R, spatial coordinates; **R**ⁱ, radius vector of the center of the trial particle; **V**, detailed velocity; t, time; w, particle diffusion motion velocity; α , distribution factor; β , $\alpha k_0/D$; β_i , $\alpha k_i/D_i$; Γ , surface concentration; δ_i , infinitesimals introduced in the definition of the structural functions θ_i ; $\varepsilon = 1 - \rho$; ρ , particle volume concentration; τ , τ_{α} , time scales; ϕ , concentration perturbation near the trial particle; the asterisk superscript denotes conditional means, and the subscript denotes equilibrium values of the concentration; the prime refers to quantities to be determined at the point **R**ⁱ, while the subscripts 0 and 1 refer to the continuous and disperse phases, respectively.

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HETEROGENEOUS MASS-TRANSFER KINETICS UNDER

DIFFUSION-CONTROLLED CONDITIONS

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Calculations have been performed on nonisothermal mass transfer with transport characteristics dependent on temperature: velocity, concentration, temperature, and mass-transfer coefficient distributions.

Topics in hydrodynamics and in heat and mass transfer are frequently handled on the assumption that the parameters representing the physical properties are constant, whereas in fact they are often dependent on temperature, so that assumption is justified only when the system is completely or nearly isothermal. If the system is essentially non isothermal, parameters characterizing the physical properties such as the viscosity may vary by substantial factors, and it is essential to incorporate the temperature dependence. However, then there can be considerable computational difficulties, whereas the corresponding isothermal treatment involves a simple analytic formula. Therefore, engineering calculations are commonly based on correcting for the nonisothermal situation by formal substitution into the theoretical formula for the isothermal case of an effective temperature, which is chosen either from rather arbitrary assumptions or from the condition that the numerical result agrees with experiment [1].

That technique sometimes gives useful results, but it has the essential disadvantage of lacking a physical basis. A basis can be provided only by solving the nonisothermal case for a sufficiently wide range of external conditions, which is considered here.

We consider the convective mass transfer from a certain substance (reagent) to a solid surface, at which there is a reaction involving the absorption of it, with the reagent dissolved in the surrounding liquid. The flow is taken as laminar and stationary, while the transport mechanism is diffusion-limited, so the concentration at the surface can be taken as zero. An example is provided by a rotating disk as commonly used in electrochemistry [2].

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Fig. 1. Relationship in dimensionless form for the axial velocity component as a function of distance from the disk at various temperatures: a) $t_{\infty} = 20^{\circ}C$; $t_{W} = 20^{\circ}C$ (1); 30 (2); 40 (3); 50 (4); 60°C (5); b) $t_{W} =$ 20°C; $t_{\infty} = 20^{\circ}C$ (1); 30 (2); 40 (3); 50 (4); 60°C (5).

Under isothermal conditions, the hydrodynamic part (Karman problem) has a self-similar solution, which is represented in terms of functions dependent only on the coordinate normal to the disk [3]. This has been used [4] in constructing a solution for the mass transfer, and for large Schmidt numbers Sc = v/D, the asymptotic result is

$$j_w = Kc_{\infty}; \ K = 0.620 D^{2/3} v^{-1/6} \omega^{1/2}.$$
⁽¹⁾

(1) has been tested repeatedly, and it has been shown [5] that it gives a systematic overestimate for the mass transfer coefficient. The error is 3% for Sc = 10^3 and increases with temperature, since the Schmidt number falls.

(1) has also been used under essentially nonisothermal conditions [6, 7], when the system has a positive heat flux $(T_W > T_{\infty})$ or a negative one $(T_W < T_{\infty})$, and in which the effective temperature for D and ν is taken either as the temperature at the disk T_W [6] or the mean temperature in the diffusion boundary layer [7].

When there is a temperature gradient, the parameters become variable and dependent on the spatial coordinates. However, the temperature dependence of the density, specific heat, or thermal conductivity for a liquid is very much less than that for the viscosity or diffusion coefficient, so ρ , c_p , and λ can be taken as constant. Estimates also show [8] that thermal-diffusion effects are small in such a system and can be neglected. It is thus assumed that the behavior is governed only by the temperature dependence of the viscosity for a liquid and the reagent diffusion. There is however no essential difficulty in incorporating all the above factors.

We now show that if one neglects the viscous dissipation (which is justified for lowviscosity liquids such as water), the nonisothermal treatment also has a self-similar solution.

Then the equations of hydrodynamics and of heat and mass transfer are

$$\nabla \cdot \mathbf{v} = 0,$$

$$(\mathbf{v} \cdot \nabla) \mathbf{v} = -\frac{1}{\rho} \nabla p + \nabla \cdot (\mathbf{v} \nabla \mathbf{v}) + \mathbf{g},$$

$$\rho c_p \mathbf{v} \cdot \nabla T = \lambda \nabla^2 T,$$

$$\mathbf{v} \cdot \nabla c = \nabla \cdot (D \nabla c).$$
(2)

We introduce a cartesian coordinate system Oxyz having the Oz axis coincident with the axis of rotation, while the flow region corresponds to positive z. We also introduce a



Fig. 2. Temperature distributions: a) $t_{\infty} = 20^{\circ}C$; $t_{W} = 30^{\circ}C$ (1); 40 (2); 50 (3); 60°C (4); b) $t_{W} = 20^{\circ}C$; $t_{\infty} = 30^{\circ}C$ (1); 40 (2); 50 (3); 60°C (4); c) distribution for the relative temperature difference (in all cases, the curves lie in the region between the curves given in the figure).

certain standard temperature $T_{0}\text{,}$ at which the kinematic viscosity is $\nu_{0}\text{,}$ and convert to the dimensionless variables

$$\xi = \frac{x}{L}, \ \eta = \frac{y}{L}, \ \zeta = \frac{z}{L};$$

$$\mathbf{u} = \frac{\mathbf{v}}{U}; \ \theta = \frac{T - T_0}{\Theta}; \ \overline{c} = \frac{c}{c_{\infty}},$$

(3)

in which $L = \sqrt{v_0/\omega}$ is the length scale, $U = \omega L = \sqrt{v_0\omega}$ the velocity scale, and Θ the characteristic temperature scale.

We also represent the viscosity and diffusion coefficients as functions of temperature in dimensionless form:

$$\mathbf{v} = \mathbf{v}_0 \mathbf{v}(\theta), \ D = D_0 \overline{D}(\theta). \tag{4}$$

With the (3) and (4) variables, (2) has the solution

$$u_{\xi} = \xi f(\zeta) - \eta g(\zeta), \ u_{\eta} = \xi g(\zeta) + \eta f(\zeta), \ u_{\zeta} = -h(\zeta); \ \theta = \theta(\zeta); \ \overline{c} = \overline{c}(\zeta),$$
(5)

in which $f(\zeta)$, $g(\zeta)$, $h(\zeta)$, $\theta(\zeta)$ and $c(\zeta)$ satisfy a system of ordinary differential equations

$$(\overline{\nu}f')' + hf' = f^2 - g^2, \ (\overline{\nu}g')' + hg' = 2fg, \ h' = 2f; \theta'' + \Pr h\theta' = 0; \ (\overline{D}c')' + Sc \ hc' = 0$$
(6)

with the boundary conditions

$$f = 0, \ g = 1, \ h = 0, \ \theta = \theta_w, \ \overline{c} = 0; \ \zeta = 0,$$

$$f = 0, \ g = 0, \ \theta = \theta_w, \ \overline{c} = 1; \ \zeta = \infty.$$
 (7)

The parameters $Pr = \rho v_0 c_p / \lambda$ and $Sc = v_0 / D_0$ are the Prandtl and Schmidt numbers, which relate to $T = T_0$; the primes in (6) denote differentiation with respect to ζ . As the mass-transport treatment does not involve calculating the pressure pattern, the corresponding equation is omitted in (6).*

We see from (6) and (7) that the solution is dependent on four numerical parameters (θ_W , θ_{∞} , Pr, Sc) and two functions ($\bar{\nu}$ (θ), \bar{D} (θ)), so it is much more complicated than for the isothermal case, where there is only one parameter, the Schmidt number.

* System (2) is not altered in form by incorporating the temperature dependence of the density, as the solution is still as in (5). The effects from free convection involve examining the stability of (5), which is not considered here.

TABLE 1. Dimensionless Diffusion Flux Density Subject to Various Boundary Temperatures

	t _{w,} °C	t∞, °C				
		20	30	40	50	60
	20 30 40 50 60	1,000 1,203 1,419 1,642 1,867	1,014 1,221 1,440 1,667 1,896	1,028 1,239 1,462 1,693 1,925	1,043 1,257 1,483 1,717 1,952	1,058 1,275 1,505 1,742 1,979



Here we restrict consideration to effects associated with variation in $T_{\rm W}$ and the temperature far from the wall $T_\infty.$

The boundary-value problem for the quasilinear system represented by the first four equations in (6) has been solved numerically by an iterative method; this gave the hydrodynamic functions f, g, and h, as well as the distribution for the temperature θ and correspondingly for the viscosity and diffusion coefficient. The results at that stage were used to calculate the reagent distribution and the mass-transfer coefficient by double numerical integration for the last equation in (6); the calculations were performed for $\theta_{\rm W}$ and θ_{∞} from 0 to 0.5 with a step of 0.05.

The standard parameters were those for water at 20°C; θ was taken as 100°, so for example t = 30°C corresponds to θ = 0.1 and so on.

The temperature dependence of the viscosity was approximated as $v(\theta) = \exp(-2.32 \ \theta + 1.09 \ \theta^2)$, which corresponds well to the tabulated viscosity for water at 20-70°C [9]. The $\tilde{D}(\theta)$ was derived from the Einstein relation [9, 10] $D\mu/T = \text{const}$, whence $\tilde{D}(\theta) = (1 + 0.34 \ \theta)/v(\theta)$. The Prandtl number was taken as 7, which also corresponds to the properties of water at 20°C; the Schmidt number was taken as 500, which corresponds to $D = 2 \cdot 10^{-9} \ \text{m}^2/\text{sec}$ at 20°C. The program incorporated scope for varying Pr and Sc, and also for modifying $v(\theta)$ and $\tilde{D}(\theta)$.

Figures 1-3 show the graphs for the axial velocity component, the concentration, and the temperature as functions of distance from the disk under various conditions at the disk and deep within the liquid. The form of the temperature difference distribution persits (Fig. 2c), which is evidently specific to a system having moderate Prandtl number.

The main interest attaches to how the nonisothermal conditions affect the mass-transfer coefficient. Table 1 gives the results, where the principal diagonal contains numbers referring to isothermal conditions. Any change in wall temperature has much more effect on the coefficient than does the corresponding temperature change at depth. For example, a rise of 40°C in liquid temperature with a fixed wall temperature of 20°C increases the mass-transfer coefficient by only 6%, whereas a fixed liquid temperature and an analogous rise in the wall temperature increases the coefficient by almost 90%. For that reason, and also because the transport coefficients are not known accurately and there may be effects from minor factors, as well as inevitable measurement errors, the effects from changes in temperature deep within the liquid may not be recorded by experiment [6].



TABLE 2. Values of A in (8) for $T_0 = T_W$ and Effective Temperatures t_{\star} for the Viscosity Corresponding to A = const = 0.620.

Fig. 4. Relative diffusion flux densities at the surface as functions of temperature difference: a) $t_{\infty} = \text{const} =$ 20°C; b) $t_{W} = \text{const} = 20$ °C; 1) numerical calculation; 2) from (1) with $T_0 = T_W$; 3) from (8); 4) from (1) with $T_0 =$ T_d , points from experiment [7].

Measurements show that the transfer coefficient increases with disk surface temperature [6, 7], so our results agree well with experiment (Fig. 4), and it is thus correct to say that the temperature dependence of the diffusion coefficient and viscosity will have a decisive effect in laminar flow under nonisothermal conditions.

We finally consider the justification for using (1) in the nonisothermal case.

If one extends the procedure [4] for deriving (1) to that case, one gets

$$K = A D_{\omega}^{2/3} v_0^{-1/6} \omega^{1/2}; \ A = 0,776 a^{1/3}, \tag{8}$$

which resembles (1) in being asymptotically true for $Sc \to \infty$. Here $D_W = D(T_W)$, while α is the coefficient in $h(\zeta) = \alpha \zeta^2 + O(\zeta^3)$, which applies for $\zeta \to 0$.

(8) shows that the effective temperature for the diffusion coefficient is naturally taken as T_W . As regards the viscosity, the concept of an effective temperature has no clearcut physical meaning, since it merely defines the linear scale L, which can be selected arbitrarily. If for example, one defines L from the viscosity at the wall, our A in (8) will be variable for a given liquid and dependent on θ_W and θ_∞ , with A = 0.620 for $\theta_W = \theta_\infty$. If, on the other hand, one selects L such as to keep A = 0.620 constant in (8), then v_0 is correspondingly variable, as is T_0 . In each case, these variable quantities should be determined by solving the hydrodynamic problem numerically.

Table 2 shows that the (8) results for a liquid such as water differ little from those from the simpler (1) if the effective temperature in the latter is taken as the wall temperature. However, there is at present no basis for saying that the same will apply for any liquid whose properties are very different from those of water, and further research is required.

We substitute for D and v taken at the mean temperature of the diffusion boundary layer [7] into (1) to get the best agreement with exact calculations (Fig. 4). However, (1) then loses its asymptotic significance and thus the original physical significance. Therefore, that substitution may be considered only as a procedure for empirically correcting (1) that does not reflect physical regularities in mass transfer under nonisothermal conditions.

NOTATION

A and α , coefficients in (8); c, reagent concentration; $c = c/c_{\infty}$; c_p , specific heat of liquid; D, diffusion coefficient; $\bar{D} = D/D_0$, f, g, h, dimensionless hydrodynamic functions from (5); j, reagent mass flux density; K, mass-transfer coefficient; L, linear scale; p, pressure; Pr, Prandtl number; Sc, Schmidt number; T and t, temperature; U, velocity scale, u = v/U; v, velocity vector; x, y, z, cartesian coordinates; ξ , η , ζ , dimensionless cartesian coordinates; θ , dimensionless temperature; Θ , temperature scale; λ , thermal conductivity; μ , viscosity; ν , kinematic viscosity; $\bar{\nu} = \nu/\nu_0$; ρ , density; ω , angular velocity. Subscripts: w, values at the wall (disk surface), ∞ , values deep in the liquid, and 0 to values at the standard temperature T_0 .

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HEAT TRANSFER IN A PLASMOCHEMICAL REACTOR .

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An empirical method is proposed for calculating heat transfer in the channel in a plasmochemical reactor when the reagents are input via a system of holes in the wall.

There is an extensive class of plasmochemical reactors in which the raw material is introduced via a system of holes in the cylindrical wall (Fig. 1). The heat transfer then occurs in an unstabilized flow section and is complicated by the jet mixing, the reaction, the recirculation in the mixing chamber, and the considerable temperature differences.

Measurements have been made on heat transfer here [1] for various geometrical and other parameters and in the presence of exothermic reactions. The quantities characterizing the heat transfer are: the Stanton number St, Reynolds number Re for a plasma flow, ratio between the flow rates of the energy carrier M_1 and the raw material M_2 , the ratio of the enthalpy H_1 in the plasma jet reckoned from 0 K to the enthalpy in the products at the wall temperature H_w , the ratio of the length of the heat-transfer section ℓ to the channel diameter d_p, and the ratio of the total area of the holes f₂ for the raw material to the area f₁ of the reaction channel. One corrects for the reaction heat as regards the transfer via the observed relationship by means of the energy criterion proposed by Suris and Shorin [2, 3]:

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