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STRUCTURES OF THE CONJUGATE SATURATION AND CONCENTRATION DISCONTINUITIES IN THE DISPLACEMENT OF OIL BY A SOLUTION OF AN ACTIVE MATERIAL

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A general description of the displacement of oil by a solution of an active material not only in the basic case of a single active factor, but also in more complicated situations is presented in [1-5]. Here a central part is played by the scope for constructing a solution in a large-scale approximation, i.e., neglecting diffusion processes of various types (capillarity, diffusion proper, and thermal conductivity). These processes have marked effects on the solution only in zones where the variables alter sharply, which correspond to discontinuities in the large-scale approximation. Here we examine the fine structure of the transition zones. The results may be of value in estimating the limits to the application of the large-scale approximation and to the failure times for the layer of active material, as well as in developing numerical and approximate methods.

1. Formulation: External Solution. We consider the one-dimensional frontal displacement of oil by a solution of an active material. We write the equations for the phase infiltration law (i = 1 for water and i = 2 for oil) and the conservation equations for water, oil, and the active material on the basis that the mass concentrations of the material in the water c and in the oil φ are small, while the porosity m, permeability k, and phase densities ρ_1 and ρ_2 are constant:

$$\begin{gathered} u_i = -(kf_i(s,\ c)/\mu_i(c))\partial p_i/\partial x\ (i = 1,\ 2), \\ p_2 - p_1 = p = \gamma(c)J(s), \\ m\partial s/\partial t + \partial u_1/\partial x = 0,\ -m\partial s/\partial t + \partial u_2/\partial x = 0, \\ m\frac{\partial}{\partial t}[\varkappa cs + \varphi(c)(1-s) + a(c)] + \frac{\partial}{\partial x}[\varkappa cu_1 + \varphi(c)u_2] = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right). \end{gathered} \tag{1.1}$$

Here s is the water content; $m\rho_2 a$, mass of sorbed material in unit volume of the porous medium; f_i, μ_i, p_i, phase permeability, viscosity, and pressure for phase i; D, diffusion coefficient for the active material; p, capillary pressure, whose dependence on the surface tension incorporates the coefficient $\gamma(c)$; J, a Leverett function; x, coordinate; t, time; and $\varkappa = \rho_1/\rho_2$.

We introduce the dimensionless variable

$$x' = x/L,\ t' = u_0 t/L,\ u_i' = u_i/u_0,\ p_i' = p_i/\Delta p,\ u_0 = k\Delta p/\mu_1(0)\,L,$$
$$\mu_i' = \mu_i/\mu_1(0),\ D' = D/D_0,\ \gamma'(c) = \gamma(c)/\gamma(0),\ \varepsilon = \gamma(0)/\Delta p,\ \nu = D_0/u_0 L,$$

where L, Δp, D_0 are the characteristic values of the size of the flow region, the external pressure difference, and the diffusion coefficient.

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We subsequently omit the primes to the dimensionless variables, eliminate the pressure from system (1.1), and take the overall volume flow rate $U = u_1 + u_2$ as constant to get

$$(1.2)\ m\frac{\partial s}{\partial t} + U\frac{\partial F}{\partial x} + \varepsilon\frac{\partial}{\partial x}(\Phi\Omega) = 0,\ F = f_1/(f_1 + f_2\mu_1/\mu_2),\ \Phi = Ff_2/\mu_2, \tag{1.2}$$

$$m\frac{\partial}{\partial t}[s(\varkappa c - \varphi) + \varphi + a] + U\frac{\partial}{\partial x}[F(\varkappa c - \varphi) + \varphi] + \varepsilon\frac{\partial}{\partial x}[(\varkappa c - \varphi)\Phi\Omega] = \nu\frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right),$$

$$\Omega = \gamma J'\partial s/\partial x + \gamma' J\partial c/\partial x,\ \gamma' = d\gamma/dc,\ J' = dJ/\partial s;$$

$$s(x, 0) = s_0,\ c(x, 0) = c_0,\ s(0, t) = s^0,\ c(0, t) = c^0. \tag{1.3}$$

We put $\varepsilon = \nu = 0$ in (1.2) to get a problem corresponding to the large-scale approximation [1]:

$$m\frac{\partial s}{\partial t} + U\frac{\partial F}{\partial x} = 0,\ m\frac{\partial}{\partial t}[s(\varkappa c - \varphi) + \varphi + a] + U\frac{\partial}{\partial x}[F(\varkappa c - \varphi) + \varphi] = 0, \tag{1.4}$$

$$s(x, 0) = s_0,\ c(x, 0) = c_0(x \geqslant 0),\ s(0, t) = s^0,\ c(0, t) = c^0(t > 0).$$

Let $c^0 > c_0$ for definiteness. The problem of (1.4) has a self-modeling solution [1-5] $s = s(\xi)$, $c = c(\xi)$, $\xi = mx/Ut$, which will be considered as constructed. As a rule, this contains discontinuities, at which the integral conservation laws apply (V is the speed of a discontinuity):

$$\xi_j[s] = [F],\ \xi_j\{s^\pm + [\varphi + a]/[\varkappa c - \varphi]\} = F^\pm + [\varphi]/[\varkappa c - \varphi], \tag{1.5}$$

$$\xi_j = mV/U,\ [f] = f^+ - f^-,\ f^\pm = f(\xi_j \pm 0).$$

An additional condition for the stability of the discontinuities amounts to the specification that the number of dimensionless characteristic velocities is three before the setup and after it, for which the following inequalities are obeyed:

$$\xi_i(s^-, c^-) \geqslant \xi_j,\ \xi_k(s^+, c^+) \leqslant \xi_j\ (i,\ k = 1,2), \tag{1.6}$$

and this condition will be refined below. Here ξ_i (i = 1, 2) are the dimensionless characteristic velocities of system (1.4). The characteristics of (1.4) $dx/dt = (U/m)\xi_i^\mp$ (i = 1, 2) that satisfy (1.6) are called those arriving at the discontinuity, while the others are called the leaving ones.

The method of constructing the self-modeling solution has been developed in [1-5], so we can take the external solution to the displacement problem corresponding to $\varepsilon = \nu = 0$ as known.

2. Internal Solution. The structure of the s steps is well known [6, 7], so we examine the structure of the conjugate s, c steps. To construct the internal solution in the neighborhood of an s, c step we transfer in (1.2) to a system of coordinates moving along with the step ($\eta = (x - Vt)/\varepsilon$, $\tau = t$) and seek a nontrivial stationary solution:

$$\left(\frac{m}{U}\frac{\partial}{\partial\tau} - \xi_j\frac{\partial}{\partial\eta}\right)s + \frac{\partial F}{\partial\eta} + \frac{1}{U}\frac{\partial}{\partial\eta}(\Phi\Omega) = 0,\ \Omega = \gamma J'\frac{\partial s}{\partial\eta} + \gamma' J\frac{\partial c}{\partial\eta}, \tag{2.1}$$

$$\left(\frac{m}{U}\frac{\partial}{\partial\tau} - \xi_j\frac{\partial}{\partial\eta}\right)[s(\varkappa c - \varphi) + \varphi + a] + \frac{\partial}{\partial\eta}[F(\varkappa c - \varphi) + \varphi] + \frac{1}{U}\frac{\partial}{\partial\eta}[(\varkappa c - \varphi)\Phi\Omega] = \frac{\nu}{\varepsilon U}\frac{\partial}{\partial\eta}\left(D\frac{\partial c}{\partial\eta}\right),$$

that satisfies the linkage conditions

$$s(\pm\infty) = s^\pm,\ c(\pm\infty) = c^\pm. \tag{2.2}$$

For $\partial s/\partial\tau = \partial c/\partial\tau = 0$ we integrate (2.1) on the basis of (2.2) to get

$$ds/d\eta = -H[BY + (c - c^-)Z]/G,\ dc/d\eta = H(c - c^-)Z, \tag{2.3}$$

$$Z(c) = F^-(\varkappa - \delta\varphi) + \delta\varphi - \xi_j[s^-(\varkappa - \delta\varphi) + \delta\varphi + (a - a^-)/(c - c^-)];$$

$$\delta\varphi = (\varphi - \varphi^-)/(c - c^-),\ Y(s, c) = F - F^- - \xi_j(s - s^-), \tag{2.4}$$

$$H(s, c) = \varepsilon U/\nu D,\ G(s, c) = \gamma J'/\gamma' J.\ B(s, c) = \nu D/\varepsilon\gamma' J\Phi.$$

Equations (2.3) correspond to the phase plane of s and c to the equation

$$dc/ds = -G(s, c)(c - c^-)Z(c)/[(c - c^-)Z(c) + B(s, c)Y(s, c)]. \tag{2.5}$$

It follows from (1.5) that $Z(c^+) = Y(s^\pm, c^\pm) = 0$, so the points (s^-, c^-) and (s^+, c^+) in the phase plane are singular points for (2.5).

The internal structure of the conjugate s, c steps is shown below to be closely related to the conditions for the stability of these and to the global structure of the solution. The latter for fixed values of c^0, c_0 and $s^0 = 1$ is completely determined by the form of F(s, c), φ(c), a(c) and by the value of the initial water content

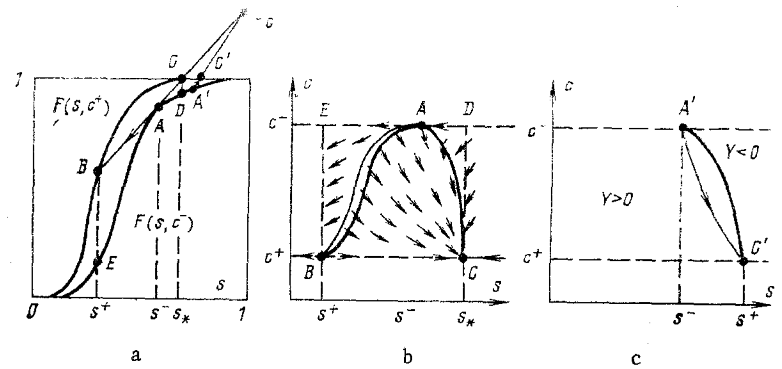


Fig. 1

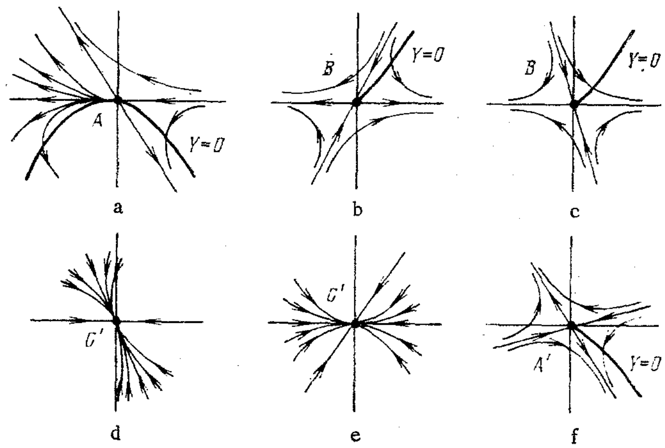


Fig. 2

s_0 [1]. We have restricted ourselves so far to the case of complete discontinuities in the concentration, where $c^-=c^0$, $c^+=c_0$; such a situation occurs for example if $\varphi_{,cc}\le 0$, $a_{,cc}\le 0$ [1].

Function $F_{,c}=\partial F/\partial c$ will subsequently be considered as of constant sign. There are two types of conjugate s, c steps for $F_{,c}\le 0$, which are dependent on the value of s_0: a) a AB step for $s_0\le s_*$, when $[s]<0$; b) a A'C' step for $s_0>s_*$ at which $[s]>0$. For these we have correspondingly

$$\xi_1^- = \xi_j < \xi_1^+,\ \xi_2^+ < \xi_j < \xi_2^-,\ \xi_1^\pm < \xi_j,\ \xi_2^+ < \xi_j < \xi_2^-. \tag{2.6}$$

In Fig. 1a, $O_c = (-[\varphi + a]/[\varkappa c - \varphi],\ -[\varphi]/[\varkappa c - \varphi])$, straight-line segment O_cC touches the curve $F(s, c^-)$ at point A, while point C corresponds to the value $s=s_*$.

We first consider the discontinuity AB. It is convenient to transfer the construction to the s, c phase plane (Fig. 1b). The curves $F(s, c^\pm)$ correspond to segments of the straight lines $c=c^\pm$, the straight-line segment BAC in the s, f plane corresponds to the curve BAC, along which $Y(s, c)=0$, while $Y<0$ above BAC and $Y>0$ below it. Also, $Z(c^+)=0$ and $Z(c^-)>0$ by virtue of (1.5) and (2.6). If $\gamma'(c)<0$ (the material reduces the interfacial tension) $B(s, c)<0$, and if $Z(c)\ge 0$ in the band $c^+<c<c^-$ we have that (2.5) has no singular points in this band apart from A, B, and C. The structure of the desired form should mean that there is a path joining point A and B. It is sufficient to use the inequalities $J'(s)<0$, $G>0$, $B<0$ and conditions (1.5) and (2.6) in order to determine the types of the singular points, in accordance with which

$$F_{,s}(s_*, c^+) < \xi_j = F_{,s}^- < F_{,s}^+,\ A^+ < 0,\ A^- > 0,$$
$$A(c) = \frac{d}{dc}\left[(c-c^-)Z(c)\right] = F^\pm(\varkappa - \varphi_{,c}) + \varphi_{,c} - \xi_j\left[s^\pm(\varkappa - \varphi_{,c}) + \varphi_{,c} + a_{,c}\right].$$

It can be shown that the point $B=(s^+, c^+)$ is a simple saddle point, while $C=(s_*, c^+)$ is a simple cusp, and $A=(s^-, c^-)$ is a double saddle-cusp with one cusp sector and two saddle ones. Figure 2 shows the general picture in the region of this point. The nonzero slopes of the paths passing through the singular points are defined by

$$k_1 = [AG + B(F_{,s} - \xi_j)]/(A + BF_{,c}), \tag{2.7}$$

so $k_1(s^-, c^-)<0$ (Fig. 2a). The signs of $k_1(s^+, c^+)$ and $k_1(s_*, c^+)$ are not established unambiguously, but since $|B(s, c)|\gg 1$ we can assume that the signs of the numerator and denominator in (2.7) will be determined by $B(s, c)$, and then $k_1(s^+, c^+)>0$, $k_1(s_*, c^+)<0$ (Fig. 2b and d).

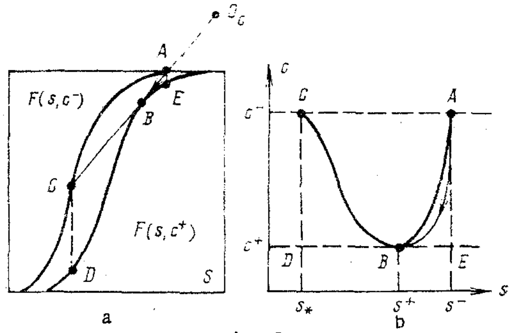


Fig. 3

The following is the asymptote of the paths for the bundle emerging from point A:

$$c - c^- \sim -c^* \exp\left[R/(s - s^-)\right](s - s^-)^2, R = 2G^-A^-/(B^-F^-_{,ss}) > 0.$$

This path exists and is unique; it is the separatrix of the saddle point B belonging to the cusp bundle of point A. This passes above the isocline to infinity.

We integrate (2.3) near points A and B to get

$$s - s^- \sim 2(G^-/B^-H^-F^-_{,ss})\eta^{-1}, c - c^- \sim \text{const}\,\eta^{-2}e^{-\chi^-\eta}, \chi^\pm = -H^\pm A^\pm, \eta \to \pm\infty, \quad (2.8)$$
$$s - s^+ \sim \text{const}\,e^{-\chi^+\eta}, c - c^+ \sim \text{const}\,e^{-\chi^+\eta} = k_1(s^+, c^+)(s - s^+).$$

For $\varphi(c) \equiv 0$ $\chi^\pm = \xi_j(\varepsilon U/\nu D^\pm)(a^\pm_{,c} - [a]/[c])$, i.e., the width of the transition zone in front of the step $1/\chi^+$ and the rate of decrease in the concentration behind the step are proportional to the speed ξ_j of the step and are dependent solely on the curvature of the sorption isotherm and the material diffusion coefficient D(c). In general, χ^+ is proportional to $\xi^+_2 - \xi_j$. Behind the step, the concentration tends to the value corresponding to the external solution in an exponential fashion, while the saturation varies more solely (in accordance with a power law). The latter feature on numerical treatment may be seen as the saturation front lagging behind the material-concentration front and having greater diffuseness.

We now consider the structure of the A'C' step (Fig. 1a and c), which corresponds to final displacement of the oil after flooding of the deposit. In that case point $A' = (s^-, c^-)$ is a simple saddle point (Fig. 2f, and $C' = (s^+, c^+)$ is a simple cusp (Fig. 2d and e), and the desired path is the separatrix of the saddle A' belonging to the cusp bundle entering point C' (Fig. 1c). The angle coefficient of the paths in the cusp bundle is dependent on the sign of $K = A^+G^+ + B^+)F^+_{,s} - \xi_j)$.

We integrate (2.3) near A' and C' for K > 0 (Fig. 2d) to get

$$s - s^\pm \sim \text{const}\,e^{-\chi^\pm\eta}, c - c^\pm \sim \text{const}\,e^{-\chi^\pm\eta} = k_1(s^\pm, c^\pm)(s - s^\pm), \chi^\pm = -H^\pm A^\pm, \eta \to \pm\infty.$$

For K < 0 (Fig. 2e) the variables ahead of the step are related by $c - c^+ \sim \text{const}\,|s - s^+|^q$, where $q = -A^+G^+/(F^+_{,s} - \xi_j) > 1$, and they vary exponentially:

$$c - c^+ \sim \text{const}\,e^{-\chi^+\eta}, s - s^+ \sim \text{const}\,e^{-(\chi^+/q)\eta}, \eta \to \infty.$$

As q > 1, the saturation tends to the value corresponding to the external solution ahead of the step more slowly than does the concentration.

These results show that no internal structure exists for the step [s] < 0 for a point A' not satisfying the condition $\xi_j = F^-_{,s}$ (two saddle points in general do not have a common separatrix). Also, to construct the desired path it was assumed that the following inequalities are obeyed for all s and c from the rectangle E bounded by the straight lines $s = s^\pm$, $c = c^\pm$:

$$\min(c^+, c^-) \leqslant w(s) \leqslant \max(c^+, c^-), Y(s, w(s)) = 0, (c - c^-)Z(c) \leqslant 0, \quad (2.9)$$

and equality occurs only at the points $(s^\pm, c^\pm)$; conditions (2.9) guarantee the absence of singular points for (2.3) in E that differ from the two vertices $(s^\pm, c^\pm)$. Violation of (2.9) means that there is no internal structure even if (2.6) are obeyed for the characteristic velocities. In fact, if Z(c) changes sign for $c^+ \leq c \leq c^-$ it is shown by (2.3) that the concentration distribution in the transition zone becomes multivalued. Violation of the first condition in (2.9) also leads to a multivalued $s(\eta)$ and/or $c(\eta)$. The second inequality in (2.9) provides a basis for constructing the c transition in the self-modeling solution for arbitrary increase in functions $a(c)$ and $\varphi(c)$ for $\varphi(c) = \varphi_0{}^c$ and $a(c) \equiv 0$ by constructing their convex (concave) shells for a given concentration range [1].

Therefore, (2.9) is to be considered as a stability condition for s, c steps refined in relation to (1.6)). This condition takes the form $Y(s, c)/(s-s^-)\geq 0$ for s steps with c = constant and has been proved rigorously in [8].

The structure of the step for $F_{,c}\geq 0$ (harmful material) can be examined similarly; for definiteness we assume that $a_{,cc}\leqslant 0$, $\varphi_{,cc}\leqslant 0$, $[c]<0$, $\gamma'(c)>0$ and consequently $B>0$, while $G<0$; the stability of such a step (Fig. 3a) is provided by conditions (2.9) and

$$\xi_1^- < \xi_j = \xi_1^+,\ \xi_2^+ < \xi_j < \xi_2^-. \tag{2.10}$$

Here the point $A = (s^-, c^-)$ is a simple saddle point, $C = (s_*, c^+)$ is a simple cusp, and $B = (s^+, c^+)$ is a simple twofold saddle-cusp with the cusp sector on the right of the straight line $c - c^+ = -A^+G^+(s-s^+)/(A^+ + B^+F^+_{,s})$ and two saddle points to the left of this, while the desired path is the separatrix arising from the saddle A and belonging to the cusp bundle of point B (Fig. 3b).

The asymptotes of the variables in the stabilized zone are described by (2.8), in which + and − changes places. Lag in the saturation behind the material concentration is here observed at the leading edge of the stabilized zone.

These features of the internal structure persist for $[c]>0$, $a_{,cc}\geqslant 0$, $\varphi_{,cc}\geqslant 0$.

If $a(c)$ and $\varphi(c)$ are of arbitrary form, it is possible for there to be steps such that the signs of the rigorous inequalities between ξ_j and $\xi_2^\pm$ in (2.6) and (2.10) are replaced by the sign of equality [1], which complicates the types of singular points in the (s, c) plane, but the form of the paths joining (s^-, c^-) and (s^+, c^+) remains as before, as does the global topological picture in the phase plane.

As an example we consider the step $[c]<0$, $[s]<0$ for $F_{,c}\leq 0$ (Fig. 1a and b). Let the following stability condition be realized:

$$\xi_1^- = \xi_j < \xi_1^+,\ \xi_2^+ = \xi_j < \xi_2^-. \tag{2.11}$$

The type of singular point A and the field of directions near it are not altered. Near B, the desired path coincides to a first approximation with the isocline at infinity and the curve $Y(s, c) = 0$. The order of the contact is determined by the order of the zero $\xi_2 - \xi_j$ at the point (s^+, c^+): s and c tend to their limiting values s^+ and c^+ for $\eta\to\infty$ in a power-law form rather than an exponential one.

From the step that satisfies the conditions

$$\xi_1^- = \xi_j < \xi_1^+,\ \xi_2^+ < \xi_j = \xi_2^-, \tag{2.12}$$

there is only a change in the type of the singular point $A = (s^-, c^-)$; the path of the nodal bundle and the isocline at infinity fuse with the parabola $c - c^- = -(1/2)(F^-_{,ss}/F^-_{,c})(s-s^-)^2$ corresponding to the curve $Y(s, c) = 0$ in the region of point A. As above, s and c vary in a power-law fashion for $\eta\to-\infty$.

If $\xi_j = \xi_2^\pm$ simultaneously in (2.11) and (2.12), these features of the distributions of s and c in the stabilized zone occur simultaneously. The desired path approximates to the $Y(s, c) = 0$ curve if the difference $\xi_2(s, c) - \xi_j$ tends to zero along it.

3. Contact-Discontinuity Structure. For $\xi_2(s, c)\equiv\xi_j$ (the case of a contact discontinuity [9]), system (2.3) does not have a solution of the desired form. This situation arises when $a(c)$ and $\varphi(c)$ are linear, and it means that (1.2) does not have a solution of traveling-wave type. This is related to the occurrence of a further small parameter that has a decisive effect on the size of the stabilized zone.

The analysis of the discontinuity is not so trivial in that case. We consider it for linear isotherms $a(c) = a_0 c$, $\varphi(c) = \varphi_0 c$; (1.2) takes the following form after obvious transformations in a coordinate system linked to the discontinuity:

$$\frac{m}{U}\frac{\partial S}{\partial\tau} + \frac{\partial f}{\partial\eta} + \frac{\varepsilon}{U}\frac{\partial}{\partial\eta}(\Phi\Omega) = 0,\ \tau = t,\ \eta = x - Vt, \tag{3.1}$$

$$\frac{m}{U} S\frac{\partial c}{\partial\tau} + f\frac{\partial c}{\partial\eta} + \frac{\varepsilon}{U}\Phi\Omega\frac{\partial c}{\partial\eta} = \frac{\nu'}{U}\frac{\partial}{\partial\eta}\left(D\frac{\partial c}{\partial\eta}\right),\ \nu' = \nu/(\varkappa-\varphi_0),$$

$$S = s + (\varphi_0 + a_0)/(\varkappa-\varphi_0),\ f = F + \varphi_0/(\varkappa-\varphi_0) - \xi_j S.$$

We take S and f as new unknowns, while c is a known function of S and f, to produce the second equation in (3.1) to

$$\frac{m}{U} S\frac{\partial f}{\partial\tau} + \delta SF_{,c}\frac{\partial f}{\partial\eta} + fL + \frac{\varepsilon}{U}\left[\Phi\Omega L + \delta SF_{,c}\frac{\partial}{\partial\eta}(\Phi\Omega)\right] = \frac{\nu'}{U}F_{,c}\frac{\partial}{\partial\eta}(DL/F_{,c}),$$

$$\Phi\Omega = M\partial S/\partial\eta + N\partial f/\partial\eta,\ M(S, f) = \Phi(\gamma J' - \delta\gamma' J),\ N(S, f) = \Phi\gamma' J/F_{,c},$$
$$L(S, f) = \partial f/\partial\eta - \delta F_{,c}\partial S/\partial\eta,\ \delta = (F_{,s} - \xi_j)/F_{,c}.$$

The external discontinuous solution satisfied the conditions $f(\tau, \pm 0) = 0$. To construct the principal term in the internal expansion we put

$$f = (\varepsilon/m\tau)^{1/2} f^0,\ \zeta = (m/\varepsilon\tau)^{1/2}\eta,\ \theta = \tau \tag{3.2}$$

and transform these equations while retaining only the terms of the same order of smallness in ε and assuming that $\nu'/\varepsilon = O(1)$; we then get a system of equations for the internal problem:

$$\theta\frac{\partial S}{\partial\theta} - \frac{1}{2}\zeta\frac{\partial S}{\partial\zeta} + U\frac{\partial f^0}{\partial\zeta} + \frac{\partial}{\partial\zeta}\left(M\frac{\partial S}{\partial\zeta}\right) = 0,$$
$$\delta\left[U\left(S\frac{\partial f^0}{\partial\zeta} - f^0\frac{\partial S}{\partial\zeta}\right) - M\left(\frac{\partial S}{\partial\zeta}\right)^2 + S\frac{\partial}{\partial\zeta}\left(M\frac{\partial S}{\partial\zeta}\right)\right] + \frac{\nu'}{\varepsilon}\frac{\partial}{\partial\zeta}\left(\delta D\frac{\partial S}{\partial\zeta}\right) = 0.$$

The desired asymptotic structure is defined by the stationary solution

$$\frac{1}{2}\zeta\frac{dS}{d\zeta} - U\frac{df^0}{d\zeta} - \frac{d}{d\zeta}\left(M\frac{dS}{d\zeta}\right) = 0,$$
$$\delta\left[\left(\frac{1}{2}\zeta S - Uf^0\right)\frac{dS}{d\zeta} - M\left(\frac{dS}{d\zeta}\right)^2\right] + \frac{\nu'}{\varepsilon}\frac{d}{d\zeta}\left(\delta D\frac{\partial S}{\partial\zeta}\right) = 0,$$
$$S(\pm\infty) = S\pm,\ f^0(+\infty) = 0. \tag{3.3}$$

Note that system (3.3) is of first order in f^0, and therefore allows only one boundary condition. It can be shown that the boundary condition is lost on the inner side of the transition zone $\zeta = -\infty$, where $\delta = (F_{,s} - \xi_j)/F_{,c} = 0$, and this corresponds to choice of the boundary condition for f^0 in the problem of (3.3). By virtue of the transformation of (3.2), this does not alter the feature that $f = 0$ for the limiting stationary asymptote ($\tau \to \infty$), for which the boundedness of $f^0(-\infty)$ is sufficient, and the linkage conditions for the internal and external solutions are met. It is notable however that one would be unable to construct as external expansion for S by seeking the stationary distribution $S(\zeta)$ with $f \equiv 0$.

Therefore, to define the main term in the internal expansion for a contact discontinuity one can first find $S(\zeta)$ and $f^0(\zeta)$ from (3.3) and then determine c by means of $f(s, c) = 0$; as in the case of a typical problem in convective thermal conduction, the characteristic size of the transition zone increases with time as $\tau^{1/2}$.

4. Structure Due to Disequilibrium. Another factor that influences the structure of the s, c steps in disequilibrium is the sorption, with redistribution of the material between the phases. We neglect diffusion and capillary forces and restrict ourselves to the case where the rates of the exchange processes are dependent only on the contents of the material in the phases and in the sorbed state. When we have

$$m\frac{\partial S}{\partial t} + U\frac{\partial F}{\partial x} = 0,\ m\frac{\partial}{\partial t}[\varkappa cs + \varphi(1 - s) + a] + U\frac{\partial}{\partial x}[\varkappa cF + \varphi(1 - F)] = 0, \tag{4.1}$$
$$\partial a/\partial t = A(c, \varphi, a),\ \partial\varphi/\partial t = \Phi(c, \varphi),\ F = F(s, c, \varphi),$$
$$s = s_0,\ c = c_0,\ a = a_0(c_0),\ \varphi = \varphi_0(c_0)\ (t = 0),$$
$$s = s^0,\ c = c^0,\ a = a_0(c^0),\ \varphi = \varphi_0(c^0)\ (x = 0),$$

where a and φ are independent variables and $a_0(c)$ and $\varphi_0(c)$ are their equilibrium values, which are the unique roots of the equation $A(c, \varphi, a) = \Phi(c, \varphi) = 0$; we introduce the dimensionless variables $x' = mx/L$, $t' = tU/L$, $A' = A/A_0$, Φ/Φ_0, $\varepsilon = U/A_0L$, $\nu = U/\Phi_0 L$ and transform (4.1) to the following form (primes subsequently omitted):

$$\frac{\partial s}{\partial t} + \frac{\partial F}{\partial x} = 0,\ \frac{\partial}{\partial t}[\varkappa cs + \varphi(1 - s) + a] + \frac{\partial}{\partial x}[\varkappa cF + \varphi(1 - F)] = 0, \tag{4.2}$$
$$\varepsilon\partial a/\partial t = A(c, \varphi, a),\ \nu\partial\varphi/\partial t = \Phi(c, \varphi),\ A(c, \varphi_0, a_0) = \Phi(c, \varphi_0) = 0,$$
$$s = s_0,\ c = c_0\ (t = 0),\ s = s^0,\ c = c^0\ (x = 0).$$

The external self-modeling solution corresponding to $\varepsilon = \nu = 0$ is taken as known. To construct the internal solution in the region of the s, c step, we transfer in (4.2) to a coordinate system moving along with the steps ($\eta = (x - Vt)/\varepsilon$, $\tau = t$) and seek a nontrivial stationary solution to

$$\left(\frac{\partial}{\partial\tau} - \xi_j\frac{\partial}{\partial\eta}\right)s + \frac{\partial F}{\partial\eta} = 0,\ \left(\frac{\partial}{\partial\tau} - \xi_j\frac{\partial}{\partial\eta}\right)[\varkappa cs + \varphi(1 - s) + a] + \frac{\partial}{\partial\eta}[\varkappa cF + \varphi(1 - F)] = 0, \tag{4.3}$$
$$\left(\frac{\partial}{\partial\tau} - \xi_j\frac{\partial}{\partial\eta}\right)a = A(c, \varphi, a),\ h\left(\frac{\partial}{\partial\tau} - \xi_j\frac{\partial}{\partial\eta}\right)\varphi = \Phi(c, \varphi),\ h = \nu/\varepsilon,$$
$$s(-\infty) = s^-,\ c(-\infty) = c^-,\ \varphi(-\infty) = \varphi_0(c^-),\ a(-\infty) = a_0(c^-).$$

We integrate the stationary equations (4.3) on the basis of (1.5) to get a second-order system:

$$da/d\eta = -\xi_j^{-1} A(\Psi(\varphi, a), \varphi, a), \; d\varphi/d\eta = -(h\xi_j)^{-1}\Phi(\Psi(\varphi, a), \varphi),$$
$$c = \Psi(\varphi, a) = c^- + \alpha(a - a_0^-) + \beta(\varphi - \varphi_0^-), \; F - F^- - \xi_j(s - s^-) = 0,$$
$$\alpha = [c - \varphi_0/\varkappa]/\omega > 0, \; \beta = [a_0/\varkappa + (1 - \xi_j^{-1})c]/\omega > 0,$$
$$a_0^- = a_0(c^-), \; \varphi_0^- = \varphi_0(c^-), \; \omega = [a_0 + (1 - \xi_j^{-1})\varphi_0], \tag{4.4}$$

which corresponds to the following equation in the (φ, a) phase plane:

$$da/d\varphi = -hA(\Psi(\varphi, a), \varphi, a)/\Phi(\Psi(\varphi, a), \varphi). \tag{4.5}$$

The path joining the singular points $(\varphi_0^{\pm}, a_0^{\pm})$ in that case always exists and is unique, which remains to be elucidated; these are conditions under which $\varphi(\eta)$ and $a(\eta)$ are single-value function of η that satisfy the boundary conditions at $\eta \to \pm\infty$. Clearly, these conditions amount to obedience to the inequalities $(c^+ - c^-)A \leq 0$, $(c^+ - c^-)\Phi \leq 0$ along the path.

If the material is not sorbed or does not dissolve in the oil, then the corresponding equation can be integrated in quadratures. We consider examples of such situations for $[c] < 0$ steps with $F_{,c} \leq 0$.

Let $\varphi \equiv 0$ and $A = A(c, a) = c - c_1(a)$, where $c_1(a_0(c)) = c$; then $\Psi(a) = c^- + (a - a_0)[c]/[a_0]$, and from the stability conditions for the step $\xi_2^- \leq \xi_j \leq \xi_2^-$ we have the inequalities $a_{0,c}^+ \geq [a_0]/[c]$ and $a_{0,c}^- \leq [a_0]/[c]$, i.e., the straight line $c = \Psi(a)$ intersects the equilibrium sorption isotherm $a_0(c)$ or touches it at the points $c^{\pm}$, $a_0^{\pm}$ (Fig. 4a). We integrate the first equation in (4.4) to get

$$\eta = \eta^* - \xi_j \int_{a_0^*}^{a} \left\{c^- + \frac{[c]}{[a_0]}(a' - a_0^-) - c_1(a')\right\}^{-1} da', \; a_0^+ < a_0^* < a_0^-,$$

where the behavior of $a(\eta)$ for $\eta \to \pm\infty$ will be determined by the order of the contacts at the points $c = c^{\pm}$ in the c, a plane between the straight line $c = \Psi(a)$ and the $a = a_0(c)$ equilibrium sorption isotherm. For $a_{0,cc} \leq 0$ we have $a - a_0^{\pm} \sim \text{const}\, e^{-\chi^{\pm}\eta}$, $\chi^{\pm} = [c]/[a_0] - c_{1,a}(a_0^{\pm}), \eta \to \pm\infty$ while when $\chi^{\pm}$ becomes zero (first-order contact) the behavior of $a(\eta)$ for $\eta \to \pm\infty$ becomes of power-law type: $a - a_0^{\pm} \sim 1/\chi_1^{\pm}\eta$, $\chi_1^{\pm} = (1/2)\, c_{1,aa}(a_0^{\pm})$.

As $c = \Psi(a)$ is linear, the same applies to the asymptotic behavior of the $c(\eta)$ in the stabilized zone. The asymptote of $s(\eta)$ for $\eta \to \pm\infty$ is found from (4.4) and the condition at the step $\xi_j = [F]/[s]$. For $[s] < 0$, $\xi_j = F_{,s}^- < F_{,s}^+$, so $s - s^- \approx -\{-2F_{,c}^-(c - c^-)/F_{,ss}^-\}^{1/2}$, $s - s^+ \approx F_{,c}^+(c - c^+)/(\xi_j - F_{,s}^+)$. At the step $[s] > 0$ $\xi_j > F_{,s}^{\pm}$, so $s - s^{\pm} \approx F_{,c}^{\pm}(c - c^{\pm})/(\xi_j - F_{,s}^{\pm})$.

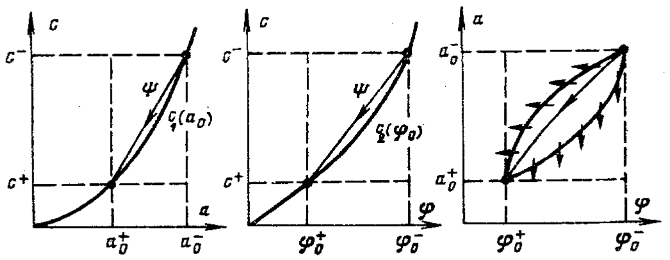
We similarly examine the structure of the stabilized zone for $a \equiv 0$ and $\Phi(c, \varphi) = c - c_2(\varphi)$, where $c_2(\varphi_0(c)) = c$; in that case $\Psi(\varphi) = c + (\varphi - \varphi_0^-[c]/[\varphi_0]$ and $\varphi(\eta)$ is determined by the form of the equilibrium isotherm $\varphi = \varphi_0(c)$ and the order of its contact with the straight line $c = \Psi(\varphi)$ in the (c, φ) plane (Fig. 4b).

Finally we consider the general case on the assumption that the material is sorbed only from the aqueous phase: $A(c, a) = c - c_1(a)$, $\Phi(c, \varphi) = c - c_2(\varphi)$; let (4.5) become

$$da/d\varphi = -h\left[c^- + \alpha(a - a_0^-) + \beta(\varphi - \varphi_0^-) - c_1(a)\right]/\left[c^- + \alpha(a - a_0^-) + \beta(\varphi - \varphi_0^-) - c_2(\varphi)\right].$$

The desired path is the separatrix of the saddle point (φ_0^+, a_0^+) belonging to the cusp of point (φ_0^-, a_0^-) and lies below the convex zero isocline $c_1(a) = \Psi(\varphi, a)$ $(\beta d^2\varphi/da^2 = c_{1,aa} > 0)$ above the concave isocline at infinity $c_2(\varphi) = \Psi(\varphi, a)$ $(\alpha d^2a/d\varphi^2 = c_{2,\varphi\varphi} > 0)$ (Fig. 4c). The directions of the path at the singular points are determined by the slopes:

$$k^{\pm} = (da/d\varphi)^{\pm} = \left[p + (p^2 + 4\alpha\beta h)^{1/2}\right]/2\alpha, \; p = c_{2,\varphi}^{\pm} - \beta - h(c_{1,a}^{\pm} - \alpha),$$



a b c

Fig. 4

where $k^{\pm} \to (c^{\pm}_{2,\varphi} - \beta)/\alpha$, if $h \to 0$ and $k^{\pm} \to \beta/(c^{\pm}_{1,a} - \alpha)$, if $h \to \infty$.

We integrate (4.4) in the region of the singular points to get $a - a_0^{\pm} \sim \text{const}\, e^{-\chi^{\pm}\eta}$, $\varphi - \varphi_0^{\pm} \sim \text{const}\, e^{-\gamma^{\pm}\eta}$, $\eta \to \pm\infty$, $\chi^{\pm} = \beta/k^{\pm} + \alpha - c^{\pm}_{1,a}$, $\gamma^{\pm} = (\alpha k^{\pm} + \beta - c^{\pm}_{2,\varphi})/h$, where $\chi^{\pm}$ and $\gamma^{\pm}$ are proportional to the differences between the slopes of the path and the reference curves (Fig. 4c) at the points $(\varphi_0^{\pm}, a_0^{\pm})$ in the $\varphi(a)$ plane.

As $c = \Psi(\varphi, a)$ is linear, the behavior of $c(\eta)$ for $\eta \to \pm\infty$ is determined by the term $\exp[\pm\eta \min(|\chi^{\pm}|, |\gamma^{\pm}|)]$, i.e., by the slower of the two nonequilibrium processes.

If the path touches one of the reference curves at the points $(\varphi_0^{\pm}, a_0^{\pm})$, the exponential behavior of the corresponding variable (φ or a) and of the concentration $c(\eta)$ for $\eta \to \pm\infty$ is replaced by a power-law form.

The results still apply for $A(c, \varphi, a)$ and $\Phi(c, \varphi)$ of arbitrary form that satisfy the conditions $A_{,c} > 0$, $A_{,\varphi} > 0$, $A_{,cc} \leqslant 0$, $A_{,\varphi\varphi} \leqslant 0$, $A_{,a} < 0$, $\Phi_{,c} > 0$, $\Phi_{,cc} \leqslant 0$, $\Phi_{,\varphi} < 0$; in that case the slopes of the path at the singular points $(\varphi_0^{\pm}, a_0^{\pm})$ and the values of $\chi^{\pm}$, $\gamma^{\pm}$ are determined by $k^{\pm} = [p + (p^2 + 4\alpha\Phi^{\pm}_{,c}R^{\pm})^{1/2}]/2\alpha\Phi^{\pm}_{,c}$, $\chi^{\pm} = P^{\pm} + R^{\pm}/k^{\pm}$, $\gamma^{\pm} = (Q^{\pm} + \alpha\Phi^{\pm}_{,c}k^{\pm})/h$, $p = hP^{\pm} - Q^{\pm}$, $P^{\pm} = \alpha A^{\pm}_{,c} + A^{\pm}_{,a}$, $Q^{\pm} = \beta\Phi^{\pm}_{,c} + \Phi^{\pm}_{,\varphi}$, $R^{\pm} = \beta A^{\pm}_{,c} + A^{\pm}_{,\varphi}$.

This problem coincides with the classical sorption problem [10] for a homogeneous liquid.

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