Prediction of Thermodynamic Properties of Dense Gas Mixtures Containing One or More of the Quantum Gases

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Effective critical constants for helium and normal hydrogen have been determined by fitting experimental volumetric data for these gases to the generalized tables of Pitzer. The effective critical temperature and pressure are found to depend on the temperature and on the molecular mass in a simple manner permitting good estimates to be made of effective critical constants for other quantum gases for which experimental data are scarce (neon, isotopes of helium and hydrogen). Pitzer's tables are used with pseudocritical mixing rules to predict thermodynamic properties of mixtures at high pressures and low temperatures. Calculated compressibility factors and enthalpies are in excellent agreement with experimental results for dense mixtures of hydrogen-methane, hydrogen-argon, and helium-nitrogen.

The volumetric properties of nonpolar or slightly polar fluids have been correlated by Pitzer et al. (*7, 19, 20*) using an extended form of the theorem of corresponding states. Pitzer's correlation excludes highly polar fluids and also those light (quantum) gases whose configurational properties must be described by quantum rather than classical statistical mechanics. In this work we describe a simple, semiempirical procedure which, in effect, extends Pitzer's correlation to the quantum gases. This extension may be useful for predicting volumetric and derived thermodynamic properties of neon and isotopes of helium and hydrogen for which experimental data are scarce. More important for technical applications, however, this extension provides a good method for predicting thermodynamic properties of dense gaseous mixtures which contain one or more of the quantum gases. Such mixtures are common in many technical operations in petroleum and related industries; since these mixtures are frequently at low temperatures and high pressures, deviations from ideal behavior are sometimes very large. The configurational property of most interest for rational design of cryogenic processes is the configurational enthalpy which, at high pressures and low temperatures, may make a significant contribution to the refrigeration load. Optimization of cryogenic separation processes requires accurate enthalpy information and, since experimental enthalpy data for dense mixtures are scarce, it is desirable to be able to predict such enthalpies with confidence.

EXTENSION OF PITZER'S CORRELATION TO QUANTUM GASES

Pitzer correlated the compressibility factors of pure gases in terms of two generalized functions, $z^{(o)}$ and $z^{(1)}$, such that

$$z = z^{(o)}\left(\frac{T}{T_c}, \frac{P}{P_c}\right) + \omega\, z^{(1)}\left(\frac{T}{T_c}, \frac{P}{P_c}\right) \qquad (1)$$

Equation (1) is a direct consequence of Pitzer's form of the theorem of corresponding states. The acentric factor, which is a constant for any given gas, is a measure of the importance of noncentral intermolecular forces and for small molecules (for example, nitrogen, methane, argon) it is very nearly zero. The functions $z^{(o)}$ and $z^{(1)}$ have been tabulated (*20*).

Pitzer's tables are not applicable to the quantum gases when the true critical constants and acentric factor are used in Equation (1), because these gases do not follow the same law of corresponding states as that followed by the classical gases (*3*). A corresponding states treatment of quantum gases must include the molecular mass in addition to the characteristic constants included in corresponding states treatments of classical gases.

A fundamental discussion of corresponding states theory for quantum gases is given by de Boer (*2* to *5*) and, more recently, Leland, Chappelear, and Leach (*12*) have considered techniques for incorporating the properties of quantum gases into correlations prepared for classical gases. As suggested thirty years ago by Newton (*17*), it appears possible to define effective critical constants for quantum gases which may be used to predict thermodynamic properties of such gases from standard correlations. In our attempt to fit the properties of normal hydrogen and normal helium to Pitzer's tables, we find that such effective critical constants depend not only on the molecular mass but also on the temperature, in agreement with theory (*12*). We find that the effective critical temperature and the effective critical pressure are given by

$$T_c = \frac{T_c^o}{1 + \dfrac{c_1}{mT}} \qquad (2)$$

$$P_c = \frac{P_c^o}{1 + \dfrac{c_2}{mT}} \qquad (3)$$

When the compressibility factors of normal hydrogen and normal helium are fitted to Equation (1) with $\omega = 0$, we find that the two constants c_1 and c_2 are the same for both gases. They are

$$c_1 = 21.8°\text{K.} \qquad (4)$$

$$c_2 = 44.2°\text{K.} \qquad (5)$$

TABLE 1. CLASSICAL CRITICAL CONSTANTS FOR QUANTUM GASES

	T_c^o, °K.	P_c^o, atm	V_c^o, cc./mole
Ne	45.5	26.9	40.3
He^4	10.47	6.67	37.5
He^3	10.55	5.93	42.6
H_2	43.6	20.2	51.5
HD	42.9	19.6	52.3
HT	42.3	19.1	52.9
D_2	43.6	20.1	51.8
DT	43.5	20.3	51.2
T_2	43.8	20.5	51.0

For a classical gas the corrections given by the denominators of Equations (2) and (3) are very small; for example, for argon they are 0.4 and 0.7%, respectively, at the (true) critical temperature.

Values of T_c^o and P_c^o for helium and hydrogen are shown in Table 1. Values are also given for deuterium, hydrogen deuteride, and other quantum gases for which volumetric data are scarce or nonexistent. Where volumetric data are not available, the values given in Table 1 were estimated from the experimental (true) critical constants. Because of the small molecular size of all quantum gases, we have set the effective acentric factor equal to zero; therefore, the effective critical compressibility factor for each quantum gas is 0.291, in the classical limit.

To determine the constants c_1 and c_2, experimental compressibility factors were taken from the work of Johnston and White (*9*) and Mann (*14*).

For hydrogen, one hundred eighty experimental values were used for ten isotherms ranging from 35° to 150°K. Pressures were as high as 150 atm., corresponding to a reduced pressure of 8.0 to 9.0. Average percent deviation between calculated and experimental results was 0.29%. A maximum error of 2.5% occurred at a temperature of 35°K. and 150 atm. Table 2 shows a comparison of calculated and experimental data for hydrogen for two isotherms, one at low temperature and one at high temperature.

For helium, nine different isotherms were used, ranging from 3° to 35°K. Pressures were as high as 45 atm. Two hundred and ten experimental compressibility factors were compared with calculated results with an average deviation of 0.85%. The maximum deviation occurred in the liquid region at 4°K. and two atmospheres; for this point the predicted and experimental compressibility factors of 0.187 and 0.182, respectively, correspond to a deviation of 3%.

TABLE 2. PREDICTED AND EXPERIMENTAL COMPRESSIBILITY FACTORS FOR HYDROGEN

Experimental data from reference *9*

	$T = 35.0$°K.		$T = 125.0$°K.	
P	z_{exp}	% deviation*	z_{exp}	% deviation*
15	0.4725	—0.13	1.0068	+0.16
25	0.3509	—0.15	1.0114	+0.09
35	0.4440	+0.19	1.0160	—0.07
45	0.5381	+0.18	1.0222	—0.32
60	0.6746	—0.27	1.0338	—0.44
80	0.8543	—0.93	1.0522	—0.28
100	1.0252	—1.09	1.0730	—0.33
150	1.4361	—2.50†	1.1357	—0.59
200	‡	‡	1.2094†	—0.08

* % deviation = $\frac{z_{exp} - z_{calc}}{z_{exp}} \times 100$.

† Extended compressibility tables given in reference *23* used for these points.

‡ No experimental data available.

DERIVED THERMODYNAMIC FUNCTIONS

Generalized tables have been given by Pitzer for three derived thermodynamic functions: fugacity coefficient, configurational enthalpy, and configurational entropy. With some modifications these tables are applicable to the quantum gases, provided the true critical constants are replaced by the effective constants of Equations (2) and (3). The fugacity coefficient is given by the well-known result

$$\ln \frac{f}{P} = \int_0^P \frac{z-1}{P} dP \tag{6}$$

where the integration is performed along an isotherm. Since Equation (6) does not depend on derivatives of the compressibility factor with respect to temperature, ln f/P for quantum gases can be determined directly from Pitzer's tables by using the same effective critical constants as those used with the generalized tables for the compressibility factor.

However, the effect of pressure on the enthalpy and entropy is determined by the temperature derivative of the compressibility factor and this depends upon the rate of change of the effective critical constants with respect to the temperature. Therefore, application of Pitzer's tables to calculate the configurational enthalpy and entropy of a quantum gas is somewhat more complicated than the corresponding calculation for a classical gas. The enthalpy function is

$$H^* - H = RT^2 \left(\frac{\partial \ln f/P}{\partial T} \right)_P \tag{7}$$

Equation (7) can be expressed as a function of the reduced pressure and temperature. The total derivative of ln f/P is

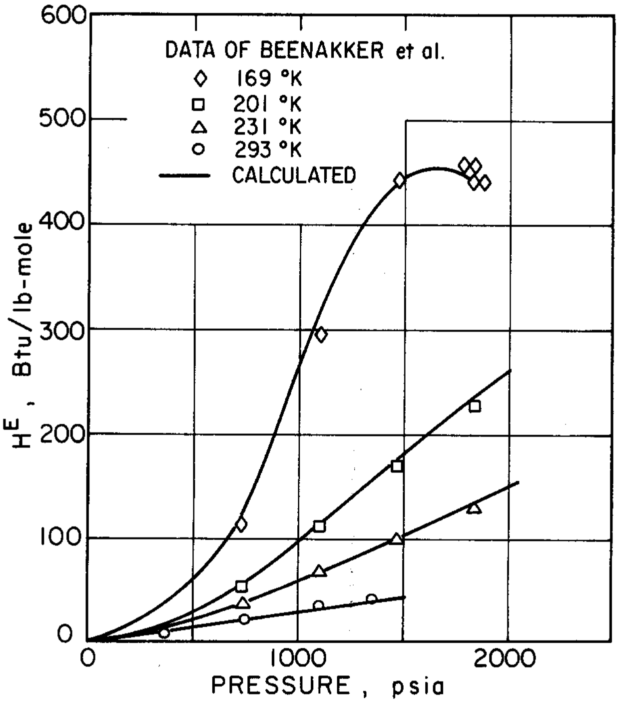

Fig. 1. Excess enthalpies for a mixture of argon and hydrogen containing 54 mole % argon.

$$d \ln f/P = \left(\frac{\partial \ln f/P}{\partial T_R}\right)_{P_R} dT_R + \left(\frac{\partial \ln f/P}{\partial P_R}\right)_{T_R} dP_R \qquad (8)$$

The partial derivative $\left(\frac{\partial \ln f/P}{\partial T}\right)_P$ as obtained from Equation (8) is

$$\left(\frac{\partial \ln f/P}{\partial T}\right)_P = \left(\frac{\partial \ln f/P}{\partial T_R}\right)_{P_R} \left(\frac{\partial T_R}{\partial T}\right)_P + \left(\frac{\partial \ln f/P}{\partial P_R}\right)_{T_R} \left(\frac{\partial P_R}{\partial T}\right)_P \qquad (9)$$

The quantities $(\partial T_R/\partial T)_P$ and $(\partial P_R/\partial T)_P$ are found from Equations (2) and (3). Using standard thermodynamic relations we obtain

$$T_R^2 \left(\frac{\partial \ln f/P}{\partial T_R}\right)_{P_R} = \left(\frac{H^* - H}{RT_c}\right)^o \qquad (10)$$

$$\left(\frac{\partial \ln f/P}{\partial P_R}\right)_{T_R} = \frac{z-1}{P_R} \qquad (11)$$

where $\left(\frac{H^* - H}{RT_c}\right)^o$ is the reduced enthalpy function for a classical gas. This quantity is found from Pitzer's enthalpy tables with the use of the effective critical temperature and pressure as given by Equations (2) and (3). The final expression for $H^* - H$ for a quantum gas is obtained by combining Equations (2), (3), (7), (9), (10), and (11):

$$\frac{H^* - H}{RT_c} = \left(\frac{H^* - H}{RT_c}\right)^o \frac{T_c}{T_c^o} + (1-z)\frac{P_c}{P_c^o}\frac{c_2}{mT_c} \qquad (12)$$

In a similar manner the effect of nonideality on entropy can be shown to be

$$\frac{S^* - S}{R} = \left(\frac{S^* - S}{R}\right)^o + \left(\frac{H^* - H}{RT_c}\right)^o \frac{T_c - T_c^o}{T_R T_c^o} + (1-z)\frac{P_c}{P_c^o}\frac{c_2}{mT_cT_R} \qquad (13)$$

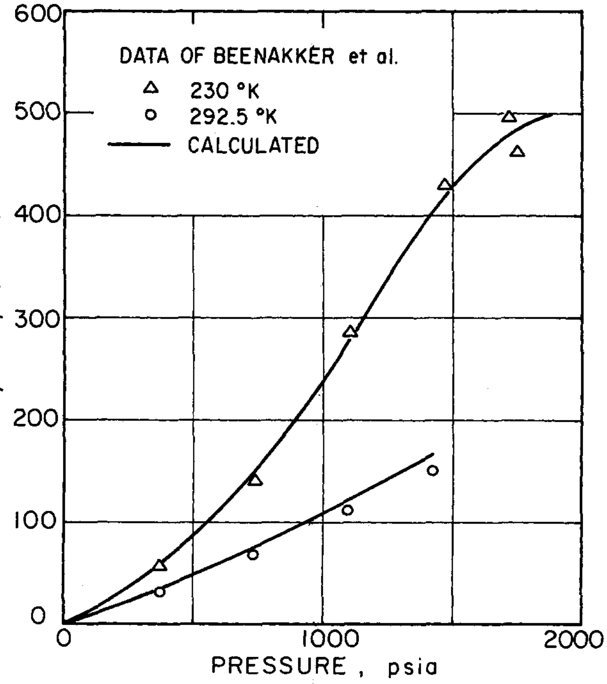

Fig. 2. Excess enthalpies for a mixture of methane and hydrogen containing 56 mole % methane.

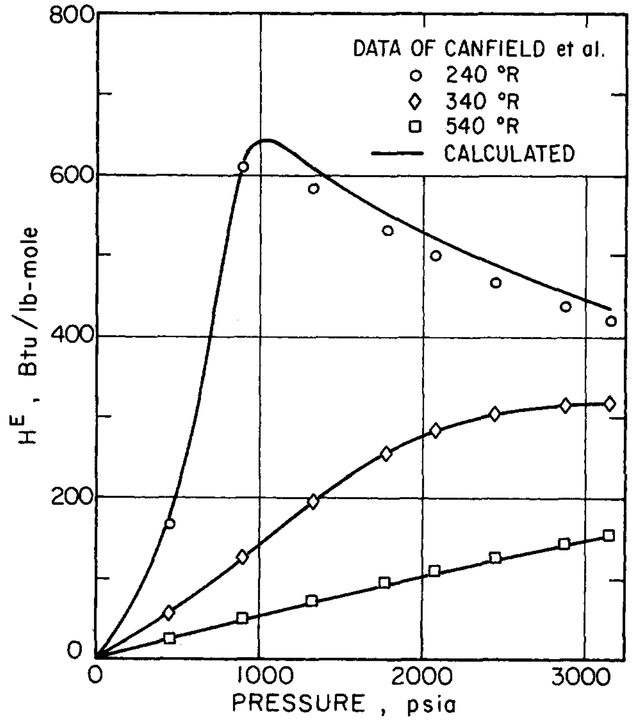

Fig. 3. Excess enthalpies for a mixture of nitrogen and helium containing 55.44 mole % nitrogen.

MIXTURES

The thermodynamic properties of normal hydrogen and helium have been determined over a wide range of pressure and temperature. However, the number of possible mixtures containing these gases is extremely large and therefore it is not likely that complete experimental data even for industrially important mixtures will be available in the near future. For this reason a real need exists for a method to predict accurately the thermodynamic properties of mixtures containing one or more of the quantum gases. Such a method is provided by the pseudocritical hypothesis, first proposed by Kay (*11*).

Although Kay's rule is the best known of the pseudocritical methods, more accurate and more complicated rules are available. A review of these has been given by Reid and Leland (*22*). The more complicated of these methods give excellent accuracy when used with characteristic binary interaction constants. In general, however, such constants are not known and without them the complicated rules are not reliable. A convenient method, proposed by Prausnitz and Gunn (*21*) retains most of the simplicity of Kay's rule but appears to be considerably more accurate. We propose here to use a straightforward extension of that rule. The pseudocritical temperature, pressure, and acentric factor are given by

$$T_{cM} = \frac{\sum_i y_i T_{ci}^o}{1 + \frac{c_1}{m_M T}} \qquad (14)$$

$$P_{cM} = \frac{R\left(\sum_i y_i z_{ci}^o\right)\left(\sum_i y_i T_{ci}^o\right)}{\left(\sum_i y_i V_{ci}^o\right)\left(1 + \frac{c_2}{m_M T}\right)} \qquad (15)$$

$$\omega_M = \sum_i y_i \omega_i \qquad (16)$$

$$\frac{1}{m_M} = \left[\sum_i \frac{y_i}{\sqrt{m_i}} \right]^2 \qquad (17)$$

For classical gases the true critical constants are used in Equations (14) and (15). For quantum gases the constants given in Table 1 must be used. By assumption, the effective acentric factor of all quantum gases is zero, and therefore the effective critical compressibility factor for all quantum gases in Equation (15) is 0.291, in the classical limit.

The pseudocritical method presented above has been tested with experimental data for three binary systems containing one of the quantum gases.

Extensive compressibility data for methane-hydrogen mixtures have been presented by Mueller, Leland, and Kobayashi (*16*). All of these experimental measurements have been compared with calculated results from Pitzer's tables for the temperature range 50° to −150°F. and up to a maximum reduced pressure of 9.0. Average and maximum deviations from 260 experimental compressibility factors is 0.88 and 2.3%, respectively. These small deviations compare favorably with an average deviation of 0.52% for predicted compressibility factors for pure methane in the same ranges of pressure and temperature as those of the mixtures.

Extensive data have also been published by Canfield, Leland, and Kobayashi (*6*) for the helium-nitrogen system. All compressibility measurements reported in that work have been tested with the proposed pseudocritical method except when the reduced temperature or reduced pressure fell beyond the range of the Pitzer compressibility tables. For 560 experimental points, average and maximum deviations were 0.25 and 2.2%, respectively.

Excess enthalpies have been calculated by means of Equation (12) for methane-hydrogen, argon-hydrogen, and nitrogen-helium mixtures. Figures 1, 2, 3, and 4 present our calculated results along with experimental data reported by Beenakker et al. (*1*) for the two hydrogen-containing systems and by Pfenning and Canfield (*18*) and Mage and Katz (*13*) for the system nitrogen-helium. Agreement is excellent for all three systems. The excess enthalpy (or heat of mixing) H^E is defined by

$$H^E = H_M - \sum_i y_i H_i \qquad (18)$$

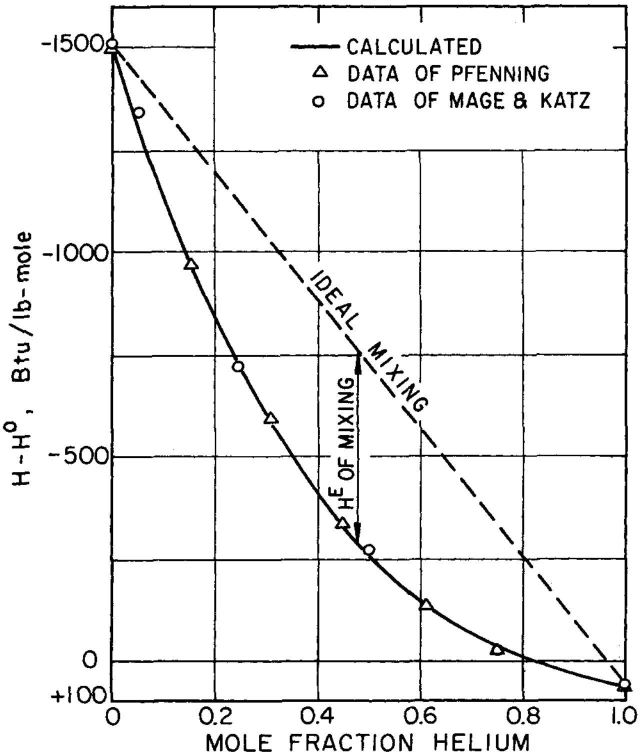

Fig. 4. Enthalpy of helium-nitrogen mixtures at 260°R. and 1,975 lb./sq.in.abs. relative to that of ideal gas at same temperature and composition.

Pure component enthalpies were taken from Jones et al. (*10*) for methane, from Dean (*8*) for hydrogen, from Michels (*15*) for argon, and from Pfenning and Canfield (*18*) for nitrogen and helium.

The favorable results shown in Figures 1 to 4 suggest that the proposed pseudocritical method can be used to predict thermodynamic properties of dense gas mixtures containing one or more of the quantum gases with sufficient accuracy for most industrial purposes.

ACKNOWLEDGMENT

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NOTATION

c_1, c_2 = constants given by Equations (4) and (5), respectively
f = fugacity
H = enthalpy of a real gas at some temperature and pressure
H^* = enthalpy of an ideal gas at the same temperature as that of the real gas
H_M = enthalpy of the mixture at some T and P
H_i = enthalpy of pure i at the same T and P as those of the mixture
H^E = excess enthalpy
$\left(\frac{H^* - H}{RT_c}\right)^o$ = reduced enthalpy function from Pitzer tables
m = molecular weight
P = pressure
P_c = critical pressure
P_{cM} = pseudocritical pressure of the mixture
P_c^o = classical critical pressure (high-temperature limit of P_c)
R = universal gas constant
S = entropy of a real gas at some T and P
S^* = entropy of an ideal gas at the same T and P as those of the real gas
$\left(\frac{S^* - S}{R}\right)^o$ = reduced entropy function from Pitzer tables
T = temperature
T_c = critical temperature
T_{cM} = pseudocritical temperature of the mixture
T_c^o = classical critical temperature (high-temperature limit of T_c)
V_c^o = classical critical volume ($V_c^o = 0.291\ RT_c^o/P_c^o$ for quantum gases)
y = mole fraction
z = compressibility factor
$z^{(o)}, z^{(1)}$ = tabulated generalized functions
z_c^o = critical compressibility factor in the classical limit
ω = acentric factor

Subscripts

c = critical
i = component i
M = mixture

LITERATURE CITED

1. Beenakker, J. J. M., B. van Eijnsbergen, M. Knoester, K. W. Taconis, and P. Zandbergen, "Advances in Thermophysical Properties at Extreme Temperature and Pressure," p. 114, Am. Soc. Mech. Engrs., New York (1965).
2. de Boer, J., and A. Michels, *Physica*, **5**, 945 (1938).
3. de Boer, J., *ibid.*, **14**, 139 (1948).
4. ———, and B. S. Blaisse, *ibid.*, **14**, 149 (1948).
5. de Boer, J., and R. J. Lunbeck, *ibid.*, **14**, 520 (1948).
6. Canfield, F. B., T. W. Leland, and Riki Kobayashi, *J. Chem. Eng. Data*, **10**, 92 (1965).
7. Curl, R. F., Jr., and K. S. Pitzer, *Ind. Eng. Chem.*, **50**, 265 (1958).
8. Dean, J. W., *Natl. Bureau Standards Tech. Note 120*, (Nov., 1961).
9. Johnston, H. L., and D. White, *Trans. Am. Soc. Mech. Engrs.*, **70**, 651 (1948).
10. Jones, M. L., Jr., D. T. Mage, R. C. Faulkner, Jr., and D. L. Katz, *Chem. Eng. Progr. Symposium Ser. No. 44*, **59**, 52 (1963).
11. Kay, W. B., *Ind. Eng. Chem.*, **28**, 1014 (1936).
12. Leland, T. W., Jr., Patsy S. Chappelear, and J. W. Leach, *U.S. Bureau Mines Rept.* (Apr., 1965).
13. Mage, D. T., and D. L. Katz, *A.I.Ch.E. J.*, **12**, 137 (1966).
14. Mann, D. B., *Natl. Bureau Standards Tech. Note 154A* (1962).
15. Michels, A., J. M. Levelt, and G. J. Wolkers, *Physica*, **25**, 1097 (1959).
16. Mueller, W. H., T. W. Leland, Jr., and Riki Kobayashi, *A.I.Ch.E. J.*, **7**, 267 (1961).
17. Newton, R. H., *Ind. Eng. Chem.*, **27**, 302 (1935).
18. Pfenning, D. B., and F. B. Canfield, *Document No. 7864*, Am. Documentation Inst., Lib. Congr., Washington, D. C.
19. Pitzer, K. S., *J. Am. Chem. Soc.*, **77**, 3427 (1955).
20. ———, D. Lippman, R. F. Curl, Jr., C. M. Huggins, and D. E. Petersen, *ibid.*, 3433 (1955).
21. Prausnitz, J. M., and R. D. Gunn, *A.I.Ch.E. J.*, **4**, 494 (1958).
22. Reid, R. C., and T. W. Leland, Jr., *ibid.*, **11**, 228 (1965).
23. Satter, A., and J. M. Campbell, *Soc. Petrol. Engrs. J.*, **3**, 333 (1963).

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Statistical Models for Surface Renewal in Heat and Mass Transfer: Part I. Dependence of Average Transport Coefficients on Age Distribution

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Average transport coefficients for different transport models are computed by using widely varying distributions of residence times of elements at the transporting surface. It is shown that for typical transport models, the shapes of the residence time and age distributions have an insignificant effect on the average transport coefficient. Operational techniques for calculating average coefficients and for constructing delayed versions of age distributions are presented.

DISCUSSION OF PREVIOUS WORK

The concept of surface renewal as a model for heat and mass transfer was first introduced by Higbie (3). In this early work, Higbie visualized heat transport as occurring by the arrival at the transport surface of fresh transporting elements from the bulk fluid, followed by unsteady state transport by conduction or diffusion during the residence of the fluid element at the surface, and eventual replacement of the stale element by a fresh fluid element. Higbie assumed that the fluid elements which arrived at the transporting surface had identical residence times. Danckwerts (2) later extended Higbie's work by assuming an age distribution of surface fluid elements with an exponential form. This is equivalent to the assumption that the probability of replacement of a surface fluid element is independent of its age. Zwieterling (8) derived a general relation between the age distribution of elements at the surface and the residence time distribution of elements which are about to enter the transporting surface. A constant total flow of elements to and from the surface was assumed in making this derivation. Perlmutter (5) investigated the effects of different age distributions upon the calculated average transport coefficients, and introduced the concept of a dead time effect resulting from stagnant pockets at the surface.

The present work consists of two parts: In Part I we review and systemize this earlier work, make appropriate modifications in the derivations to extend validity to transport in systems where a constant total flow cannot be assumed (such as in fluidized beds), point out some inconsistencies in interpretation of this previous work, justify the conclusion that for much of the work in transport phenomena only the average residence time (and not the shape of the residence time distribution) is needed for prediction of transport coefficients, and finally apply the results to an example situation which involves prediction of heat transfer coefficients at surfaces in a fluidized bed. In Part II, two simple but accurate statistical techniques are derived for computing the average residence time from information *only* on the *total number* of tagged elements present at the transporting surface as a function of time. (Interest in the average residence time only is justified by Part I.) The method is applied both to computer-simulated residence time distributions and to experimental data generated by a system of black and white fluidized particles. For exceptional cases wherein knowledge of only the average residence time is insufficient, a more

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