$K$ = thermodynamic equilibrium constant

$k_1$ = reaction velocity constant in flow

$k_2$ = reaction velocity constant on catalyst surface

$L$ = $\dfrac{C_o}{C_e} + M - 1$

$M$ = $1 - \dfrac{C_o}{C_o}\left(\dfrac{1}{K+1}\right)$

$N_{Re}$ = Reynolds number, $d\,Um\,\rho/\mu$

$N_{Pe}$ = Peclet number, $N_{Re} \times N_{Sc}$

$N_{Sc}$ = Schmidt number, $\mu/\rho D$

$N^*_\infty$ = ratio of mass transfer rate with irreversible reaction to that without reaction at $\beta = \infty$

$U_m$ = maximum velocity at $\epsilon = 0$

$x$ = axial distance from entrance

$y$ = radial distance from center of channel

$Y_n$ = eigenfunctions

**Greek Letters**

$\alpha_1$ = homogeneous reaction parameter, $\sqrt{\dfrac{k_1 d^2}{D}\left(\dfrac{K+1}{K}\right)}$

$\alpha_2$ = heterogeneous reaction parameter, $\sqrt{\dfrac{k_2 d}{D}\left(\dfrac{K+1}{K}\right)}$

$\beta$ = dimensionless axial distance, $x/N_{Pe}d$

$\epsilon$ = dimensionless radial distance, $y/d$

$\theta$ = dimensionless concentration function, $\dfrac{(K+1)(C/C_o)-1}{K}$

$\theta_1$ = dimensionless concentration function, $\dfrac{C}{C_e} - 1$

$\lambda_n$ = eigenvalues

$\mu$ = viscosity

$\rho$ = density

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# Dual Variational Statements Viewed from Function Space

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In a recent note (*2*) W. E. Stewart exploited certain dual variational principles, developed by Hill and Johnson to obtain bounds for the volumetric flow rate $Q$ of an incompressible, homogeneous, Newtonian fluid in steady, rectilinear motion. More general methods are available however for obtaining bounds in linear problems; these methods are developed in functional analysis (*3*, *4*). The purpose of this communication is to point out the correspondence which exists between dual variational statements and geometric constructions in a function space and to suggest the power of the more general approach.

### BASIC EQUATIONS

The mathematical representation of an incompressible, rectilinear motion in a conduit is

$$\nabla^2 w = -\frac{\mathcal{P}}{\mu}; \quad \frac{\partial w}{\partial z} = 0; \quad \text{in } S_o \qquad (1)$$

$$w = 0 \quad \text{on walls of duct}$$

Green's identity combined with Equation (1) yields

$$Q \equiv \int_{S_o} w\, dA = \frac{1}{\mathcal{P}} \int_{S_o} \mu \nabla w \cdot \nabla w\, dA = \frac{1}{\mathcal{P}} D(w, w) \qquad (2)$$

In order to obtain bounds for the volumetric flow rate $Q$ it is necessary to obtain bounds for the rate of viscous dissipation per unit length of duct $D(w, w)$.

### PROBLEM IN FUNCTION SPACE

The natural setting of a variational problem is a space (or set) composed of functions which represent conceivable dynamic states (velocity fields in the present example). Such a space of functions is infinitely dimensional, yet can be pictured in the same manner as the space of free vectors in three-dimensional analytic geometry by imagining a function as a vector. In this spirit the scalar product of two functions $u$ and $v$ in the space is defined to be

$$D(v, u) \equiv \int_{S_o} \mu \nabla v \cdot \nabla u\, dA \quad \mu > 0 \qquad (3)$$

The positive square root of the quadratic form $D(v, v) \geqslant 0$ constitutes a distance measure in units of viscous dissipation, in function space; consequently the dynamic states in the space can be partially ordered by assigning them specific units of dissipation. The most important item in function space analysis is Schwarz's inequality, which in the present case takes the form

$$D^2(v, w) \leqq D(v, v)\, D(w, w) \qquad (4)$$

If $D(u, v) = 0$, $u$ and $v$ are said to be orthogonal, $u \perp v$. With these tools available, Equation (1) can be recast in a function space setting.

Let $v$ be a space of continuous functions (in $x$ and $y$) which possess continuous derivatives inclusive of the second order and let $N$ represent the set of all those functions in $v$ which vanish on the walls of the duct; that is

$$N = [v : v = 0 \text{ on the walls of the duct}] \qquad (5)$$

Now all those functions in $v$ which are orthogonal to every function in $N$ are sorted out and placed in a set $N\perp$. To do this requires finding all $u \epsilon v$ (where $\epsilon$ means 'contained in') and $v \epsilon N$ such that

$$D(v, u) = 0$$

Every $v \epsilon N$ vanishes on $L_o$ (the periphery of the duct), and consequently by the definition of $D(v, u)$ it is required that

$$\nabla^2 u = 0 \quad \text{in } S_o \qquad (6)$$

for all $u \epsilon N\perp$; that is

$$N\perp = [u : \nabla^2 u = 0 \text{ in } S_o]$$

Thus Equation (1) recast in a function space setting becomes

$$w \epsilon N \quad w - w_o \epsilon N\perp \qquad (7)$$

where $w_o$ is any function satisfying

$$\nabla^2 w_o = -\frac{\mathcal{P}}{\mu} \quad \text{in } S_o \qquad (7a)$$

This formulation is represented geometrically in Figure 1, where any line perpendicular to $N$ represents $N\perp + w_i$ and $\alpha$ is an arbitrary constant. From the orthogonality of $N$ and $N\perp$ it follows that

$$D(w - w_1, w) = 0 \quad w_1 - w_o \epsilon N\perp \qquad (8)$$

Inequality (6) yields the desired upper bound for $D(w, w)$:

$$D(w, w) \leqq D(w_1, w_1) \qquad (9)$$

Therefore any function satisfying the differential equation but not the boundary conditions of (1) yields an upper bound when used in calculating the viscous dissipation of the system. The

(*Continued from page 276*)

## INFORMATION RETRIEVAL

**Key Words:** A. Residence Time Distribution Function-9, Laminar Flow-5, Unpacked Tube-, Molecular Diffusion-4, Convection-4, Moments-8, Dispersion-8, Mixing-8. B. Moments-2, Computer-10. C. One Dimensional Model-2, Two Dimensional Model-2, Residence Time Distribution Function-2, Moments-, Variance-, Skew-.

**Abstract:** The residence time distribution function for laminar flow in an unpacked tube was obtained analytically by consideration of the simultaneous effects of convection and radial molecular diffusion. The results, unlike those of previous studies, are not generally reducible to an equivalent one-dimensional model, and the unique characteristics of the two-dimensional form provide an explanation for the tails found on residence time distributions obtained experimentally. The method of solution is general and may be extended to other diffusional situations involving tube flow and radially varying axial velocities.

**Reference:** Farrell, M. A., and E. F. Leonard, **A.I.Ch.E. Journal, 9,** No. 2, p. 190 (1963).

**Key Words:** Dispersed Phase-1, Mixing-8, Organic Liquids-1, Water-5, Stirred Tank-10, Reactor-10, Light Transmission-10, Power Input-6, Phase Fraction-6, Impeller Type-6, Vessel Scale-6, Mixing Rate-7, Reactor Design-9, Coalescence-9.

**Abstract:** Mixing rates were measured for various organic phase dispersions in water with a dye transfer light transmission technique. The variables studied were power input per unit volume, phase fraction, impeller type, and vessel scale. Mixing rates were found to be in the range where they can significantly affect chemical reactions. The information given here and in Part 1 shows for the first time the importance of dispersed phase mixing in affecting average reaction rate and product selectivity.

**Reference:** Miller, R. S., J. L. Ralph, R. L. Curl, and G. D. Towell, **A.I.Ch.E. Journal, 9,** No. 2, p. 196 (1963).

**Key Words:** A. Drying-8, Adsorption-8, Mass Transfer-8, Air-1, Water-1, Molecular Sieves-1, Fixed Bed-10, Dew-Point-6, Feed Composition-6, Temperature-6, Mass Velocity-6, Bed Height-6, Mass Transfer Zone-7, Dry Air-7. B. Design-8, Adsorbers-10, Dehumidifiers-10, Fixed Bed-10, Air-1, Water-1, Molecular Sieves-1, Adsorbent-5, Adsorption Mechanisms-10, Reaction Kinetics-10, Mass Transfer Coefficients-6, Pore Diffusion-10, Solid Diffusivities-6.

**Abstract:** The rate of drying of air in a fixed bed of molecular sieves was investigated. Effluent concentration as a fuction of time was measured at several values of inlet concentration, flow rate, bed height, and bed temperature. The constant mass transfer zone independent of bed height method of data analysis was found to be applicable. Published combined external and internal diffusion and pore diffusion models were also found to be applicable over a considerable portion of the breakthrough curve. The experimental data correlated well with calculated values obtained from material balances and rate equations. The data reported are useful for design purposes.

**Reference:** Nutter, James I., and George Burnet, Jr., **A.I.Ch.E. Journal, 9,** No. 2, p. 202 (1963).

**Key Words:** Diffusion-8, Mutual Diffusion-8, Transport Processes-9, Liquid Diffusion-8, Absolute Rate Theory-9, Liquid Viscosity-9, Solute-Solvent Effects in Diffusion-6.

**Abstract:** A method for estimating the difference in the free energies of activation for the viscous and mutual diffusion processes has been proposed. The correction factor is obtained by subdividing the viscosity into its kinetic and volumetric components, each of which were found to contribute equally to the total free energy of activation. Incorporation of this correction into the absolute rate theory of the transport processes improves the predicted values of the group $D\mu/T$.

**Reference:** Olander, Donald R., **A.I.Ch.E. Journal, 9,** No. 2, p. 207 (1963).

(*Continued on page 280*)

function space equivalent of the preceding statement is that the length of $w_1$ is larger than the length of $w$, unless $w_1 = w$—a fact which is obvious from Figure 1.

It is also evident in Figure 1 that the length of $\alpha v - w_o$ is greater than the length of $w - w_o$:

$$D(w - w_o, w - w_o) \leq D(\alpha v - w_o, \alpha v - w_o) \qquad (10)$$

Since $w \epsilon N$ and $w - w_o \epsilon N\perp$, application of the definition of $D$ yields

$$D(w, w) \geqq 2\alpha D(v, w_o) - \alpha^2 D(v, v) \qquad (11)$$

The right-hand side of (11) must be maximized with respect to $\alpha$ in order to obtain the best possible lower bound. Maximization gives

$$D(w, w) \geqq \frac{D^2(w_o, v)}{D(v, v)} \quad v \epsilon N \qquad (12)$$

It should be noted that any $\alpha$ in (11) would yield a lower bound. Relations (9) and (12) combined with (2) provide the desired upper and lower bounds for the volumetric flow rate:

$$\frac{1}{\wp} \frac{D^2(w_o, v)}{D(v, v)} \leq Q \leq \frac{1}{\wp} D(w_1, w_1) \qquad (13)$$

where $v \epsilon N$ and $w_o$ satisfy ($7a$).

Sometimes a solution to Equation ($7a$) is difficult to obtain. The difficulty can be overcome by an invariant imbedding of the space $v$ in a larger space $v'$. The imbedding is accomplished by associating elements $u \epsilon v$ with elements in the space $v'$ in such a manner that the operations of addition and multiplication by scalars in the space $v$ are preserved, and the length of functions in $v$ is not changed. These restrictions insure that angles are preserved, and consequently the orthogonality of the sets $N$ and $N\perp$ is preserved.

In the present example all the functions in $v$ are associated with vector—valued functions in a space $v'$ by the following linear, isometric mapping:

$$v \epsilon v \rightarrow \mathbf{q} = \nabla v \epsilon v'$$

The scalar product in $v'$ is

$$D'(p, q) = \int_{S_o} \mu \mathbf{p} \cdot \mathbf{q} \, dA$$

Functions in $N\perp$ may be difficult to obtain; consequently $N\perp$ is enlarged

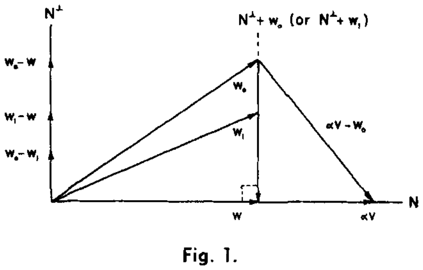

Fig. 1.

by constructing the orthogonal complement of $N$ (all vectors in $N$ are gradients of scalar functions) in $v'$. If $\mathbf{p} = \nabla v \epsilon N$ and $\mathbf{q} \epsilon N\perp'$, then

$$0 = \int_{S_o} \mu\, \mathbf{q}\cdot\nabla v\, dA =$$

$$-\int_{S_o} \mu\, v \nabla\cdot\mathbf{q}\, dA + \int_{S_o} \mu v\, \mathbf{q}\cdot\vec{dl} =$$

$$-\int_{S_o} \mu\, v \nabla\cdot\mathbf{q}\, dA$$

Consequently $N\perp$ has been enlarged to

$$N\perp' = [\mathbf{q} : \nabla\cdot\mathbf{q} = 0 \text{ in } S_o]$$

by invariant imbedding and

$$N = [\mathbf{p} : \mathbf{p} = \nabla v, v = 0 \text{ on walls of duct}]$$

Note that $N\perp'$ still includes the previous set $N\perp$.

The previous upper and lower bounds for the volumetric flow rate become

$$\frac{D'^2(\mathbf{q}_o, \nabla v)}{\wp\, D'(\nabla v, \nabla v)} \leq Q \leq \frac{1}{\wp} D'(\mathbf{q}_1, \mathbf{q}_1)$$

$$\mathbf{q}_1 - \mathbf{q}_o \epsilon N\perp' \tag{14}$$

where $v \epsilon N$ and $\mathbf{q}_o(x, y)$ is any function satisfying

$$\nabla\cdot\mathbf{q}_o = \frac{-\wp}{\mu}$$

## FUNCTION SPACE EQUIVALENT OF DUAL VARIATIONAL STATEMENTS

In this section the bounds for the volumetric flow rate which were obtained by Stewart (*2*) are viewed in function space. In so doing the correspondence between the method of dual variational statements and the geometrical constructions in a function space becomes apparent.

From the definition of $\mathbf{q}_o$ and $v \epsilon N$ it follows that

$$D'(\mathbf{q}_o, \nabla v) = \int_{S_o} \mu\, \mathbf{q}_o\cdot\nabla v\, dA =$$

$$-\int_{S_o} \mu\, v \nabla\cdot\mathbf{q}_o dA = \wp \int_{S_o} v\, dA$$

and consequently (15)

$$2D'(\nabla v, \mathbf{q}_o) - D'(\nabla v, \nabla v) =$$

$$2\wp \int_{S_o} v\, dA - \mu \int_{S_o} \nabla v\cdot\nabla v\, dA \tag{16}$$

Because of Equation (16) and the definition of $\wp$, the bound (11) for the special case $\alpha = 1$ yields

$$(p_1 - p_o) \int_{S_o} v\, dA +$$

$$\frac{\mu L}{2} \int_{S_o} \nabla v\cdot\nabla v\, dA \geqq$$

$$\frac{-(p_o - p_1)}{2} Q \geqq -\frac{L}{2} D'(\mathbf{q}_1, \mathbf{q}_1) \tag{17}$$

which is identical to Stewart's statement of bounds for $J = \frac{-1}{2}(p_o - p_1)\, Q$. It was pointed out above that inequalities (14), not (11) with $\alpha = 1$, give the narrowest possible bounds. Thus an immediate reward for viewing the problem in a function space is finding that Stewart's lower bound for the volumetric flow rate is not the best possible; however it does simplify numerical computations.

From the above reconstruction of Stewart's bounds it is apparent that dual variational statements represent statements about the projections of function-space vectors onto specific hyperplanes in function space. The utility of function space methods is twofold. Firstly, they afford a clear picture of the approximation and narrowness of the bounds, and secondly, they can be extended to yield bounding techniques for the pointwise value of a function. Moreover, they are, in the words of Synge (*3*, pp. 33 to 34), "in tune with physical space intuitions which are sometimes indispensable for discovery and rapid understanding."

## NOTATION

$dA$ = differential element of area
$D$ = integral defined by (3)
$L$ = axial distance
$L$ = periphery of duct cross section
$p$ = value of thermodynamic pressure referred to a given datum
$\wp$ = $\frac{p_o - p_1}{L}$
$Q$ = volumetric flow rate through duct
$S_o$ = cross-sectional area of duct
$w$ = local value of axial component of velocity field
$\nabla$ = two dimensional gradient $\left(\frac{\partial}{\partial x}\hat{i} + \frac{\partial}{\partial y}\hat{j}\right)$
$\nabla^2$ = two dimensional Laplacian $\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$
$\mu$ = viscosity

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# Flow of Liquids in Horizontal Capillary Tubes

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Behavior of liquid-gas systems in the absence of gravitational forces presents interesting problems for the engineer who must design equipment for space flight. Utilization of surface tension forces which are independent of gravity to control the position of the liquid has considerable promise. Flow of several liquids in horizontal glass capillary tubes has been studied in order to predict flow under zero gravity conditions.

Prime purpose of the study was to determine whether or not capillary tubes could be used to pump liquid oxygen from a mass of liquid. The capillary could be either a conventional tube or a porous material. If a capillary tube is placed in a horizontal position, then it may be assumed that the gravity forces acting on a liquid flowing in the tube may be negligible. Based on this assumption it may be speculated that the behavior of a liquid in a capillary tube which is in a zero gravity environment can be estimated by studying the flow of liquids in horizontal capillary tubes.

## PREVIOUS ANALYSIS

During initial considerations of the surface tension properties of LOX (liquid oxygen), it was thought that the rate of movement of LOX in a horizontal capillary could be calculated from known data. It was postulated that, under zero gravity conditions, the LOX would be drawn into the capillary until the tube would be filled or the surface tension forces would be balanced by a contrary force such as the viscous drag on the liquid.