri dishes about 100 mm in diameter, with a solution layer about 2 mm deep.

Fig. 1 shows a series of sixteen photographs taken at one-minute intervals. In the first photograph, the catalyst is completely reduced, and subsequent photographs show it starting to be oxidized at particular points (leading centres), from which circular waves of oxidation are propagated. The fourth photograph shows oxidation taking place in areas not reached by these waves. The time when these transitions take place is determined by the oscillation period (T_0) of the main part of the space, which is equal to the system oscillation period in the case of forced synchronization by stirring. The next photographs show waves coming from leading centres (with $T < T_0$) oxidizing all the space step by step. When the waves coming from different leading centres collide, mutual annihilation takes place, with the point of collision, situated on a straight line between two leading centres, gradually moving towards the leading centre with the longer period. When a wave from a high-frequency leading centre reaches a low-frequency centre, the latter disappears, and, in the ideal case, a single leading centre with the highest frequency eventually synchronizes the whole space. In most experiments, however, some fronts break at the end of the process and space disorganization takes place (photographs 12–16).

Qualitatively distinctive patterns, for example, radial symmetric and small-cell patterns, are observed at other initial reactant concentrations. Those shown in Fig. 1 resemble Liesegang rings (LR), but it should be emphasized that the phenomenon described differs from LR in two significant features. First, in this case, there are progressive concentration waves while the sediment rings in the LR phenomenon are motionless. Second, LR-pattern in a fixed imprint of a reaction which has proceeded, but in our case the space structure is supported at the expense of redox reaction energy.

We consider here the simplest model of wave propagation in the system. In a one-dimensional system (a thin tube with length L , filled by solution), see Fig. 2, let all

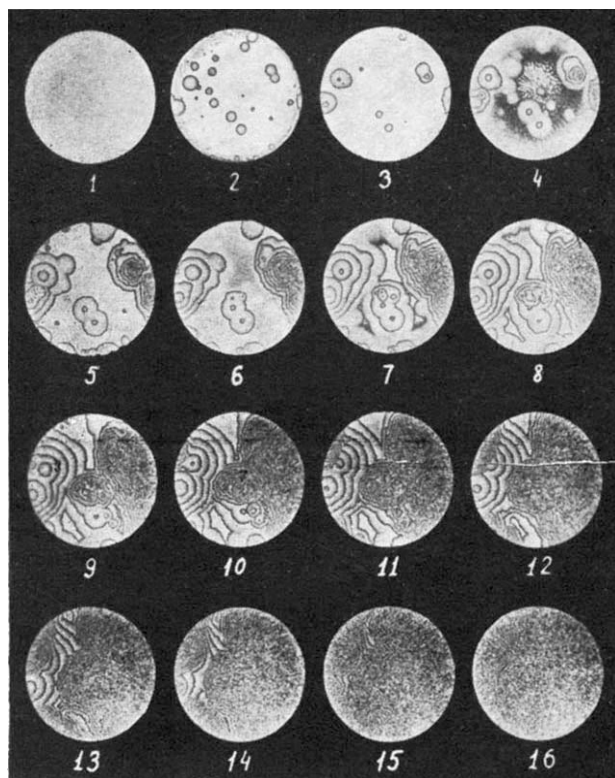


Fig. 1. Concentration wave propagation in two-dimensional self-oscillatory chemical system. Ring diameter equals 100 mm. Initial reactant concentrations (in mol/l.): $[BMA]=0.125$; $[NaBrO_3]=0.3$; $[Fe(phen)_3]=0.003$; $[H_2SO_4]=0.37$.

the points in the system (except X_A and X_B) possess a period of self-oscillation equal to T_0 . Leading centres (A and B) have periods equal to T_A and T_B

$$T_A < T_B < T_0$$

The following features of the system, obtained experimentally, form the basis of the model. Relaxation oscillations take place at every point in the space. The period of oscillation is distinctly divided into two phases: an oxidation phase and a reduction phase. The catalyst exists in oxidized form during a small part of the oscillation period. In Fig. 2 the oxidized state is represented by black lines (in the same manner as in Fig. 1) and the line width corresponds to the duration of the oxidation phase. The velocity of wave propagation (V_0) is constant throughout the space and oscillation periods (T_A , T_B and T_0) are constant. When two waves collide, they cancel each other out.

In this model, waves spread in the following manner. All the space is initially in the reduced state, and at $t = 0$ all the points pass into the oxidized state and then the system returns to the reduced state. At $t = T_A$ transition into the oxidized state occurs at the point X_A from which a wave begins to spread with velocity equal to V_0 . At $t = T_B$ the same process occurs at X_B . At $T = T_0$, transition into the oxidized state occurs in all parts of space free from waves coming from leading centres, and this annihilates one (external) wave from every leading centre. In the absence of this general oxidation, the velocity of propagation of the zone synchronized by one particular leading centre equals V_0 . With general oxidation, the mean velocity of propagation of the zone by leading centres is given by

$$V_i = V_0 \left(1 - \frac{T_i}{T_0}\right); \text{ with period } T_i$$

At

$$t = \frac{T_0}{V_0} \cdot \frac{X_B - X_A}{2T_0 - T_A - T_B}$$

waves from centres A and B collide, and the point of collision then moves towards X_B with mean velocity

$$V = V_0 \frac{T_B - T_A}{T_B + T_A}$$

The complete development of the picture in time is accompanied by the appearance of some characteristic points in X, t -space (Fig. 2). At point G , time t_G , general oxidation ceases to the left, from centre A .

$$X_G = 0; t_G = T_0 \frac{X_A}{V_0(T_0 - T_A)}$$

At C , general oxidation ceases between A and B .

$$X_C = \frac{X_B(T_0 - T_A) + X_A(T_0 - T_B)}{2T_0 - T_B - T_A}; t_C = \frac{T_0(X_B - X_A)}{V_0(2T_0 - T_B - T_A)}$$

At D , the centre B is captured by higher-frequency centre A .

$$X_D = X_B; t_D = \frac{T_B(X_B - X_A)}{V_0(T_B - T_A)}$$

It should be noted that the time at which this takes place (t_D) does not depend on general oxidation being present in the system. At E , despite the disappearance of the centre B , its waves continue to propagate in the triangle DEH , and waves from centre A begin to interact with the general oxidation patterns.

$$X_E = \frac{X_B(T_0 - T_A) - X_A(T_0 - T_B)}{T_B - T_A}; t_E = \frac{T_0(X_B - X_A)}{V_0(T_B - T_A)}$$

At F , waves from the higher-frequency centre A fill the whole tube.

$$X_F = L; t_F = \frac{T_0(L - X_A)}{V_0(T_0 - T_A)}$$

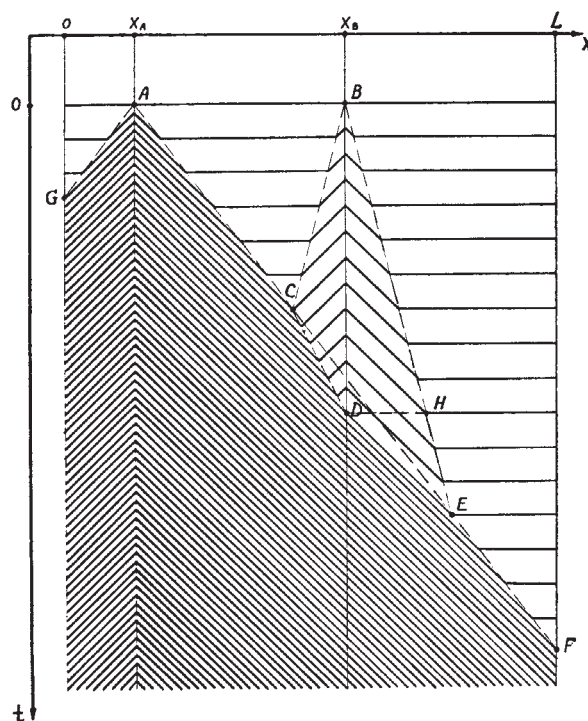


Fig. 2. Wave propagation in one-dimensional model.

It should be noted that t_F does not depend on the existence of the centre B .

All these events may be observed in a two-dimensional model on the straight line passing through two leading centres.

Similar models have been applied to the explanation of impulse propagation in cardiac muscle¹²⁻¹⁴.

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A. N. ZAIKIN
A. M. ZHABOTINSKY

Institute of Biological Physics,
Academy of Sciences of the USSR,
Puschino, Moscow Region.

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Solid State Chemistry and Colloid Chemistry

THE properties of the solid state are often ignored in studies of lyophobic colloidal phenomena. Colloid chemists concentrate on the liquid phase when trying to interpret experiments, and consider the solid phase as relevant only in the role of an adsorbent or of a charged surface.

In 1947, Grimley and Mott¹ pointed out how solid state properties, in particular the type and the number of lattice defects, might influence colloidal phenomena. Until recently, very little attention was paid to their article, except by Mackor² and by Ottewill and Woodbridge³, who rekindled the interest in Grimley and Mott's article. Recent experiments carried out in our laboratory have shown that the introduction of divalent anions or cations to AgBr crystals causes a considerable shift of the point of zero charge (p.z.c.) of AgBr⁴. The p.z.c. of AgBr is defined as that concentration of silver ions in solution (Ag_1^+) for which the crystals carry no net charge. According to Grimley and Mott the net charge in the crystals depends on the equilibrium $Ag_2^+ \rightleftharpoons Ag_1^+$, or the p.z.c. depends on the concentration of interstitial silver ions (Ag_1^+) in the crystals. The introduction of S^{2-} in the crystals increases $[Ag_1^+]$ and hence the p.z.c. is expected to shift to a higher $[Ag_2^+]$ (lower $pAg^{p.z.c.}$). Conversely, the introduction of Pb^{2+} in the crystals decreases $[Ag_1^+]$, and the p.z.c. is expected to shift to a lower $[Ag_2^+]$, in agreement with the experimental data presented in Table 1.

A second property of the solid phase, which has to be considered, is the potential difference which exists between

the surface and the bulk of the crystal due to a surface charge in the crystal, as pointed out by Lehoc⁵, Kliever⁶ and Trautweiler⁷. We note that the origin of this surface charge is not the same as the surface charge usually assumed in colloid chemistry. The "colloid chemical" version of the boundary charge is an adsorption or desorption of ionic species on the surface from the solution. The "solid state chemical" version of the boundary charge is a different concentration of interstitials and vacancies in the surface region compared with the bulk of the crystals.

The existence of this surface charge leads to a modification of Grimley's theory^{4,8,9}. From measurements of the p.z.c. of AgBr it is then possible to calculate the concentrations of lattice defects and the surface charge of AgBr. It turned out that the fraction of the lattice defects at 25° C in pure AgBr is $10^{-7.2}$ and the surface charge is $-0.011 \mu Ci/cm^2$. From measurements of the latent image Trautweiler found $10^{-7.6}$ and $-0.03 \mu Ci/cm^2$ respectively, while the extrapolated value from conductivity measurements is $10^{-7.5}$ for the fraction of lattice defects. There is fair agreement between these data. In our case it has thus been possible to deduce data of the "dry state" from "wet" experiments.

Generally speaking, the interaction between the disciplines of colloid chemistry and of solid state chemistry is two-fold. First, the properties of the solid phase do influence the colloidal properties when such a solid is dispersed in a liquid, and second the magnitude of certain parameters of the solid phase can be deduced from colloidal measurements. In the previous section this point of view was demonstrated: the p.z.c. of AgBr is determined by the concentrations of lattice defects in AgBr, and these concentrations can be calculated from the measured p.z.c. of AgBr.

A second example is the relationship between the net charge of AgI and the silver ion concentration in solution. Instead of the usual assumption of a Stern layer in the liquid phase, with a dielectric constant of about 5 and a capacity which is a function of charge, the experimental data could be explained fairly well by a theory based on lattice defects and a fixed surface charge in AgI⁹. The fraction of lattice defects of AgI at 20° C is $10^{-2.8}$ and the surface charge is $-1.2 \mu Ci/cm^2$ —deduced from fitting the experimental data to the theory.

As a third example, consider measurements of the time necessary for equilibration in a colloidal system. If diffusion in the solid is the rate determining process, it should be possible to calculate the diffusion coefficient D of the most mobile type of lattice defects from the time for equilibration, which is roughly equal to $V\epsilon RT/16\pi F^2D$, where V is the molar volume, ϵ the dielectric constant of the solid, and R , T and F have their usual significance⁴.

As a fourth example, a better understanding of the magnitude of the zeta potential might be obtained by noting that only part of the total potential jump between the bulk solid phase and the bulk liquid phase is situated in the liquid^{8,9}.

Not only colloidal phenomena but also electrochemical phenomena are influenced by lattice defects, as pointed out by Awad¹¹, who measured the overpotential at silver anodes covered with anodically deposited AgBr layers, and by Hall and Bruner¹², who measured the electrical resistance of thin AgBr membranes between two AgNO₃ solutions.

Whether a secondary electrode of the type metal/insoluble metal salt behaves as a reproducible and accurate electrode probably also depends on the solid state properties of the salt. In particular the concentrations and the diffusion coefficients of the lattice defects must have a certain minimum value in order for equilibrium to be quickly established. Silver halides, for example, which make very good secondary electrodes, have a large concentration of lattice defects with high diffusion coefficients. It may

Table 1. POINTS OF ZERO CHARGE AT 25° C OF SULPHUR AND LEAD-DOPED AgBr

Dope	—	S	S	Pb	Pb	Pb	Pb
Dope, mole fraction (units 10^{-4})	—	0.44	4.7	1.35	1.45	1.45	5.0
$pAg^{p.z.c.}$	5.40	3.47	2.63	9.61	9.56	9.62	10.37