TABLE 1. CALCULATED VALUES OF THE VELOCITY GRADIENT AT THE WALL FOR VARIOUS N_2 AND $f(0)$ AND $N_{Pr} = 0.72$

N_2	$f(0)$	$\phi(0)$
0.000	1.000	2.917
0.000	0.500	2.092
0.000	0.250	1.701
0.000	0.000	1.328
0.000	–0.250	0.979
0.000	–0.500	0.658
0.000	–1.000	0.143
0.250	1.000	3.007
0.250	0.500	2.222
0.250	0.250	1.690
0.250	0.000	1.529
0.250	–0.250	1.233
0.250	–0.500	0.982
0.250	–1.000	0.633
0.500	1.000	3.095
0.500	0.500	2.346
0.500	0.250	2.009
0.500	0.000	1.705
0.500	–0.250	1.431
0.500	–0.500	1.217
0.500	–1.000	0.900
–0.250	1.000	2.823
–0.250	0.500	1.952
–0.250	0.250	1.521
–0.250	0.000	1.082
–0.250	–0.250	0.562
–0.250	–0.350	—
–0.500	1.000	2.727
–0.500	0.500	1.800
–0.500	0.250	1.312
–0.500	0.000	0.701
–0.500	–0.150	—

to iterate on ϕ until $\phi(0)$ is determined to the desired accuracy. However, as seen in Equation (8), $\int_0^\eta f\, d\eta$ will be negative for larger η if ϕ is negative in the region near the wall. This effect accumulated with successive iterations, and the expression for $\phi(0)$ yields increasingly large negative values. Therefore if $\phi(0)$ is negative, the iterative procedure employed diverges; also, as N_2 approaches the value required for stagnation, the number of iterations needed increases markedly. The exact values of $\phi(0)$, with various N_2, required for stagnation were not determined owing to the excessive numerical work required. However these may be estimated by extrapolating the data in Table 1 graphically and noting the smallest values of the parameters used in the calculation for which $\phi(0)$ is negative.

Figure 2 shows several representative temperature profiles. Clearly, the effect of N_2 is more pronounced for negative $f(0)$ or when there is mass transfer into the stream.

ACKNOWLEDGMENT

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LITERATURE CITED

1. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," p. 608, Wiley, New York (1960).
2. Eckert, E. R. G., and R. M. Drake, "Heat and Mass Transfer," McGraw Hill, New York (1959).
3. Eichhorn, R., *Trans. Am. Soc. Mech. Engrs., Series C,* **82,** 260 (1960).
4. Gill, W. N., and Eduardo del Casal, *A.I.Ch.E. Journal,* to be published.

Application of Reciprocal Variational Principles to Laminar Flow in Uniform Ducts

WARREN E. STEWART

University of Wisconsin, Madison, Wisconsin

The usefulness of variational principles in solving steady flow problems is well known; a variety of Newtonian and non-Newtonian problems have been so treated (*1, 10, 11, 12, 13, 14*). The problem of determining the accuracy of variational flow calculations however has not received much attention. The present note shows how such a determination can be made, with reciprocal variational principles developed by Hill (*5, 6*) and independently by Johnson (*7, 8*).

The variational theorems of Hill and Johnson are quite general with regard to system geometry, rheological behavior, and boundary conditions. To focus attention on the reciprocal aspects of the theorems the present discussion deals only with rectilinear Newtonian flow, and the basic equations are specialized accordingly. The notation and terminology here parallel those used by Johnson.

BASIC EQUATIONS

Consider the steady flow of a Newtonian fluid, of constant viscosity and density, in a long, cylindrical duct of arbitrary cross section S_0 under a known pressure gradient. The flow is assumed to be parallel to the z-axis, except for a small region at each end of the duct. Determine Q, the volumetric rate of flow.

For this system the equations of continuity and motion (*2*) become

$$\frac{\partial v_z}{\partial z} = 0 \tag{1}$$

$$0 = -\frac{\partial \mathcal{P}}{\partial x} \tag{2a}$$

$$0 = -\frac{\partial \mathcal{P}}{\partial y} \tag{2b}$$

$$0 = -\frac{\partial \mathcal{P}}{\partial z} - \frac{\partial \tau_{xz}}{\partial x} - \frac{\partial \tau_{yz}}{\partial y} \tag{2c}$$

The nonvanishing components of the viscous stress tensor are given by

$$\tau_{xz} = \tau_{zx} = -\mu \frac{\partial v_z}{\partial x} \tag{3a}$$

$$\tau_{yz} = \tau_{zy} = -\mu \frac{\partial v_z}{\partial y} \tag{3b}$$

and the boundary conditions are

$$\text{at } z = 0, \quad \mathcal{P} = \mathcal{P}_0 \tag{4a}$$

$$\text{at } z = L, \quad \mathcal{P} = \mathcal{P}_L \tag{4b}$$

$$\text{at the walls, } v_z = 0 \tag{5}$$

where the region $0 < z < L$ lies inside the region of fully developed flow.

Hill (*5, 6*) and Johnson independently (*7, 8*) have given two methods for variational solution of this problem. By applying both methods one obtains upper and lower bounds on the quantity

$$J_0 = -\frac{1}{2}(\mathcal{P}_0 - \mathcal{P}_L)Q \tag{6}$$

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INFORMATION RETRIEVAL*

Key Words: Catalysis-4, Gas-5, Diffusion-8, Thermal Conduction-8, Heat Transfer-8, Reaction Kinetics-8, Mass Transfer-8, Material Balance-8, Mathematics-10, Computations-10, Reactors-10, Thermodynamics-10, Film Theory-.

Abstract: Film-theory solutions are presented for the effect of a gas-phase chemical reaction upon the rate of heat transfer between the reacting gas and a solid wall. Both homogeneous reaction and heterogeneous reaction on the wall are considered. Restricting the analysis to the case of a small temperature-driving force and to the case in which the bulk gas is in chemical equilibrium, one obtains results that can be presented in general terms involving partial derivatives of arbitrary chemical kinetic expressions. The assumption that the bulk gas is essentially in chemical equilibrium is justified for the case of a homogeneous reaction.

Reference: Brian, P. L. T., and R. C. Reid, **A.I.Ch.E. Journal, 8,** No. 3, p. 322 (July, 1962).

Key Words: Diffusion-8, Coefficients-8, Liquid Phase-8, Predicting-8, Estimating-8, Binary-9, Mass Transfer-9, Transport-9, Properties (Characteristics)-9, Physical Properties-9, Correlations-9, Concentration-6, Diffusion-7, Rates-7, Coefficients-7, Models-10.

Abstract: A new approach has been developed for calculating diffusion coefficients in binary liquid systems. The proposed equation is based on the results obtained from the statistical mechanics of transport phenomena in dense media. The fundamental variables required for the calculation are the free volume of a molecule, obtainable from physical measurements such as the velocity of sound, and the heat of vaporization of the solute. Viscosity is not included explicitly. The results predicted by the proposed correlation are compared with experimental data on fifty-six different systems. The effect of concentration on the diffusion coefficient is discussed.

Reference: Kamal, Musa R., and L. N. Canjar, **A.I.Ch.E. Journal, 8,** No. 3, p. 329 (July, 1962).

Key Words: Flow-8, Fluid Flow-8, Emulsions-8, Dispersions-8, Laminar Flow-9, Turbulence-9, Viscosity-9, Properties (Characteristics)-9, Physical Properties-9, Petroleum-9, Solvents-9, Water-9, Fluids-9, Liquid Phase-9, Friction-9, Factors-, Rates-6, Quantity-6, Proportions-6, Diameter-6, Orientation-6, Viscosity-7, Solutions (Mixtures)-9, Capillaries-10, Tubes-10.

Abstract: Liquid-liquid emulsions of a petroleum solvent dispersed in water have been studied under laminar and turbulent flow conditions. On the assumption that the dispersions behave as a single phase fluid, effective viscosities are calculated from measured friction factors. Calculated viscosities are presented as functions of flow rate, volume fraction of solvent, tube diameter, and tube orientation.

Reference: Cengel, J. A., A. A. Faruqui, J. W. Finnigan, C. H. Wright, and J. G. Knudsen, **A.I.Ch.E. Journal, 8,** No. 3, p. 335 (July, 1962).

Key Words: Heat Transfer-8, Fluid Flow-8, Flow-8, Thermal Conductivity-8, Properties (Characteristics)-8, Physical Properties-8, Correlations-8, Gases-9, Fluids-9, Solids-9, Carbon Dioxide-1, Oxides (Inorganic)-1, Nitrogen-1, Helium-1, Hydrocarbons-1, Flow Rates-6, Thermal Conductivity-7, Beds-10, Packed-, Beads-10, Glass-10.

Abstract: Effective thermal conductivities have been evaluated for beds of fine glass beads from experimental data on heat transfer perpendicular to the direction of fluid flow. Results were obtained for a bead size range of 29 to 940 μ and for carbon dioxide, nitrogen, helium, and a C_7 hydrocarbon liquid. Over the range of flow rates studied, 0 to 80 lb. (hr. sq. ft.), there is no effect of flow on the conductivity. Hence the measured stagnant conductivity also satisfactorily represents heat transfer for flow conditions. Methods of predicting the stagnant conductivity have been re-examined, and a revised prediction method is proposed. The equations are compared with literature data.

Reference: Willhite, G. P., Daizo Kunii, and J. M. Smith, **A.I.Ch.E. Journal, 8,** No. 3, p. 340 (July, 1962).

(*Continued on page 427*)

and correspondingly bounds are obtained for the volumetric flow rate Q.

An upper bound for J_0 is obtained by evaluating the functional

$$J_v = \frac{\mu L}{2} \int\!\!\int_{S_0} \left[\left(\frac{\partial v_z}{\partial x} \right)^2 + \left(\frac{\partial v_z}{\partial y} \right)^2 \right] dxdy + (\mathcal{P}_L - \mathcal{P}_0) \int\!\!\int_{S_0} v_z \, dxdy \qquad (7)$$

for any trial function $v_z(x, y)$ which satisfies Equations (1) and (5) and is sufficiently differentiable. That trial function which renders J_v an absolute minimum relative to all other admissible trial functions is the exact solution for $v_z(x, y)$ in Equations (1) through (5). That is the variational problem $\delta J_v \geqq 0$, with Equations (1) and (5) as admissibility conditions for the trial functions and with the stresses given by Equations (3), has Equations (2) as Euler equations and Equations (4) as natural boundary conditions. The absolute minimum value of J_v obtainable with admissible trial functions is J_0. This variational procedure follows from the Helmholtz principle of minimum energy dissipation (9), as well as from the more general formulations of Johnson and Hill for non-Newtonian fluids.

A lower bound for J_0 is obtained by evaluating the functional

$$H_\tau = -\frac{L}{2\mu} \int\!\!\int_{S_0} [\tau_{xz}{}^2 + \tau_{yz}{}^2] \cdot dxdy \qquad (8)$$

for any set of trial functions τ_{xz}, τ_{yz}, and $\mathcal{P}$ which satisfies Equations (2) and (4) and is sufficiently differentiable. That set of trial functions which renders H_τ an absolute maximum, relative to all other admissible sets, is the exact solution for $\mathcal{P}$, τ_{xz}, and τ_{yz} in Equations (1) through (5). That is the variational problem $\delta H_\tau \leqq 0$, with Equations (2) and (4) as admissibility conditions and with the velocity gradients given by Equations (3) has Equation (1) as its Euler equation and Equation (5) as a natural boundary condition. The absolute maximum value of H_τ obtainable with admissible trial functions is J_0.

Notice that the admissibility conditions for either of the above variational problems are the Euler equations and natural boundary conditions for the other; that is the two variational problems are reciprocal to each other (7) It is this reciprocal relationship which causes J_v and H_τ to approach the same limit from opposite sides when increasingly accurate trial functions are used. Reciprocal variational problems offer similar advantages in other physical problems, for example in the theory of elasticity. The formulation and properties of reciprocal variational problems are treated in Courant and Hilbert (3).

The selection of admissible trial functions for Equation (8) may be simplified by setting

$$\mathcal{P} = \mathcal{P}_0 - (\mathcal{P}_0 - \mathcal{P}_L)\,\frac{z}{L} = \mathcal{P}_0 - mz \tag{9}$$

$$\tau_{xz} = (\mathcal{P}_0 - \mathcal{P}_L)\,\frac{x}{2L} + \frac{\partial F}{\partial y} = \frac{mx}{2} + \frac{\partial F}{\partial y} \tag{10}$$

$$\tau_{yz} = (\mathcal{P}_0 - \mathcal{P}_L)\,\frac{y}{2L} - \frac{\partial F}{\partial x} = \frac{my}{2} - \frac{\partial F}{\partial x} \tag{11}$$

where F is a sufficiently differentiable function of x and y. Equations (2) and (4) are identically satisfied by these equations, and no other solutions exist. Thus Equation (8) may be rewritten in the form

$$H_\tau = -\frac{L}{2\mu}\int\!\!\int_{S_0}\left[\left(\frac{mx}{2} + \frac{\partial F}{\partial y}\right)^2 + \left(\frac{my}{2} - \frac{\partial F}{\partial x}\right)^2\right] dx\,dy \tag{12}$$

and now only one quantity $F(x, y)$ needs to be represented by a trial function.

The following example illustrates the use of the reciprocal principles $\delta J_v \geqq 0$ and $\delta H_\tau \leqq 0$, in conjunction with the Rayleigh-Ritz procedure (3) for determining the constants in the trial functions.

FLOW IN A SQUARE DUCT

Consider a square duct with walls at $x = \pm a$ and $y = \pm a$. The following trial function satisfies Equations (1) and (5):

$$v_z = c_1\left[1 - \frac{x^2}{a^2}\right]\left[1 - \frac{y^2}{a^2}\right] \tag{13}$$

For this trial function Equation (7) gives

$$J_v = \frac{128}{45}\,\mu L c_1^2 - \frac{16}{9}\,(\mathcal{P}_0 - \mathcal{P}_L)\,a^2 c_1 \tag{14}$$

Minimizing J_v with respect to c_1 one gets

$$c_1 = \frac{5}{16}\,\frac{(\mathcal{P}_0 - \mathcal{P}_L)a^2}{\mu L} \tag{15}$$

from which

$$J_v = -\frac{5}{18}\,\frac{(\mathcal{P}_0 - \mathcal{P}_L)^2 a^4}{\mu L} \geqq -\frac{1}{2}\,(\mathcal{P}_0 - \mathcal{P}_L)Q \tag{16}$$

or

$$\frac{5}{9}\,\frac{(\mathcal{P}_0 - \mathcal{P}_L)a^4}{\mu L} \leqq Q \tag{17}$$

That is the upper bound on J_0 provides a lower bound on the volumetric flow rate.

The simplest trial function usable in Equation (12) is $F = 0$; this gives

$$H_\tau = -\frac{(\mathcal{P}_0 - \mathcal{P}_L)^2 a^4}{3\,\mu L} \leqq -\frac{1}{2}\,(\mathcal{P}_0 - \mathcal{P}_L)Q \tag{18}$$

or

$$\frac{2}{3}\,\frac{(\mathcal{P}_0 - \mathcal{P}_L)a^4}{\mu L} \geqq Q \tag{19}$$

When one considers the crude trial function used, this result is surprisingly good; it exceeds the lower bound in Equation (17) by only 20%. The deviation from the exact solution is therefore less than 20%.

To obtain a closer upper bound on Q an adjustable F function may be used. Because of the symmetry of the problem the simplest polynomial F-function which gives any change from the above result is

$$F = c_2\,(x^3y - y^3x) \tag{20}$$

Equation (12) then gives

$$H_\tau = -\frac{4a^2L}{\mu}\left[\frac{m^2}{12} - \frac{2c_2m}{15} + \frac{12}{35}\,c_2^2\right] \tag{21}$$

Maximizing this result with respect to c_2 one obtains finally

$$\frac{76}{135}\,\frac{(\mathcal{P}_0 - \mathcal{P}_L)a^4}{\mu L} \geqq Q \tag{22}$$

Combining Equations (17) and (22) one obtains

$$0.5556\,\frac{(\mathcal{P}_0 - \mathcal{P}_L)a^4}{\mu L} \leqq Q \leqq 0.5630\,\frac{(\mathcal{P}_0 - \mathcal{P}_L)a^4}{\mu L} \tag{23}$$

which determines Q accurately enough for most purposes. Narrower bounds could of course be obtained by including more adjustable constants in the trial functions.

The exact solution, according to Boussinesq (4), is

$$Q = 0.5622\,\frac{(\mathcal{P}_0 - \mathcal{P}_L)a^4}{\mu L} \tag{24}$$

which is consistent with the bounds in Equation (23).

DISCUSSION

The determination of upper and lower bounds in variational calculations gives a useful test of accuracy and is therefore strongly recommended. It should be remembered of course that the computed local values of v_z and F tend to be less accurate than the corresponding functionals J_v and H_τ when incomplete trial functions are used. For example the center line velocity in the duct according to Boussinesq (4) is

$$v_{z,\,\max} = 0.2945\,\frac{(\mathcal{P}_0 - \mathcal{P}_L)a^2}{\mu L} \tag{25}$$

and the value of $v_{z,\,\max}$ predicted by Equations (13) and (15) is therefore about 6% too low, in spite of the excellent lower bound obtained for Q.

Upper and lower bounds can also be obtained for variational solutions under more general conditions, with the theorems of Hill (5, 6) and Johnson (7, 8). For most non-Newtonian rheological models the quantity J_0 has no simple physical significance; however the comparison of J_v and H_τ should still give a useful test of accuracy. In problems of rectilinear non-Newtonian duct flow Equations (9), (10), and (11) will remain useful.

NOTATION

a = half width of walls of square duct

F = integral stress function defined in Equations (10) and (11)

H_τ = functional defined in Equation (8)

J_v = functional defined in Equation (7)

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INFORMATION RETRIEVAL*

Key Words: Mass Transfer-8, Diffusion-8, Transport-8, Rates-8, Fluids-9, Liquids-9, Non-Newtonian-, Slurries-9, Dispersions-9, Suspensions-9, Benzoic Acid-4, Acids (Carboxylic)-4, B-Naphthol-4, 2-Naphthol-4, Alcohols-4, Naphthols-4, Water-5, Estimating-8, Predicting-8, Properties (Characteristics)-9, Physical Properties-9, Theory-10, Eyring-.

Abstract: The general Eyring rate theory is extended to predict diffusivities in slurries and in non-Newtonian solutions. The predicted diffusivities are compared with experimental values. Data are provided on slurries and a polymer solution. Benzoic acid and B-naphthol were employed as the diffusing solutes. Only aqueous systems were investigated.

Reference: Clough, S. B., H. E. Read, A. B. Metzner, and V. C. Behn, **A.I.Ch.E. Journal, 8,** No. 3, p. 346 (July, 1962).

(*Continued on page 428*)

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INFORMATION RETRIEVAL*

Key Words: A. Extraction-8, Liquid-, Spontaneous-2, Convection-2, Interfacial-8, Patterns-8, Acetic Acid-1, Ethylene Glycol-1, Ethyl Acetate-1, Photography-10, Schlieren-, Motion Pictures-10, Concentration-6, Time-6. B. Size-7, Velocity-7, Stationary-, Propagating-, Polygons-2, Cells-2, Clusters-2, Stripes-2, Ripples-2.

Abstract: Spontaneous interfacial cellular convection accompanying the extraction of acetic acid out of ethylene glycol with ethyl acetate was studied photographically with a Schlieren technique. A flat liquid-liquid interface at room temperature was photographed straight down with motion picture and still cameras. The interface exhibited a dominant pattern of stationary and propagating polygonal cells, accompanied by stripes, cell cluster boundaries, and confined or unconfined ripples. The time dependence of the average wave length (size) of the different patterns, their average speed of propagation, and their frequency was determined with initial acetic acid concentration range of 0.1 to 10%, over a time span of 72 hours.

Reference: Orell, Aluf, and I. W. Westwater, **A.I.Ch.E. Journal, 8,** No. 3, p. 350 (July, 1962).

Key Words: Vapor Pressure-8, Properties (Characteristics)-8, Physical Properties-8, Relationships-8, Equations-8, Paraffins-9, Olefins-9, Aromatics-9, Hydrocarbons-9, Predictions-9, Critical-9, Constants-, Temperature-9, Pressure-9.

Abstract: A vapor pressure equation is presented which involves the reduced pressure, the reduced temperature, and a charactistic constant for each pure substance. The relationship has been applied to fifty-four hydrocarbons including normal paraffins, isoparaffins, olefins, diolefins, acetylenes, naphthenes, and aromatics. The equation can be used to predict vapor pressures of pure hydrocarbons up to the critical point, or, if reliable vapor pressure data are available, to predict the critical constants.

Reference: Reynes, Enrique G., and George Thodos, **A.I.Ch.E. Journal, 8,** No. 3, p. 357 (July, 1962).

Key Words: Porosity-8, Voids-8, Properties (Characteristics)-8, Physical Properties-8, Beds-9, Packed-, Spheres-9, Balls-9, Diameter-6, Boundaries-6, Concave-, Convex-, Porosity-7, Voids-7, Properties (Characteristics)-7, Physical Properties-7, Variations-7, Radial-.

Abstract: The radial variation of void fraction in a packed bed of uniform spheres has been studied. Results are presented for various D/d ratios, and for concave and convex boundary walls. An improved experimental technique is described in detail.

Reference: Benenati, R. F., and C. B. Brosilow, **A.I.Ch.E. Journal, 8,** No. 3, p. 359 (July, 1962).

(*Continued on page 430*)

J_0 = quantity defined in Equation (6)
L = axial distance over which $(\mathcal{P}_0 - \mathcal{P}_L)$ is measured
m = $(\mathcal{P}_0 - \mathcal{P}_L)/L$
$\mathcal{P}$ = static pressure referred to a constant elevation = $p + \rho\Phi$
Q = volumetric flow rate through duct
S_0 = cross section of the duct
v_z = local fluid velocity in the z-direction
x,y,z = rectangular coordinates

Greek Letters

δ = variation operator
μ = viscosity
ρ = density
τ_{xz},τ_{yz} = components of the viscous stress tensor
Φ = potential energy per unit mass of fluid

LITERATURE CITED

1. Bird, R. B., *Physics of Fluids,* **3,** 539 (1960).
2. ———, W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," Wiley, New York (1960).
3. Courant, R., and D. Hilbert, "Methods of Mathematical Physics," Vol. 1, Chap. 4, Interscience, New York (1953).
4. Dryden, H. L., F. D. Murnaghan, and H. Bateman, "Hydrodynamics," p. 197, Dover, New York (1956).
5. Hill, R., *J. Mech. and Phys. Solids,* **5,** 66 (1956).
6. ———, *Quart. J. Mech. and Appl. Math.,* **9,** 313 (1956).
7. Johnson, M. W., Jr., *Physics of Fluids,* **3,** 871 (1960).
8. ———, *Mathematics Research Center Summary Report 208,* Univ. Wisconsin, Madison, Wisconsin (1960).
9. Lamb, H., "Hydrodynamics," 6 ed., pp. 617-619, Dover, New York (1932).
10. Pawlowski, J., *Kolloid-Zeitschrift,* **138,** 6-11 (1954).
11. Schechter, R. S., *A.I.Ch.E. Journal,* **7,** 445 (1961).
12. Sparrow, E. M., and R. Siegel, *J. Heat Transfer,* **81,** Series C, p. 157 (1959).
13. Tomita, Y., *Bull. Japan Soc. Mech. Engrs.,* **2,** 469 (1959).
14. Ziegenhagen, A. J., R. B. Bird, and M. W. Johnson, Jr., *Trans. Soc. Rheology,* **5,** 47-49 (1961).

Immiscibility of Hydrocarbons and Liquid Methane

A. J. DAVENPORT, P. I. FREEMAN, and J. S. ROWLINSON

Imperial College of Science and Technology, London, England

J. P. Kohn (3) has recently reported a study of the phase equilibria of the system methane + *n*-heptane. He observed that the system separated into two liquid phases and reported the temperature and pressure of the quadruple point [solid heptane + liquid I + liquid II + gas]. It is very rare for two hydrocarbons to be partially immiscible, and the purpose of this paper is first to confirm Kohn's results and secondly to report some similar obser-

TABLE 1. QUADRUPLE POINT OF METHANE + *n*-HEPTANE

	Temperature, °K.	Pressure, atm.	Weight fraction of CH_4 in liquid phases	
Kohn	169.6	23.0	0.227	~1
D, F, and *R*	169.6	—	0.17	>0.93

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