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DETECTION OF INTERPHASE INSTABILITY FROM LUMINESCENCE OF REACTION PRODUCTS

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The reaction between chlorine and an alkaline solution of hydrogen peroxide is suggested for the investigation of chemothermocapillary convection [1].

In recent years there has been growing interest in problems connected with interphase instability. The reason is, in particular, that this effect can intensify mass transfer by an order of magnitude [2]. However, the number of experimental methods for studying the effect is limited.

In the present paper a method based on recording the luminescence of the reaction products is proposed for studying the interphase instability in gas-liquid systems.

Mass transfer processes in gas-liquid systems with chemical reactions accompanied by interphase instability are characterized by convective motion initiated in the liquid phase and directed normal to the interface. In this case the most suitable systems for studying interphase instability are those where the reactions proceed almost instantaneously, i.e., the dissolved gas reacts instantaneously with the dissolved reagent and below the gas-liquid interface there is a plane with zero concentrations of both components and the process rate is only determined by the rate of diffusion of the reacting components toward this plane. The theory of an instantaneous reaction process and experimental verification of the existence (under these conditions) of a plane where the reaction proceeds can be found in [3, 4]. If in the reaction system with instantaneous reaction there exists interphase instability, a decrease in the speed of motion of the reaction plane into the bulk of the solution can be expected.

In the experimental verification of this hypothesis, difficulties arise that are associated with the location of the reaction plane. The difficulty can be overcome to a great extent by considering systems in which the reaction products have luminescent characteristics. In this case the region where the excited reaction products exist will depend on their lifetime in the liquid phase.

The system chlorine-alkaline solution of hydrogen peroxide was chosen as a model for testing the method proposed. The peculiarity of the system is that the reaction

$$H_2O_2 + 2NaOH + Cl_2 = 2H_2O + 2NaCl + O_2^* + 27.5 \quad \text{kcal/mole} \tag{1}$$

yields 100% of excited $O_2^* - O_2('\Delta_g)$ oxygen, emitting at $\lambda = 1.27$ μm [5]. The lifetime of O_2^* in this solution is probably close to that in water, $\tau_{H_2O} = (3.09 \pm 0.06) \cdot 10^{-6}$ sec [6], and the lifetime in the gas phase is many orders of magnitude longer and depends on the partial pressure of O_2^* due to homogeneous quenching processes:

$$O_2^* + O_2^* \xrightarrow{K_1} O_2^{**} + O_2,$$

$$O_2^{**} + H_2O \xrightarrow{K_2} O_2^* + H_2O,$$

$$O_2^* + H_2O \xrightarrow{K_3} O_2 + H_2O,$$

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where $O_2^{**} - O_2('\Sigma_g^-)$, $K_1 = (2.0 \pm 0.5) \cdot 10^{-17}\ \mathrm{cm^3/sec}$, $K_2 = (6.7 \pm 0.5) \cdot 10^{-12}\ \mathrm{cm^3/sec}$, and $K_3 = (5.6 \pm 0.4) \cdot 10^{-18}\ \mathrm{cm^3/sec}$ [7].

In [8] it is shown that the probability of the yield of singlet oxygen from the solution at depth x without quenching is

$$P(x) = \frac{\alpha}{\alpha + \sqrt{D_{O_2}^{\mathrm{liq}}/\tau}} \exp\left(-\frac{x}{\sqrt{D_{O_2}^{\mathrm{liq}}\tau}}\right). \tag{2}$$

According to the instantaneous reaction model, the motion of the reaction plane deeper into the solution is governed by the law

$$x = 2\beta\sqrt{t}, \tag{3}$$

where β for reaction (1) with $D_{O_2}^{\mathrm{liq}} = D_{Cl_2}^{\mathrm{liq}}$ has the form

$$\beta = \frac{[Cl_2]_{\mathrm{liq}}}{[Cl_2]_{\mathrm{liq}} + [HO_2^-]} \sqrt{D_{Cl_2}^{\mathrm{liq}}}\ . \tag{4}$$

Substituting (4) and (3) into (2), we obtain the probability of the yield of excited oxygen as a function of time for the instantaneous reaction (1):

$$P(t) = \frac{\alpha}{\alpha + \sqrt{D_{O_2}^{\mathrm{liq}}/\tau}} \exp\left(-\frac{2\,[Cl_2]_{\mathrm{liq}}}{[Cl_2]_{\mathrm{liq}} + [HO_2^-]} \sqrt{\left(\frac{D_{Cl_2}^{\mathrm{liq}}}{D_{O_2}^{\mathrm{liq}}}\,\frac{t}{\tau}\right)}\right).$$

Let us consider the conditions under which reaction (1) can be assumed instantaneous. According to [3, 4] the following condition should be observed:

$$\sqrt{\left(\frac{\pi}{4} K B t\right)} \gg E_i, \tag{5}$$

where K is the constant of the second-order reaction rate; B is the concentration of the reagent reacting with the dissolved gas (chlorine) in the main liquid.

According to [9] O_2^* is produced directly as a result of the second-order reaction

$$HO_2^- + Cl_2 \xrightarrow{K} O_2^* + Cl^- + HCl \tag{6}$$

with $K \gtrsim 10^8$ liter/(mole·sec). Therefore, the HO_2^- ion produced rapidly in the reaction

$$H_2O_2 + OH^- \rightleftarrows HO_2^- + H_2O$$

should be considered as the component B.

The acceleration coefficient E_i for reaction (6) has the form

$$E_i = 1 + \frac{[HO_2^-]}{[Cl_2]_{\mathrm{liq}}} \tag{7}$$

provided $D_{O_2}^{\mathrm{liq}} = D_{Cl_2}^{\mathrm{liq}}$. It should be noted that for $D_{O_2}^{\mathrm{liq}} \neq D_{Cl_2}^{\mathrm{liq}}$ the results obtained numerically from relations (4) and (7) can differ by 12% at most.

In view of the above, condition (5) has the form

$$\sqrt{\left(\frac{\pi}{4} K [HO_2^-] t\right)} \gg 1 + \frac{[HO_2^-]}{[Cl_2]_{\mathrm{liq}}},$$

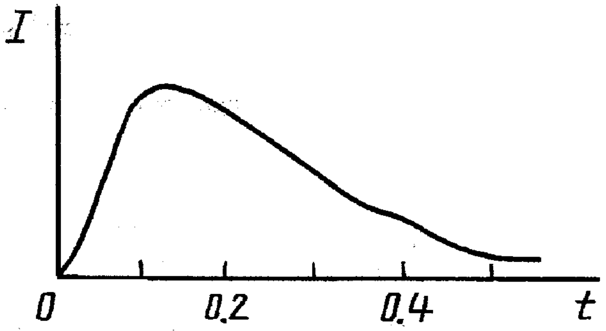

Fig. 1. Luminescence intensity of singlet oxygen I (rel. units) versus time (sec).

from which with $[HO_2^-]/[Cl_2]_{liq} \approx 10$

$$t \gg \frac{4}{\pi}\frac{1}{K}\frac{[HO_2^-]}{[Cl_2]^2_{liq}} \approx \frac{[HO_2^-]}{[Cl_2]^2_{liq}} \cdot 10^{-8} \approx \frac{1}{[Cl_2]_{liq}} \cdot 10^{-7}.$$

Thus, reaction (1) can be considered instantaneous for $[Cl_2]_{liq} = 0.1$ mole/liter (at a chlorine pressure of 10^5 Pa), if $[HO_2^-] \approx 1$ mole/liter and the observation time $t \geq 10^{-5}$ sec.

With these parameters and the purely diffusive mechanism of the process, the reaction plane will reach the depth $x \approx 10^{-5}$ cm, from which O_2^* cannot yield into the gas phase for time $t = 10^{-2}$ sec, which exceeds substantially the minimum period, after which the reaction can be considered instantaneous. As was noted earlier here, with interphase instability the time necessary to reach this depth should increase.

It should also be noted that after O_2^* stops yielding into the gas phase, the signal from the gas phase will be observed for some more time and should decay following an exponential law, since the lifetime of O_2^* in the gas phase is many orders of magnitude longer than that in the liquid phase and depends on the partial pressure of O_2^*.

The authors carried out some initial experiments to verify the possibility of observing the appearance of the interphase instability by recording the luminescence of O_2^*.

The experimental setup consisted of a source of chlorine, supplied via a glass tube with 6 mm inner diameter at a rate of 10 cm/sec and atmospheric pressure. The tube end was placed 1 cm above the surface of an alkaline solution of hydrogen peroxide ([NaOH], 1.2 mole/liter), which was poured into a test tube of diameter 20 mm to a height of 6 cm. An FD-5G photosensor was placed in the phase interface plane, and its signal was applied to an F-8024/S amplifier and then to an ENDIM 622.01 graph plotter with a scanning rate of 10 cm/sec. The typical shape of the recorded signal is shown in Fig. 1.

This scheme of supplying chlorine to the liquid surface was chosen to facilitate appearance of interphase instability in the system. The initial period to $t \approx 0.1$ sec actually corresponds, to the time of spreading chlorine over the surface from the center to the test tube walls. After the time $t \approx 0.4$ sec the luminescence is recorded only from the liquid phase. The substantially longer time of the signal recording compared with the expected one for the strictly diffusion mechanism of the reaction and a virtually linear time function of the signal decay are indicative of the appearance of interphase instability in the system.

The present preliminary results allow us to hope that the system chlorine-alkaline solution of hydrogen peroxide will be used with the appropriate experimental equipment for thorough investigation of the processes at the gas-liquid interface. An indisputable advantage of the method proposed is obtaining information about the state of the system from the luminescence of the reaction products.

NOTATION

λ, O_2^* radiation wavelength, μm; τ, O_2^* lifetime, sec; K_1, K_2, K_3, reaction rate constants, cm^3/sec; x, distance measured from the interface plane to the liquid depth, cm; α, speed, at which oxygen passes the interface, cm/sec; D, diffusivity, cm^2/sec; $P(x)$, probability of yielding O_2^* into the gas phase; β, quantity determined from equation (4); t, time, sec; E_i, absorption acceleration coefficient in the instantaneous reaction; K, rate constant of the second-order reaction, liter/(mole·sec); B, concentration of the reacting component in the liquid phase, mole/liter; I, recorded signal intensity, rel.units.

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