LITERATURE CITED

Hulburt, H. M., and S. Katz, "Some Problems in Particle Technology. A Statistical Mechanical Formulation," *Chem. Eng. Sci.*, 19, 555 (1964).

Randolph, A. D., and M. A. Larson, *Theory of Particulate Processes*, Academic Press, New York (1971).

——————, "Transient and Steady State Size Distributions in Continuous Mixed Suspension Crystallizers," *AIChE J.*, 8, 639 (1962).

Sikdar, S. K., and A. D. Randolph, "Secondary Nucleation of Two Fast Growth Systems in a Mixed Suspension Crystallizer: Magnesium Sulfate and Citric Acid Water Systems," *ibid.*, 22, 110 (1976).

Weed, D. R., "Growth and Nucleation Studies for a Batch, Isothermal, Suspension Crystallizer" M.S. thesis, Clarkson College of Technology, Potsdam, N.Y. (1972).

Wey, J-S, and J. Estrin, "Modeling the Batch Crystallization Process. The Ice-Brine System," *Ind. Eng. Chem. Process Design Develop.*, 12, 236 (1973).

Manuscript received January 20, 1977; revision received October 14, and accepted October 27, 1977.

Vapor Pressures of High-Boiling Liquid Hydrocarbons

A. B. MACKNICK
JACK WINNICK
and
J. M. PRAUSNITZ
Chemical Engineering Department
University of California,
Berkeley, California

Owing to the rising importance of coal-derived fluids and heavy petroleum in emerging technology, the vapor pressures of heavy hydrocarbons are becoming of increasing interest in chemical process design. In this note we consider how limited liquid vapor-pressure data, obtained at near-ambient temperatures, can be used to predict vapor pressures at elevated temperatures where industrial processes often occur but where it is difficult to make experimental measurements.

We consider four methods for extrapolating vapor pressures P to higher temperatures T:

1. The linear method, wherein a plot of log P vs. T^{-1} is assumed to be a straight line.
2. The method of Riedel (1954) which requires critical temperature, critical pressure, and one vapor-pressure datum.
3. The method of Zia and Thodos (1974) which also requires critical temperature, critical pressure, and one vapor-pressure datum.
4. The SWAP method (Smith et al., 1976) which requires only approximate information on the molecular structure of the hydrocarbon and one vapor-pressure datum.

Critical temperatures and pressures can be estimated using the method of Foreman and Thodos as described in Reid and Sherwood (1966), provided the molecular structure of the hydrocarbon is known. Particularly important is the number of carbon atoms per molecule.

Detailed consideration was not given to the Antoine equation because a preliminary study showed that when the Antoine parameters were determined from limited vapor-pressure data, the resulting equation, while good for interpolation, is extremely poor for extrapolation.

For our study we used five representative hydrocarbon liquids that have been studied experimentally. They are eicosane (I), 1,1 dicyclohexyl heptane (II), 2,2,4,10,12,12 hexamethyl-7-(3,5,5,-trimethylhexyl)-6-tridecane (III), perhydrochrysene (IV) and 9-N-butylanthracene (V).

Table 1 gives the measured temperature corresponding to a vapor pressure of 0.01 Torr. This temperature, always above the melting point, is the experimental datum used in all four extrapolation methods.

Table 1 also gives estimated critical temperatures and pressures and, where appropriate, the fraction of carbon atoms which are aromatic (F_A), naphthenic (F_N), or branched (F_B). These fractions are required in the SWAP method.

Calculated and experimental vapor pressures are compared in Table 1 which gives the percent error at two temperatures: T_1 and T_{10} where the subscript refers to the observed pressure in torr. All experimental data are from American Petroleum Institute Projects 42 and 44, except $T_{0.01}$ for eicosane which was measured in our own laboratory.

The simplest manner for using the linear method, log P vs. T^{-1}, is to interpolate between $T_{0.01}$ and the estimated critical point. However, this procedure calculates pressures in error by an order of magnitude. Instead, several experimental data in the region 0.001 to 0.01 torr were fit to a straight line. The equation of this line was then used to estimate T_1 and T_{10}.

Calculations using the method of Riedel are described by Reid et al. (1977). Calculations using the method of Zia and Thodos are described by those authors (Zia and Thodos. 1974).

Calculations using the SWAP method are essentially those described by Smith et al. (1976) but require, in addition, an empirical relation between T_{760} and $T_{0.01}$ for normal paraffins. From available experimental data, this relation is

$$T_{760} = 3.22 + 2.089\, T_{0.01} - 1.035 \times 10^{-3}(T_{0.01})^2 \quad (1)$$

Equation (1) above replaces Equation (13) in the article by Smith et al. (1976).

The results in Table 1 indicate that the linear method is poor; the other three methods are consistently better, but it appears that of these three, no one method is significantly better than the others. However, the method of Riedel and that of Zia and Thodos require detailed information on molecular structure, in particular, the number of carbon atoms per molecule; this information is

---

Jack Winnick is at the University of Missouri, Columbia, Missouri 65201.

0001-1541-78-1001-0731-$00.75. © The American Institute of Chemical Engineers, 1978.

TABLE 1. PERCENT ERRORS IN CALCULATED VAPOR PRESSURES

Hydrocarbon	I	II	III	IV	V
Experimental $T_{0.01}$, °K	356.68	341.51	370.96	341.10	367.64
Estimated T_c, °K	749.3	790.5	873.1	800.1	887.6
Estimated P_c, atm	11.03	15.00	11.32	17.56	22.01
F_A, F_N, F_B	0, 0, 0	$0, \frac{12}{19}, 0$	$0, 0, \frac{15}{28}$	$0, \frac{18}{18}, 0$	$\frac{14}{18}, 0, 0$
Percent error in pressure					
Method 1, at T_1	—	52.6	35.1	149.9	−24.5
at T_{10}	94.4	135.8	96.7	465.8	15.4
Method 2, at T_1	—	−4.6	−36.0	25.3	−27.3
at T_{10}	12.1	−2.2	−45.2	60.3	−6.7
Method 3, at T_1	—	9.6	−26.7	45.3	−15.0
at T_{10}	21.0	10.8	−37.6	80.8	8.0
Method 4, at T_1	—	−5.0	−15.2	10.9	−12.4
at T_{10}	13.1	−8.7	−22.9	26.3	13.0

necessary to estimate critical temperatures and critical pressures.

When interest is directed at petroleum fractions (or, similarly ill-defined, fossil-fuel cuts), it is not possible to specify detailed molecular structure or the number of carbon atoms per molecule. Therefore, the SWAP method, which does not require critical temperatures or critical pressures, is more easily applied to petroleum fractions. To illustrate, Table 2 presents results for the five hydrocarbons in Table 1 obtained after the molecular structure (including the carbon number) is deliberately changed. For example, for hydrocarbon I (eicosane) we assume that we do not know the molecular structure, and we make calculations using two erroneous structures: octadecane and 1-cyclohexyl tetradecane. In the first case we decrease the carbon number by two but retain the correct normal paraffin structure; in the second case we retain the correct carbon number but change the molecular structure, that is, the spatial arrangement of the carbon atoms.

The results shown in Table 2 indicate that serious errors may result when the method of Riedel or of Zia and Thodos is used to predict vapor pressures at T_1 and T_{10} using, as before, experimental values of $T_{0.01}$. The SWAP method is now more reliable because, unlike the others, it is not primarily sensitive to the carbon number or to details in molecular structure.

Finally, similar vapor-pressure calculations were made for all five hydrocarbons with a reversal in the direction of prediction. In these calculations the input data were, as before, the molecular structure (correct as in Table 1 or erroneous as in Table 2), but now, unlike before, the experimental value of T_{10} was given and the pressure at $T_{0.01}$ was calculated. The average errors were as follows: linear method 66.7%, method of Riedel 62.8%, method of Zia and Thodos 55.8%, SWAP method 29.4%. In the linear method several experimental data in the region of 10 torr were fit to a straight line, and this equation was then used to estimate $T_{0.01}$.

The results summarized here suggest, first, that the linear method is often poor for extrapolation of vapor pressure data for highboiling hydrocarbons; second, that the methods of Riedel and of Zia and Thodos and the SWAP method give fair results when the carbon number and molecular structure are known; and third, that the SWAP method is likely to be better than the others for petroleum fractions where carbon number and molecular structure are not well known.

TABLE 2. PERCENT ERRORS IN CALCULATED VAPOR PRESSURES USING ERRONEOUS MOLECULAR STRUCTURE

	Method					
	2		3		4	
Hydrocarbon	at T_1	at T_{10}	at T_1	at T_{10}	at T_1	at T_{10}
I						
Octadecane	—	41.4	—	50.5	—	13.1
1-Cyclohexyl-tetradecane	—	0.1	—	9.8	—	−10.8
II						
1,1-Dicyclohexyl-pentane	11.0	19.7	25.6	34.7	5.6	6.0
1,1-Diphenylheptane	−14.7	−16.1	−0.6	−3.0	7.3	8.2
III						
2,2,4,10,12,12-Hexamethyl-7(Hexyl)-6-Tridecene	−23.7	−29.6	−13.6	−21.2	−13.3	−20.5
Octacosane	−26.3	−33.6	−17.8	−27.0	11.0	11.3
IV						
Perhydrophenanthrene	87.1	183.8	112.2	211.7	12.6	26.3
Chrysene	−25.7	−22.9	−11.7	−8.2	30.2	57.3
V						
9-Ethylanthracene	−20.9	6.2	−7.2	23.8	−9.3	18.3
1,3-Di-*n*-butyl-naphthalene	−8.2	30.7	4.5	46.2	−7.8	21.1

ACKNOWLEDGMENT

The authors are grateful to the Fossil Energy Division, Department of Energy for financial support.

LITERATURE CITED

Reid, R. C., and T. K. Sherwood, *The Properties of Gases and Liquids*, 2 ed., McGraw-Hill, New York (1966).

Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3 ed., McGraw-Hill, New York (1977).

Research Project 42 of the American Petroleum Institute, "Properties of Hydrocarbons of High Molecular Weight," American Petroleum Institute, New York (1940-1966).

Riedel, L., "Eine Neue Universelle Dampfdruckformel," *Chem. Ing. Tech.*, **26**, 83 (1954).

Smith, G., Jack Winnick, D. S. Abrams, and J. M. Prausnitz, "Vapor Pressures of High-Boiling, Complex Hydrocarbons," *Can. J. Chem. Eng.*, **54**, 337 (1976).

Zia, T., and G. Thodos, "A Generalized Vapor Pressure Equation for Hydrocarbons," *ibid.*, **52**, 630 (1974).

Zwolinski, B. J., and R. C. Wilhoit, *Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds*, Thermodynamic Research Center and American Petroleum Institute Research Project 44, College Station, Tex. (1971).

Manuscript received August 11, 1977; revision received November 8, and accepted December 1, 1977.

Fully Developed Laminar Incompressible Flow in an Eccentric Annulus

J. TERRY WILSON

Department of Mathematics
San Jacinto College, Pasadena, Texas

Past investigators of laminar incompressible fluid flow in eccentric annular ducts have concentrated on the fully developed problem. Each investigation yielded a different expression for the fully developed velocity, which was then used to determine other information pertinent to fully developed flow. Snyder and Goldstein (1965), for example, used their expression to determine local wall shear stress and various friction factors. A summary of heat transfer and fluid flow research in eccentric annular and various other ducts has been compiled by Shah and London (1971). The purpose of this paper is to present a different representation of the fully developed velocity which proves quite useful in the analysis of the entrance region problem. A brief description of the general entrance region problem and an explanation of the role of our representation in solving this problem for an eccentric annular duct follow.

In 1964, Sparrow et al. proposed a linearized version of the entrance region problem for a straight duct with an arbitrary cross section. A method of solution, which represented the entrance region velocity as the sum of the fully developed velocity and a difference velocity, was also proposed and, in fact, applied to the parallel plate and circular tube problems. The application of their method to other geometries is warranted by the close agreement of their analytical results with experimental data.

The author has recently solved the equation which governs the difference velocity in an eccentric annular duct using the Galerkin method. The coordinate functions used to represent the difference velocity are used in this paper to represent the fully developed velocity. Thus, the entrance region velocity can be expressed in terms of a single set of coordinate functions. Furthermore, our representation allows for the calculation of all Galerkin inner products, difference velocity coefficients, and fully developed velocity coefficients in closed form.

ANALYSIS

The geometry under consideration is shown in Figure 1. The equation governing the flow is given by

$$\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}=\frac{1}{\mu}\frac{dp}{dz} \qquad (1)$$

where the pressure gradient dp/dz and the viscosity μ are constants. We impose the nonslip boundary condition $u = 0$ on C, the duct walls. Symmetry considerations allow us to solve Equation (1 only in, say, the lower half of the annulus. It also follows from symmetry that $\partial u/\partial y = 0$ on B, the plane of symmetry of the duct. If we define

$$c_1=\frac{r_2^2-r_1^2-e^2}{2e}$$

and

$$c_2=\frac{r_2^2-r_1^2+e^2}{2e}$$

then the bipolar transformation given by

$$\xi=\frac{1}{2}\ln\left[\frac{(x+h)^2+y^2}{(x-h)^2+y^2}\right]-k_2$$

$$\eta=\arctan\left[\frac{-2hy}{x^2+y^2-h^2}\right]$$

maps the lower half of the annulus onto the rectangle shown in Figure 2. In terms of the $\xi-\eta$ coordinates, Equation (1) is given by

$$\frac{\partial^2 v}{\partial \xi^2}+\frac{\partial^2 v}{\partial \eta^2}=\frac{-1}{[\cosh(\xi+k_2)-\cos\eta]^2} \qquad (2)$$

where

$$v=\frac{-u}{\dfrac{h^2}{\mu}\dfrac{dp}{dz}}$$

is the dimensionless velocity. The boundary conditions for

0001-1541-78-9995-0733-$00.75. © The American Institute of Chemical Engineers, 1978.