

## MASS TRANSFER WITH FAST CHEMICAL REACTION IN A FALLING DROP

P. NEKOVÁŘ<sup>a</sup> and V. VACEK<sup>b</sup>

<sup>a</sup> *Chemical Engineering Department,  
Institute of Chemical Technology, 166 28 Prague 6*

<sup>b</sup> *Institute of Inorganic Chemistry,  
Czechoslovak Academy of Sciences, 250 68 Prague - Řež*

Received May 10th, 1973

Mass transfer into a single drop in a system of two immiscible liquids is studied. Inside the drop a fast chemical reaction takes place with mass transfer remaining the controlling operation. At mass transfer from the continuous phase into the drop there exists a region in the drop where the reactant is present and the region where due to the reaction it is absent. Both these regions were visualized by using a dye and the change of their volume was determined in dependence on time, drop size and concentration of reacting components. The effects of surface active agents and of stirring the continuous phase were also studied. A comparison has been made of the process during the drop formation and during the subsequent motion through continuous phase. The experimental results are compared with simplified theoretical models.

For experimental studies on mass transfer into the drop in a system of two immiscible liquids it is especially necessary to prevent changes in hydrodynamic conditions of the system by the experimental technique used. The experimental procedure must also respect the fact that mass transfer takes place both at the time of formation of the drop as well as during its motion through the continuous phase and at the drop coalescence. From the hydrodynamic point of view these are different stages but it is difficult to determine the mass of component transferred in these individual stages. Here, a simple optical method for determination of mass transfer in a drop is presented, where in the drop a fast chemical reaction takes place between the transferred component and the reactant originally present in the drop but where mass transfer remains the controlling operation. By distinguishing in colour the reactant from the remaining part of the drop, information on this process can be obtained.

A similar problem has been studied experimentally by Tyroler and coworkers<sup>1</sup> for stationary and circulating viscous drops under conditions when the numerical solutions of mass transfer equations for the given problem could have been verified. Mathematically a similar problem has been solved by Sherwood and Pigford<sup>2</sup> for the simple case of absorption into a thick stationary planary layer in which a fast chemical reaction takes place. This approach leads to the solution of the problem with a moving boundary. Analogous derivation for a drop in which, moreover, internal streaming takes place is a problem rather complex<sup>3</sup> and its simple solution can be obtained only for very simplified cases<sup>4</sup>.

## THEORETICAL

In a stationary continuous phase the substance A having the mean molar concentration  $c_{Ac}$  is present in the solvent C. The dispersed phase in which the component B of concentration  $c_{BD}$  in the solvent D is fed by a nozzle immersed into the continuous phase. The solvents C and D are immiscible. When both phases are brought into contact the component A is transferred into the forming drop in which a fast chemical reaction of the form



takes place.

On separation of the drop from the nozzle the reaction proceeds during the motion of the drop in the continuous phase, of course without supply of component B until all the component B undergoes the reaction (Fig. 1).

Let us assume that in the drop exist two regions  $\mathcal{A}$  and  $\mathcal{B}$ . As a fast chemical reaction is considered, the region  $\mathcal{A}$  is limited by the space where no component B, is present, region  $\mathcal{B}$  by the space without the component A. The regions  $\mathcal{A}$  and  $\mathcal{B}$  are separated by a moving reaction boundary  $\mathcal{S}$  at which the concentrations of both components are nil. Further is assumed that the concentrations of components A and B and AB in the solvent D are low.

The continuity equation

$$\partial c_i / \partial t = \nabla(D_i \nabla c_i) - \mathbf{v} \nabla c_i \quad (2)$$

can be written for the component  $i = A$  in the region  $\mathcal{A}$  and for component  $i = B$  in the region  $\mathcal{B}$ . For solution it is necessary to know the components of the vector of the streaming velocity inside the drop. This description leads to the moving boundary problem with a joint boundary condition for regions  $\mathcal{A}$  and  $\mathcal{B}$

$$c_i = 0 \quad (i = A, B) \quad (\text{point on the reaction boundary}). \quad (3)$$

For a point on this reaction boundary the balance relation holds

$$D_A \nabla c_A = -D_B \nabla c_B \quad (\text{point on the reaction boundary}). \quad (4)$$

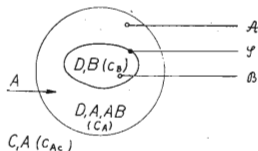


FIG. 1  
Operation and Symbols Used

Analytical solution of such system of equations with the usual initial conditions and with the boundary condition on the drop surface has not been found even for one-dimensional problem in a spherical symmetry without flow. But there exists a method how with additional simplification the complication of the moving boundary can be eliminated. Let us assume that at the reaction boundary holds

$$D_A = D_B = D \quad (\text{point on the reaction boundary}). \quad (5)$$

Concentrations of components are expressed by use of a new concentration  $c$ :

$$c = c_A \quad \text{for component A in the region } \mathcal{A}, \quad (6)$$

$$c = -c_B \quad \text{for component B in the region } \mathcal{B}. \quad (7)$$

Diffusivity  $D$  can be then considered a continuous function of concentration  $c$ . From Eq. (4) results equality of concentration gradients of  $c$  on both sides of the plane  $\mathcal{S}$ . It is possible to use the known solutions of the mass transfer equation as the moving reaction boundary area does not need to be considered.

The boundary condition on the drop surface results from the equation for flux of component across the interface

$$\dot{n} = k_c s (c_{Ac} - c_{Ac}^*) = V(d\bar{c}/dt). \quad (8)$$

For the introduced concentration  $c$  holds

$$\bar{c}(t) = 1/V \int c \, dV. \quad (9)$$

Concentrations on the interface are related by the equilibrium relation

$$c^* = m c_{Ac}^*, \quad (10)$$

with the concentration  $c_{Am}$  defined by

$$c_{Am} = m c_{Ac}. \quad (11)$$

Let us further assume that the drop is spherical and symmetrical along the vertical axis. Changes in the concentration gradient are not considered in the continuous phase along the drop surface during its motion. The origin and way of formation of the drop is not considered as well and, on the contrary, we assume that the drop forms so that at the moment of its origin the concentration in the whole volume is  $c_{BO}$ . The quantities  $c_{Am}$ ,  $c_{BO}$ ,  $m$ ,  $D$ ,  $k_c$  are considered constant. Next, two simplified limiting cases of stationary and turbulent drops are given.

For a stationary, spherical, axially symmetrical drop an equation can be derived (see Appendix) describing the motion of the reaction boundary

$$C_s = 1 - \frac{2L}{R} \sum_{n=1}^{\infty} \frac{\sin(\beta_n R) \exp(-\beta_n^2 T)}{\sin \beta_n [\beta_n + L(L-1)]}, \quad (12)$$

where the dimensionless variables are

$$C_s = c_{BO}/(c_{Am} + c_{BO}), \quad R = r/a, \quad T = Dt/a^2, \quad L = ak_c/md. \quad (13)$$

Equation for the dimensionless time in which the reaction is completed  $T_r$  is obtained from Eq. (12) for  $R = 0$

$$C_s = 1 - 2L \sum_{n=1}^{\infty} \frac{\beta_n \exp(-\beta_n^2 T_r)}{\sin \beta_n [\beta_n + L(L-1)]}. \quad (14)$$

As the second limiting case for a turbulent drop can be considered the modification of the model according to Handlos and Baron<sup>5</sup> (or by Wellek and Skelland<sup>6</sup>) which together with the resulting relation for calculation of the mass transfer coefficient on the side of the dispersed phase is most frequently used and which is in good agreement with the experimental data. According to the authors of this model an existence of a circulating toroide is assumed which is symmetrical around the vertical axis of a spherical drop and the sphere is substituted by this toroide. On this basis the relation of the effective turbulent diffusivity is derived.

After introducing the mean value of turbulent diffusivity in the toroidal symmetry an equation can be derived (see Appendix) describing the motion of the reaction boundary

$$C_s = 1 - 2L' \sum_{n=1}^{\infty} \frac{I_0(\beta'_n R') \exp(-\beta'^2_n T')}{(\beta'^2_n + L'^2) I_0(\beta'_n)}, \quad (15)$$

where the dimensionless variables are

$$T' = \frac{4\bar{D}t}{a^2} = \frac{1}{256(1+M)} \frac{ut}{a}, \quad (16)$$

$$L' = \frac{ak_c}{2m\bar{D}} = 512(1+M) \frac{k_c}{mu}, \quad (17)$$

$$M = \eta_d/\eta_c, \quad R' = 2r'/a, \quad (18)$$

and  $r$  is the radial variable in toroidal coordinates with the origin in the middle of radius of a spherical drop. The equation for the dimensionless time in which the reaction is completed  $T_r$  is obtained after substituting for  $R = 0$

$$C_s = 1 - 2L' \sum_{n=1}^{\infty} \frac{\exp(-\beta'^2_n T_r)}{(\beta'^2_n + L'^2) I_0(\beta'_n)}. \quad (19)$$

## EXPERIMENTAL

*Substances employed.* Both regions  $\mathcal{A}$  and  $\mathcal{B}$  were distinguished in colour by adding the indicator E into the dispersed phase so that the region  $\mathcal{B}$  was coloured and disappearance of this colour in the drop was observed. In some of experiments the surface active agent was added into the dispersed phase. In the experiments were used: A — acetic acid or formic acid, B — sodium hydroxide, C — benzene, D — water, E — 1% solution of phenolphthalein in ethyl alcohol (40 drops in 100 ml of the dispersed phase), F — sodium diisobutyl-naphthalensulfonate. Analytical grade compounds which were further purified by a repeated rectification and saturated solvents were used.

*Apparatus.* From the nozzle the dispersed phase was expelled at a constant (though variable) flow rate in a form of drops into a column filled with the continuous phase by use of a linear doser coupled with a syringe. The system was kept at constant temperature  $25^\circ \pm 0.1^\circ\text{C}$ .

The flow rate was determined by measuring the volume expelled in a time unit, volume of the drop by measuring the time necessary for its formation. The syringe was connected by a polyethylene hose with the nozzle made of a syringe needle by working of its edge into a conical shape so that spherical drops would form on the sharp edge of the nozzle. The internal diameters of the nozzles were 0.21 to 0.81 mm, radius of the formed drops was in the range of 1.75 to 2.75 mm, the steady terminal velocity was 10.5–12.6 cm/s and the corresponding range of the Reynolds number was 510 to 935. The column was formed by a glass tube (inside diameter 34 mm for the set of experiments 1, 74 mm for the set of experiments 2 and 3, length 1200 mm) situated in a jacket of rectangular cross-sectional area with two glass walls situated on opposite sides. To prevent an optical distortion, the space between the jacket and the column was filled with a continuous phase identical with that inside the column. On the back wall of the column jacket was situated a scale by which it was possible to determine the distance of the drop from the nozzle. The rim of the nozzle was submerged 10 mm below the liquid surface in the column. After the drop was separated a stop watch was put into operation and the doser was switched off. On reaching the chosen distance from the nozzle the drop was photographed and the stop watch switched off automatically.

## RESULTS AND DISCUSSION

### REACTION TIME

In the first series of experiments the distance from the nozzle was measured at which the colour of the drop disappeared. The effect of the drop size on hydroxide concentration in the dispersed phase at its inlet, and acid concentration in the continuous phase for two different acids was studied.

The experiments were arranged so that the drop diameters were in the range of 3 to 6 mm. The velocity in the nozzle was as high as possible under the condition that formation of individual drops was preserved. The range of Reynolds numbers ( $2ua \rho_c / \eta_c$ ) 516 to 780 should have corresponded to the turbulent flow regime, the Peclet number ( $au/D_A$ ) was large, with its order of magnitude  $10^5$ . At its fall the drop has reached on a relatively short path (4 cm) approximately a constant terminal velocity. In the experiments with formic acid its concentrations in the continuous

phase were 0.05 mol/l and 0.11 mol/l, initial concentrations of sodium hydroxide  $5 \cdot 10^{-4}$  to 9.2 mol/l. In the experiments with acetic acid its concentrations in the continuous phase were 0.45 to 0.67 mol/l, initial concentrations of sodium hydroxide  $5 \cdot 10^{-4}$  to 0.21 mol/l. The colour of drops has disappeared at the distance 22 to 112 cm (set of experiments 1).

For the time dependence the dimensionless time

$$T'' = ut/a, \quad (20)$$

was used, where the time  $t = 0$  corresponded to the moment of separation of the drop from the nozzle. In Fig. 2 are plotted experimental times of colour disappearance  $T_r'' = ut_r/a$  in dependence on dimensionless concentration  $C_s$  on area  $\mathcal{S}$  for two different acids, two concentrations of acids, and two drop diameters.

It is obvious from this figure that for low acid concentrations an approximately linear dependence was obtained in logarithmic coordinates. Dependence for both acids used are different which corresponds to different values of the term  $k_c a/mD$ . In Fig. 2 are further plotted curves corresponding to Eqs (15) and (19). The dimen-

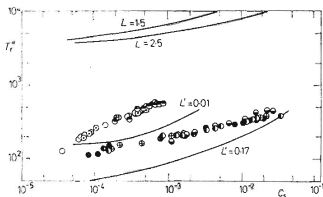


FIG. 2

Dependence of the Dimensionless Time in which the Reaction is Accomplished on Dimensionless Concentration on Phase Boundary

Conditions in the series 1: ●  $a = 0.185$  cm,  $u = 10.9$  cm/s,  $c_{Ac} = 0.05$  mol/l,  $c_{BO} = 1.0$  to  $9.2 \cdot 10^{-3}$  mol/l,  $l_r = 28.4-108.0$  cm; ○  $a = 0.185$  cm,  $u = 10.9$  cm/s,  $c_{Ac} = 0.11$  mol/l,  $c_{BO} = 2.1-9.2 \cdot 10^{-3}$  mol/l,  $l_r = 18.5-106.0$  cm; ⊙  $a = 0.245$  cm,  $u = 12.5$  cm/s,  $c_{Ac} = 0.05$  mol/l,  $c_{BO} = 0.7-5.2 \cdot 10^{-3}$  mol/l,  $l_r = 47.2-112.0$  cm; ○  $a = 0.245$  cm,  $u = 12.5$  cm/s,  $c_{Ac} = 0.11$  mol/l,  $c_{BO} = 0.5-5.2 \cdot 10^{-3}$  mol/l,  $l_r = 31.4-103.3$  cm, formic acid; ●  $a = 0.175$  cm,  $u = 10.8$  cm/s,  $c_{Ac} = 0.45$  mol/l,  $c_{BO} = 5.1-125.4 \cdot 10^{-3}$  mol/l,  $l_r = 30.7-80.3$  cm; ●  $a = 0.175$  cm,  $u = 10.8$  cm/s,  $c_{Ac} = 0.67$  mol/l,  $c_{BO} = 1.0-209.0 \cdot 10^{-3}$  mol/l,  $l_r = 22.7-67.3$  cm; ⊗  $a = 0.265$  cm,  $u = 12.4$  cm/s,  $c_{Ac} = 0.45$  mol/l,  $c_{BO} = 0.8-102.3 \cdot 10^{-3}$  mol/l,  $l_r = 36.0$  to  $105.0$  cm; ●  $a = 0.265$  cm,  $u = 12.4$  cm/s,  $c_{Ac} = 0.67$  mol/l,  $c_{BO} = 0.5-124.0 \cdot 10^{-3}$  mol/l,  $l_r = 29.4-93.6$  cm, acetic acid. The curves correspond to Eq. (19) for the formic acid ( $L' = 0.01$ ) and acetic acid ( $L' = 0.17$ ), equation (14) for the formic acid ( $L = 1.5$ ) and acetic acid ( $L = 2.5$ ), both last two for  $a = 0.25$  cm.

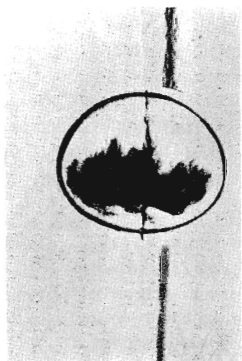
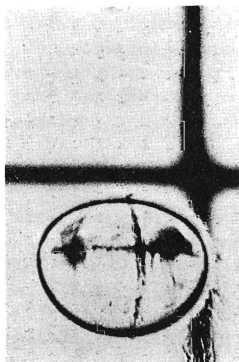
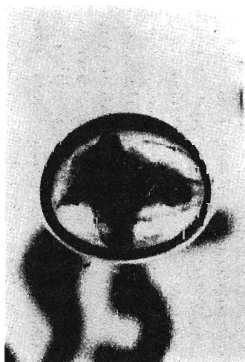
*a**b**c*

FIG. 4

## Colour Disappearance of the Drop

*a* Drop at the distance 8 cm from the nozzle; *b* drop at the distance 16 cm from the nozzle ( $a = 0.23$  cm,  $c_{Ac} = 0.53$  mol/l,  $c_{BO} = 6.8 \cdot 10^{-3}$  mol/l); *c* drop with the surface active agent present ( $a = 0.22$  cm,  $c_{Ac} = 0.36$  mol/l,  $c_{BO} = 4.7 \cdot 10^{-3}$  mol/l,  $c_F = 3.5 \cdot 10^{-5}$  mol/l, distance from the nozzle 35 cm).

sionless time  $T$  from Eq. (15) was recalculated to  $T''$  for the smaller drop diameter and for  $D = D_A$ . The curves for formic acid have smaller values of  $L$  and  $L'$ . For calculation of  $L$  and  $L'$  the quantities  $m$ ,  $D$ ,  $k_c$  were determined or calculated from literature,  $k_c$  was calculated from the relation by Garner and Tayeban which was recommended by Wellek and Skelland<sup>6</sup>. The terminal velocity and viscosities were measured. The plotted curves represent boundaries within which the experimental results should be situated and according to our expectations the results are closer to the boundary representing the turbulent drop model.

### Presence of the Surface Active Agent

In the next experimental series the effect of surface active agent in the dispersed phase has been studied. As the surface active agent sodium diisobutyl naphthalenesulfonate was used. Its concentrations were  $3.5 \cdot 10^{-5}$ ,  $2.9 \cdot 10^{-8}$  mol/l and the zero concentration. The acid was acetic acid with concentration in the continuous phase 0.36 mol/l. Initial concentration of sodium hydroxide were  $4.7 \cdot 10^{-3}$  to 0.085 mol/l and they were chosen so that the colour of drops had disappeared on the path corresponding to the length of the column (experimental series 2).

The effect of the surface active agent on time in which the reaction was accomplished is plotted in Fig. 3. There is also plotted the curve corresponding to the results

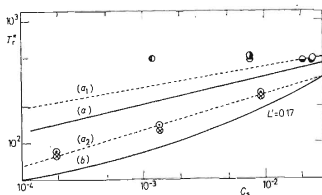


FIG. 3

Effect of Presence of the Surface Active Agent, Mixing of the Continuous Phase and Rate of Drop Formation on Dimensionless Time of Reaction Termination

Conditions in the series 2:  $\circ$   $a = 0.195$  cm,  $c_F = 0$  mol/l,  $c_{Ac} = 0.32$  mol/l,  $c_{BO} = 76.2 \cdot 10^{-3}$  mol/l,  $l_r = 96.0$  cm;  $\bullet$   $a = 0.277$ ,  $c_F = 0$ ,  $c_{Ac} = 0.35$ ,  $c_{BO} = 82.2 \cdot 10^{-3}$ ,  $l_r = 91.0$  cm;  $\ominus$   $a = 0.196$ ,  $c_F = 2.9 \cdot 10^{-8}$ ,  $c_{Ac} = 0.36$ ,  $c_{BO} = 85.3$ ,  $l_r = 96.0$  cm;  $\oplus$   $a = 0.213$ ,  $c_F = 2.9 \cdot 10^{-8}$ ,  $c_{Ac} = 0.36$ ,  $c_{BO} = 29.03 \cdot 10^{-3}$ ,  $l_r = 109.0$  cm;  $\otimes$   $a = 0.198$ ,  $c_F = 3.5 \cdot 10^{-5}$ ,  $c_{Ac} = 0.38$ ,  $c_{BO} = 30.9 \cdot 10^{-3}$ ,  $l_r = 99.0$  cm;  $\odot$   $a = 0.215$ ,  $c_F = 3.6 \cdot 10^{-5}$ ,  $c_{Ac} = 0.36$ ,  $c_{BO} = 4.7 \cdot 10^{-3}$ ,  $l_r = 103.0$  cm. Experiments with the continuous phase mixed  $\otimes$   $a = 0.23$  cm,  $\dot{V}_d = 19.8 \cdot 10^{-3}$  cm<sup>3</sup>/s,  $\odot$  extrapolation for  $\dot{V}_d \rightarrow \infty$ . Straight line (a) corresponds to the experimental dependence for acetic acid from Fig. 2 with (a<sub>1</sub>) being the upper and (a<sub>2</sub>) the lower limit of experimental points in series 1, which were not averaged, curve b corresponds to Eq. (19).



given in Fig. 2 and also points of the experiments with three concentrations of the surface active agent (one of them is nil). To get approximately the same time of disappearance of colour it was necessary to reduce the concentration  $c_{BO}$  (and  $C_s$ ) in respect to that in the experiments performed in absence of the surface active agent. The slower reaction rate in presence of the surface active agent is more profound for larger drops. The corresponding points are situated above the curve representing the results of the series 1 which is in agreement with the considerations made on increase of the resistance to mass transfer and reduced mixing in the drop.

### *Mixing of the Continuous Phase*

Points in Fig. 2 represent the average value of 200 measurements. They are replotted in Fig. 3 from Fig. 2 as a solid line. The individual experimental values had a wide spread. Dashed lines are boundaries within which the individual experimental values varied. In the next (third) experimental series it was studied whether longer times of disappearance of colour affecting the mean value were not affected by the nonhomogenities in concentration of component A in the continuous phase. In this experimental series 50 values were used for obtaining the mean time of colour disappearance with the continuous phase being mixed each time after five drops have been observed. In these experiments acetic acid at the concentration 0.54 mol/l in the continuous phase was used and the initial concentrations of sodium hydroxide in the continuous phase were in the range  $9 \cdot 10^{-4}$  to  $4.8 \cdot 10^{-2}$  mol/l. These results are plotted in Fig. 3. It is obvious that these experimental points correspond to the above mentioned lower boundary of results of the series 1 and is also close to the curve plotted according to Eq. (19).

### *Rate of Drop Formation*

For comparison of disappearance of colour of the drop during its formation on the nozzle and after its separation the series of experiments 3 was made. In this series the flow rate of the dispersed phase was in the range 3.2 to 32.9 mm<sup>3</sup>/s (this corresponds to velocities in the nozzle 2.3 to 24.5 cm/s and to Reynolds numbers for flow in the nozzle from 19 to 55). At low flow rates where the time of drop formation was longer the disappearance of colour during the fall took less time than at fast formation. Exception made the drops formed from the nozzle of the smallest diameter. At low concentration  $c_{BO}$  a considerable change in colour has been observed during the formation which is the result of thorough mixing of the liquid contained in the drop before its separation accompanied by its oscillations. At higher concentrations  $c_{BO}$  this phenomenon has been observed only irregularly and not for all drops. Points in Fig. 2 (especially at higher dimensionless concentrations  $C_s$ ) are affected

by an error resulting from mass transfer at the formation and at extrapolation to the zero time of drop formation at which the obtained dimensionless times of colour disappearance should be greater. The method of such extrapolation is discussed in the following part. In Fig. 3 are plotted for comparison points obtained by extrapolation to the zero time of drop formation and the points with the corresponding flow rate of the dispersed phase through the nozzle  $\dot{V}_d = 19.8 \text{ mm}^3/\text{s}$ . From this Figure it is also obvious that the distance of these points from the curve corresponding to Eq. (19) is approximately constant. The character of the dependence is thus well represented by the proposed simplified model.

#### COURSE OF REACTION DURING THE FALL OF DROP IN THE CONTINUOUS PHASE

When observing the changes in colour of regions in the drop, partial changes could be seen already during the formation of the drop. After its separation from the nozzle the coloured part did not reach the contour of the drop. At the fall of the drop, mixing of the coloured part has been observed together with reduction in its size. Also the intensity of colour in the whole coloured region has decreased. The change in colour at the fall of the drop continued much faster than at its formation. The moving boundary between the coloured and non-coloured parts was rather irregular as can be seen from Fig. 4.

In Fig. 4a the situation is demonstrated at the distance of 8 cm of the drop path. It can be seen that in the drop an intensive circulation and mixing of the internal space take place. In Fig. 4b is a similar drop twice as far from the nozzle. Here, already considerable change in colour took place and the coloured part was situated around the assumed circulation centers.

Somewhat different picture is obtained in the presence of the surface active agent in the dispersed phase (Fig. 4c). In the front part of the drop a discoloured region forms which spreads farther. In the given figure it is the bottom part of the drop, where the drop moves downwards. The other part of the drop seems to be stagnant; no differences have been observed in the intensity of the colour inside the coloured part. Contours of projection of the coloured region during the fall of the drop correspond well to the shape of isotherms as Head and Hellums<sup>7</sup> have found in the drop with a fully developed and suppressed circulation.

#### *Ratio of Colour Disappearance*

As the contour of the projection of the coloured part of drop is irregular the ratio of colour disappearance has been chosen as an indication how the reaction proceeds which is further on denoted as  $P$ . It is defined as the ratio of projection of that part

See insert facing p. 2762.

of drop which is without colour to the total area of drop projection. It was determined from coloured photographs with the average value calculated from 10 snaps.

An example of the dependence of ratio of colour disappearance on time is given in Fig. 5. Straight lines connecting individual points can be drawn with the change in their slope at the time of separation of the drop from the nozzle. From slopes of these straight lines is obvious that the colour disappearance is slower at the drop formation than at its fall. In the figure are presented changes in the colour disappearance for drops of various sizes with differing times of their formation at a low initial concentration of hydroxide. At higher hydroxide concentrations the differences in ratios of colour disappearance at the drop formation are not so great.

In solutions of the experimental series 3 the ratio of colour disappearance in the interval of drop formation has been affected by all the studied variables (*i.e.* drop diameter, rate of formation and the hydroxide concentration), the colour disappearance in the interval of the drop fall has been affected especially by the initial hydroxide concentration.

It can be expected for the fall of the drop that according to Eq. (15) the ratio of colour disappearance would be a function  $P = P(T'', C_s, L')$ . This dependence is plotted in Fig. 6, with  $L'$  assumed to be constant.

The origin of the time scale  $T'' = 0$  was obtained by extrapolation from the dependence given in Fig. 5 for  $P = 0$ . From this figure can be seen that in the experiments of the series 3 approximately linear dependences were obtained. Small drops

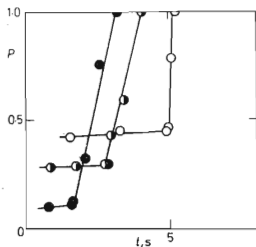


FIG. 5

Effect of Velocity of the Dispersed Phase in the Nozzle on Rate of Colour Disappearance of the Drop

○  $v = 3.9$  cm/s, ◐  $7.1$  cm/s, ●  $10.7$  cm/s,  
( $d = 0.049$  cm,  $a = 0.20$  cm,  $c_{BO} = 6.8 \cdot 10^{-3}$  mol/l).

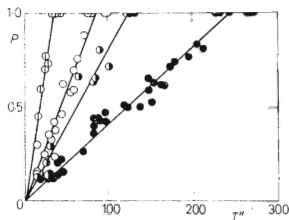


FIG. 6

Dependence of the Ratio of Colour Disappearance on Dimensionless Time

●  $C_s = 9.1 \cdot 10^{-3}$ , ◐  $1.3 \cdot 10^{-3}$ , ○  $0.2 \cdot 10^{-3}$ ,  $a = 0.16$  cm.

behaved differently as there just before separation an intensive mixing inside the drop took place which had already been described earlier (dashed line in Fig. 6).

As the dependence  $P = P(T'')$  can be considered to be linear for the given arrangement on basis of the known time of drop formation, time of completion of the reaction and value of ratio of the colour disappearance at separation of the drop  $P_b$  it is possible to determine the time interval of fall of a drop equivalent to the time of drop formation. This enables to include also the contribution of the phenomenon during the drop formation and to relate the individual results on a comparable basis enabling comparison with the equations for mass transfer at the fall of a drop. The equivalent time is then

$$T_e'' = [P_b/(1 - P_b)](T_r'' - T_b'') \quad (21)$$

and the time in which the reaction is accomplished corrected by the equivalent time corresponding to the formation is

$$T_r'' + T_e'' = (T_r'' - T_b'')/(1 - P_b). \quad (22)$$

So corrected times of reaction completion are plotted in Fig. 3 as the extrapolation for the zero time of drop formation.

Comparison of results with the curve corresponding to the model for a turbulent drop for  $L = 0.20$  is given in Fig. 7. For the projection of the coloured toroide according to Fig. 2 is the ratio of colour disappearance given by

$$P = (R'^2/4) - (R'/\pi). \quad (23)$$

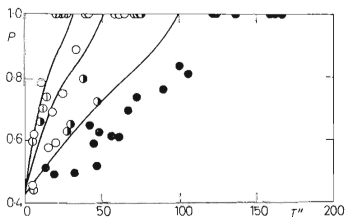


FIG. 7

Comparison of the Rate of Colour Disappearance with the Dependence for Turbulent Drop

●  $C_s = 9.1 \cdot 10^{-3}$ , ○  $1.3 \cdot 10^{-3}$ , ○  $0.2 \cdot 10^{-3}$ , ○  $0.2 \cdot 10^{-3}$ ,  $a = 0.16$  cm ( $L' = 0.20$ ).

For the origin of the scale of the dimensionless time was taken the value corresponding to the maximum size of toroide  $P = 0.432$  i.e. up to this value the change in colour is compared with the turbulent model (this was also used in Figs 2 and 3 for recalculation of the time of colour disappearance for the curve corresponding to the turbulent model). It can be also seen from Fig. 7 that the studied operation is slower than corresponds to the calculation in agreement with the results of the series 1. The operation was faster only in the experiments with the already mentioned intensive mixing inside the drop.

### Presence of the Surface Active Agent

As had already been said, the presence of the surface active agent did not stop the motion inside the drop but a significant retardation of the operation took place.

In evaluation of the results of the series 2 a similar dependence of ratio of colour disappearance on dimensionless time has been obtained as in the case without the surface active agent present which can be seen from comparison of Figs 7 and 8.

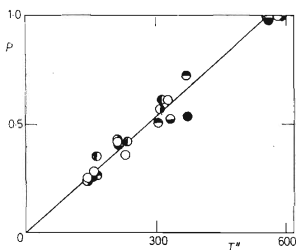


FIG. 8

Dependence of Ratio of Colour Disappearance on Dimensionless Time in Presence of Surface Active Agent

○  $c_F = 0$ ,  $a = 0.20$  cm,  $c_{BO} = 0.076$  mol/l,  
 ●  $c_F = 0$ ,  $a = 0.22$  cm,  $c_{BO} = 0.082$  mol/l,  
 ◐  $c_F = 2.9 \cdot 10^{-8}$  mol/l,  $a = 0.20$  cm,  $c_{BO} = 0.85$  mol/l,  
 ◑  $c_F = 2.9 \cdot 10^{-8}$  mol/l,  $a = 0.22$  cm,  $c_{BO} = 0.29$  mol/l,  
 ⊙  $c_F = 3.5 \cdot 10^{-5}$  mol/l,  $a = 0.20$  cm,  $c_{BO} = 0.30$  mol/l,  
 ⊚  $c_F = 3.5 \cdot 10^{-5}$  mol/l,  $a = 0.22$  cm,  $c_{BO} = 0.05$  mol/l.

It can be seen from Fig. 8 that about linear dependence has been again obtained which does not differ for different drop sizes and concentrations of the surface active agent (nil concentration inclusive), when about the same time of reaction completion has been preserved. Therefore also the straight line in Fig. 8 does not correspond in the presence of the surface active agent to a single dimensionless concentration  $C_s$  but to different values according to Fig. 3 at which about the same dimensionless time of reaction completion is obtained as in the absence of the surface active agent.

## APPENDIX

The continuity equation for a stagnant, spherical, centrally symmetrical drop can be written by use of dimensionless variables (13) with the initial and boundary conditions

$$\partial c/\partial T = \partial^2 c/\partial R^2 + (2/R)(\partial c/\partial R), \quad (A1)$$

$$C = 0 (T = 0, R < 1); \quad C = 1 - (1/L)(\partial c/\partial R) (T \geq 0, R = 1), \quad (A2)$$

where the dimensionless variable  $C$  is given by

$$C = (c + c_{BO})/(c_{Am} + c_{BO}). \quad (A3)$$

The boundary condition (A2) results from Eqs (8) to (11) and equation for the intensity of zero flux across the interphase boundary is

$$\dot{n}_A/s = D(\partial c/\partial r), \quad (r = a). \quad (A4)$$

By solving the system of equations according to Crank<sup>8</sup> holds

$$C = 1 - \frac{2L}{R} \sum_{n=1}^{\infty} \frac{\sin(\beta_n R) \exp(-\beta_n^2 T)}{\sin \beta_n [\beta_n + L(L-1)]}, \quad (A5)$$

where  $\beta_n$  are positive roots of the equation

$$\beta \cot \beta + L - 1 = 0. \quad (A6)$$

For the average value of turbulent diffusivity<sup>5</sup>, for the dimensionless radial distance from the centre of circulation, holds

$$\frac{\bar{D}}{au} = \int_0^1 \frac{6R'^2 - 8R' + 3}{1024(1+M)} dR' = \frac{1}{1024(1+M)}. \quad (A7)$$

In a toroidal symmetry the system of equations in dimensionless variables (A3), (16) to (18) is

$$\partial c/\partial T' = \partial^2 c/\partial R'^2 + (1/R')(\partial c/\partial R'), \quad (A8)$$

$$C = 0, \quad (T' = 0, R' > 1), \quad C = 1 - (1/L')(\partial c/\partial R'), \quad (T' > 0, R' = 1) \quad (A9)$$

and has the solution<sup>8</sup>

$$C = 1 - 2L' \sum_{n=1}^{\infty} \frac{I_0(\beta'_n R') \exp(-\beta'^2_n T')}{(\beta'^2_n + L'^2) I_0(\beta'_n)}, \quad (A10)$$

where  $\beta'_n$  are positive roots of the equation

$$\beta' I_1(\beta') - L' I_0(\beta') = 0. \quad (A11)$$

Equations describing the motion of the reaction boundary are obtained by substituting into the above given equations the dimensionless concentrations  $C_s$  corresponding to the zero concentration  $c$  on the reaction surface.

## LIST OF SYMBOLS

$a$	radius of drop
$c$	molar concentration defined by Eqs (6) and (7)
$c_i$	molar concentration of component $i$
$C$	dimensionless concentration defined by Eq. (A3)
$d$	nozzle diameter
$D$	diffusivity
$k_c$	mass transfer coefficient in continuous phase
$l$	distance
$L$	term defined by Eq. (13)
$L'$	term defined by Eq. (17)
$m$	equilibrium distribution ratio
$M$	term defined by Eq. (18)
$\dot{n}$	molar flux
$P$	ratio of colour disappearance
$r$	radial variable, spherical coordinate
$r'$	radial variable, cylindrical coordinate
$R$	dimensionless coordinate defined by Eq. (13)
$R'$	dimensionless coordinate defined by Eq. (18)
$Re_n$	Reynolds number for flow through the nozzle
$s$	surface
$t$	time
$T$	dimensionless time defined by Eq. (13)
$T'$	dimensionless time defined by Eq. (16)
$T''$	dimensionless time defined by Eq. (20)
$u$	terminal velocity of drop
$v$	velocity of flow inside the drop
$V$	volume of drop
$\dot{V}$	volumetric flow rate through the nozzle
$\beta$	term defined by Eq. (A6)
$\beta'$	term defined by Eq. (A11)
$\eta$	viscosity

## Subscripts

A, B	components	$i$	component
$b$	separation of drop the from nozzle	$m$	equilibrium value
$c$	continuous phase	$0$	initial value
$d$	dispersed phase	$r$	termination of reaction
$e$	equivalent value	$s$	reaction boundary

## Superscripts

*	on the interphase boundary
—	average value

## REFERENCES

1. Tyroler G., Hanielec A. E., Johnson A. I., Leclair B. P.: *Can. J. Chem. Eng.* 49, 56 (1971).
2. Sherwood T. K., Pigford R. L.: *Absorption and Extraction*. McGraw-Hill, New York 1952.
3. Nekovář P.: *Sborník Vysoké školy chemicko-technologické, Praha K 4*, 163 (1971).
4. Nekovář P., Vacek V.: *Sborník Vysoké školy chemicko-technologické, Praha K 6*, 215 (1972).
5. Handlos A. E., Baron T.: *A.I.Ch.E.J.* 3, 127 (1957).
6. Wellek R. M., Skelland A. H. P.: *A.I.Ch.E.J.* 11, 557 (1965).
7. Head H. N., Hellums J. D.: *A.I.Ch.E.J.* 12, 553 (1966).
8. Crank J.: *Mathematics of Diffusion*. McGraw-Hill, New York 1952.

Translated by M. Rylek.