Theorem of Corresponding States Applied to Saturated Liquids and Vapors

MERK HOBSON and JAMES H. WEBER

University of Nebraska, Lincoln, Nebraska

The existence of a single generalized compressibility-factor relationship for univariant systems has long been denied because reduced variables do not provide a generalized vapor-pressure relationship. The present study demonstrates that a saturation curve depends on the ability of the theorem of corresponding states to correlate the reduced temperature as a function of reduced pressure and the critical compressibility factor. Saturation curves for both the liquid and the vapor phases are established from compressibility data on a variety of systems, substantiating this conclusion.

The compressibility factors of saturated mixtures are correlated with pseudoreduced properties based upon Kay's pseudocritical concept. The results indicate that the compressibility factors of saturated liquid mixtures can be predicted with reasonable precision over the entire two-phase region. For pseudoreduced isotherms of unity and above, the same isotherms apply to both phases and are approximately consistent with published compressibility charts for pure gases.

The theorem of corresponding states has been discussed many times in connection with the generalized correlation of *PVT* data for gases (*6*, *7*, *22*, for example). The correlation of compressibility-factor data for the univariant states along the vapor-liquid phase boundary for pure substances has, however, received a relatively small amount of emphasis.

Cope, Lewis, and Weber (*6*) denied the existence of a simple general reduced equation of state along the saturation curve despite the fact that a single independent variable is sufficient to define the state of a pure substance under these conditions. This argument was based upon conclusive experimental evidence indicating that reduced vapor pressures are not a unique generalized function of reduced temperature. As a result, two reduced-state variables have been used to define the univariant state (*8*, *20*).

The present work studies the significance of the critical compressibility factor as a correlating parameter for the two-phase boundary. The problem of predicting compressibility factors for the saturated vapor and liquid phases is considered for both pure compounds and mixtures.

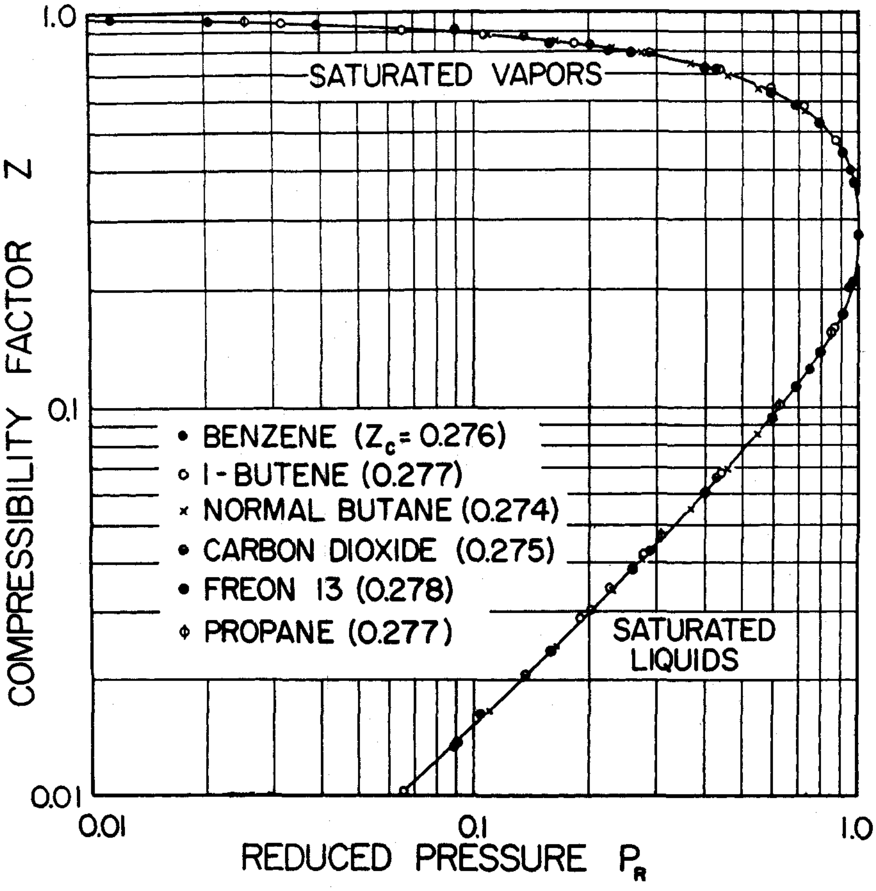

Fig. 1. Compressibility factors vs. reduced pressure for saturated pure compounds with Z_c values of approximately 0.275.

COMPRESSIBILITY FACTORS UNDER SATURATED CONDITIONS

Pure Compounds

The compressibility factor, defined by the equation

$$Z = \frac{PV}{RT} \tag{1}$$

is a state property of the system. Equation (1) may also be expressed in reduced form,

$$Z = \frac{P_r V_r Z_c}{T_r} \tag{2}$$

without affecting the exactness of the functional relationship between *Z* and the independent variables.

With discussion limited to the boundary of a two-phase region, specification of any one of the state variables is sufficient to define the state of the system. If P_r is arbitrarily selected as the independent variable, it follows from the principles of phase behavior that

$$V_r = f_1(P_r) \tag{3}$$

$$T_r = f_2(P_r) \tag{4}$$

Combining these relationships with Equation (2) gives

$$Z = f_3(P_r)Z_c \tag{5}$$

Equation (5) is of interest because it demonstrates the restriction imposed upon the theorem of corresponding states for successful correlation of the compressibility factor under saturated conditions, namely, that the same function of reduced pressure can apply only to those substances which have the same critical compressibility factor. Although Equation (5) applies specifically to univariant states, an analogous expression exists regardless of the number of independent variables required to define the state. This fact has long been recognized and several methods have been suggested for improving the generalized correlation for gases by compensating for the variations in Z_c. Su (*37*), following the principle of Onnes (*24*), has combined Z_c and V_r.

Meissner and Seferian (*21*) use Z_c as an additional variable to establish correction factors for the generalized chart based upon an average value of Z_c. Nelson and Obert (*22*), however, contend that differences in molecular structure may impair the correlation for substances with identical critical compressibility factors, and they suggest a molecular theorem of corresponding states as the more fundamental approach.

Cope, Lewis, and Weber (*6*) emphasized that f_2 is not a generalized function applicable to all compounds. In view of the restriction imposed by Equation (5), it is reasonable to assume that a similar restriction applies to the other state properties and that Equation (4) should be expressed in the form

$$T_r = f_2(P_r)_{\text{constant } Z_c} \tag{6}$$

or, more generally,

$$T_r = f_4(P_r, Z_c) \tag{7}$$

The general expression for the compressibility factor under saturated conditions would then include Z_c as an independent variable.

$$Z = f_5(P_r, Z_c) \tag{8}$$

Equation (8) is fundamentally equivalent to Meissner and Seferian's procedure in establishing correction factors for the generalized chart for gases. In the current study, however, Z_c is considered as a unique property of the system which will justify the use of a single reduced-state variable to define the vapor-liquid equilibrium state for all substances with the same critical behavior.

Equation (7) is consistent with the work of Riedel (*29*), which presents a generalized reduced vapor-pressure equation in terms of an additional variable, α_c, defined as the slope of the logarithmic vapor-pressure curve at the critical point. In the present work the critical compressibility factor, Z_c, is considered analogous to Riedel's variable, α_c. Hougen and coworkers (*12*) have shown that the constant, A, in the reduced form of the Gamson and Watson (*9*) vapor-pressure relationship can be expressed as a unique function of the critical compressibility factor, lending additional support for the validity of Equations (7) and (8).

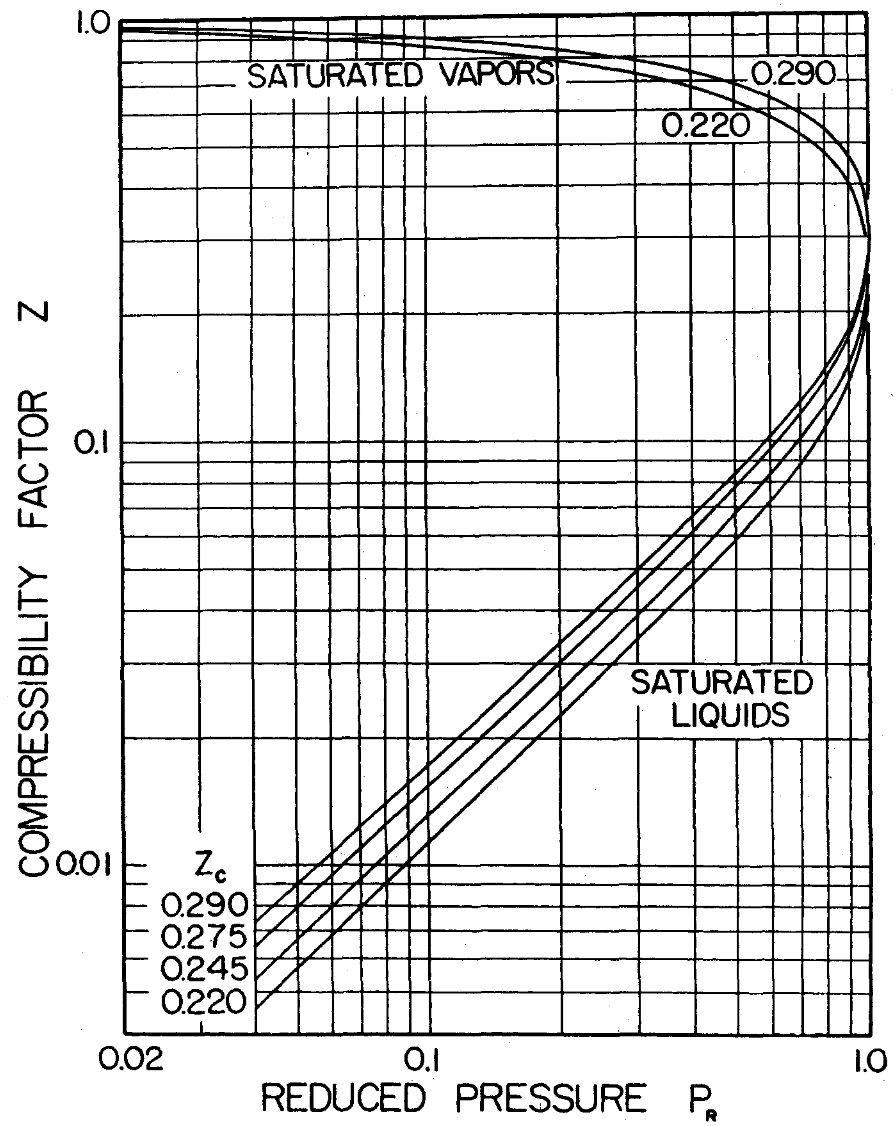

Fig. 2. Effect of Z_c on the compressibility factors for saturated pure compounds.

Correlation of Compressibility—Factor Data for Saturated Pure Compounds. The critical compressibility factors for most substances fall within the range of approximately 0.2 to 0.33. A large number of these show near constancy in their behavior at the critical point with a Z_c value of about 0.270. The various light-hydrocarbon series exhibit this property. While emphasizing the lack of any theoretical justification for a general reduced equation of state along the saturation curve, Cope, Lewis, and Weber (*6*) noted the excellent correlation between the compressibility factors for a number of saturated hydrocarbon vapors and the ratio P_r/T_r. Since the majority of these compounds have similar critical compressibility factors, and the use of P_r/T_r is equivalent to a single independent variable, $1/V_r$, their correlation is consistent with Equation (8). Equation (8), however, represents a more practical form for the graphical presentation of the same data.

The experimental volumetric data for the substances listed in Table 1 were considered in both the saturated vapor and liquid phases. The compressibility factors for six compounds having essentially similar values of Z_c are presented in Figure 1 to demonstrate the consistency of the data. The result is a single saturation curve expressed as a function of reduced pressure. The average absolute deviation is probably about 1% and the maximum deviation approximately 2%. The compressibility factors for the balance of the substances listed in Table 1 were found to deviate in a regular manner from the curve in Figure 1 in accordance

TABLE 1. SUMMARY OF VOLUMETRIC DATA FOR SATURATED PURE COMPOUNDS

Compound	Z_c	Literature reference
1-Butene	0.277	*24a*
Benzene	0.276	*25a*
Normal butane	0.274	*26*
Carbon dioxide	0.275	*30*
Ethane	0.285	*3*
Ethanol	0.248	*30a*
Ethylene	0.27	*42*
Freon 13	0.278	*1*
Normal heptane	0.260	*37*
Hydrogen sulfide	0.283	*27*
Methane	0.290	*19*
Methanol	0.220	*35a*
Nitrogen	0.291	*3a*
Normal pentane	0.269	*4*
Propane	0.277	*36*
Propylene	0.274	*5*
Sulfur dioxide	0.269	*31*
Water	0.230	*17a*

with the value of Z_c. Compounds with values of Z_c above 0.275 showed progressively higher compressibility factors over the entire range of reduced pressures consistent with the increased values of Z_c. A similar trend was noted below the curve.

The variation of the compressibility factors with Z_c is shown in Figure 2. Unique saturation curves are established for various values of the critical compressibility factor. The consistency between data for compounds having essentially the same value of Z_c was excellent over the entire range. Some inconsistencies were noted for water vapor, however, which would tend to substantiate Nelson and Obert's suggestion that differences in molecular structure may impair the correlation. The agreement in the liquid phase was found to be even better than in the vapor phase. This is of particular interest since the theorem has not been successfully applied to the correlation of liquid compressibility factors up to the present time. Watson (*40*) pointed out that deviations in the compressibility factors of liquids may vary as much as 20% at the same reduced conditions. The differences in critical compressibility factor may well account for these variations. It may be concluded from Figures 1 and 2 that a simple reduced equation of state for the vapor-liquid phase boundary is supported by the experimental volumetric data for any specific value of the critical compressibility factor. Theoretically, there would seem to be as much justification for a saturation curve based upon an average value of Z_c as there is for a generalized-compressibility-factor chart for the gas phase based upon an average value of Z_c. There is little question but that the accuracy of the compressibility-factor correlation under all conditions can be greatly improved by consideration of various values of Z_c. Under these conditions a unique saturation curve may be included.

Mixtures

Kay's empirical pseudocritical concept (*14*) has been widely used as a means of estimating the volumetric behavior of mixtures from the compressibility factors of the pure components. The method is based upon the concept of a hypothetical pure material the critical properties of which are so defined as to produce isometrics which coincide with those for the mixture. The critical constants of the hypothetical substance have been termed the *pseudocritical* properties of the mixture. In the following discussion reduced conditions for mixtures have been evaluated by use of pseudocritical properties rather than the actual critical properties of the mixture. This procedure permits direct comparison of the compressibility factors for mixtures with those of pure substances under the same reduced conditions.

Kay found that a simple summation of the products of the mole fractions and critical properties of the pure components provided a reasonable estimate of the pseudocritical constants. These summations may be expressed in the form of equations:

$$T_{pc} = \sum X_i T_{ci} \qquad (9)$$

$$P_{pc} = \sum X_i P_{ci} \qquad (10)$$

Kay's method is analogous to combining the equation-of-state constants for pure materials to obtain constants for the mixture.

Several other procedures, such as the one proposed by Joffe (*13*), have been suggested for estimating the pseudocritical properties of mixtures with a greater degree of precision. These relationships are much more complex than the simple linear molal average suggested by Kay, and since the latter method produces results close to the correct average, its use has continued.

The importance of the critical compressibility factor in correlating the volumetric behavior of saturated pure compounds suggests the need for an average value of Z_c for the mixture. Since most of the experimental volumetric data available for mixtures are for binary hydrocarbon systems, however, the present study was restricted to the use of Kay's method for predicting the volumetric behavior of saturated mixtures with an average critical compressibility factor of approximately 0.270.

Saturated Vapor Mixtures. The volumetric data for various mixtures of the ten systems listed in Table 2 were considered over a range of vapor pressures from approximately 1 atm. up to the actual critical point of the mixture. Cross plotting the experimental data for the saturated vapors of each mixture established eight reduced isotherms between 0.85 and 1.2. Each reduced isotherm was then plotted and compared with the compressibility factors published by Watson and Smith (*41* and *11*). Two typical isotherms have been illustrated in Figure 3. The saturation curve for pure compounds which was developed in the previous section is also included in Figure 3 for comparison.

A number of general conclusions may be reached on the basis of these comparisons. The data for reduced isotherms between 0.85 and 1.00, inclusive, show rather poor consistency. Deviations of more than 20% from the Watson and Smith curves were not uncommon and the errors in estimating the compressibility factors for saturated vapors are much larger than those normally encountered with the use of Kay's method in the superheated region. It was concluded, however, that the Watson and Smith relationships represent the data about as well as they can be represented at reduced pressures above 0.3 and reduced temperatures up to and including 1.0. Below

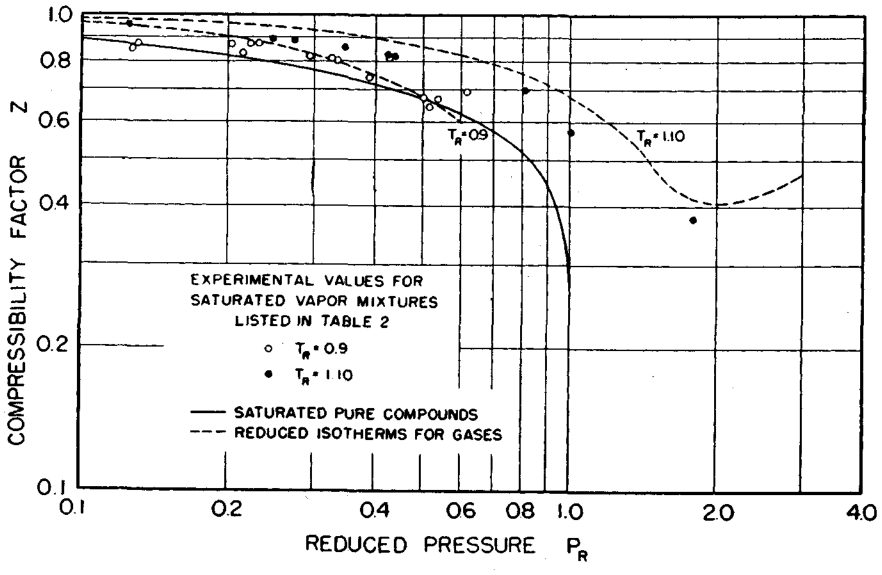

Fig. 3. Comparison of compressibility data for saturated vapor mixtures correlated by Kay's method (*14*) with reduced isotherms for pure gases (*41*).

TABLE 2. SUMMARY OF VOLUMETRIC DATA FOR SATURATED MIXTURES

Components	Number of compositions used	Literature reference
Methane—normal butane	3	*34*
Methane—normal pentane	4	*35*
Methane—decane	3	*33*
Methane—carbon dioxide	4	*24*
Methane—hydrogen sulfide	3	*27*
Ethylene—normal heptane	3	*17*
Ethane—normal butane	5	*16*
Ethane—normal heptane	5	*15*
Propane—normal butane	4	*23*
Propane—normal pentane	5	*32*
Propane—benzene	3	*10*

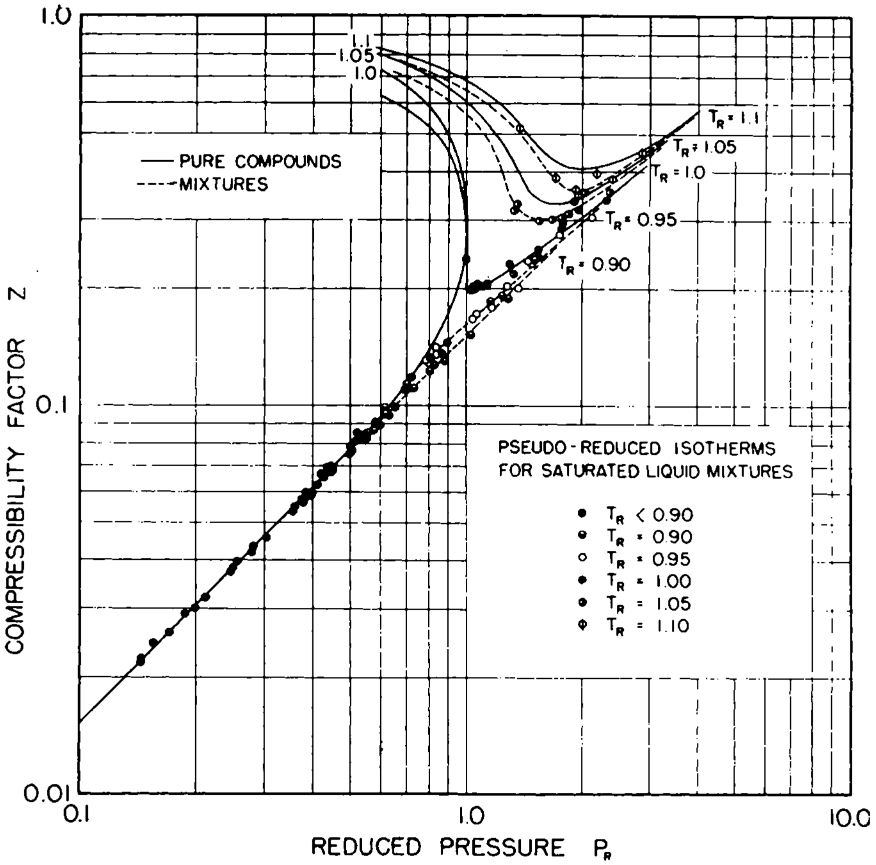

Fig. 4. Comparison of compressibility data for saturated liquid mixtures correlated by Kay's method (*14*) with the compressibility factors of pure compounds

0.3 P_r the experimental compressibility factors are consistently lower than those which would be predicted by the curves.

Above 1.0 T_r the experimental compressibility factors show excellent internal consistency, as indicated by the data in Figure 3 for 1.1 T_r. The experimental data, however, fall below the Watson and Smith curves. This was generally true for all the reduced isotherms greater than unity. The difference is probably due to the approximate nature of Kay's method for estimating the pseudocritical properties of mixtures. The experimental data show much the same configuration as the existing gas-phase parameters, and it is reasonable to assume that a more accurate estimate of the pseudocritical point might bring the curves together. In this connection it would be interesting to study the effectiveness of Joffe's relationships; however this was not attempted in the present study.

Saturated Liquid Mixtures. The experimental data for saturated liquid mixtures were analyzed by the methods reported in the previous section. The binary systems indicated in Table 2 were also used as sources for liquid compressibility factors.

The results of the study are presented in Figure 4. Below a reduced temperature of 0.9 the compressibility factors for saturated liquid mixtures appear to be directly proportional to the reduced pressure and are independent of reduced temperature. This corresponds to the behavior of an incompressible fluid, and so the conclusion is undoubtedly an approximation. Over a wide range of reduced pressures, however, the compressibility factors for saturated liquid mixtures may be estimated by the relationship

$$Z = (0.153)P_r \qquad (11)$$

with reasonable accuracy. At lower reduced pressures the data for mixtures are superimposed on the relationship established for pure saturated liquids with a critical compressibility factor of 0.27. It will be noted that for mixtures the direct proportionality extends above a pseudoreduced pressure of 1.0. The effect of pseudoreduced temperature becomes significant above 0.9 T_r.

To illustrate the high degree of reproducibility of the data the experimental compressibility factors have been plotted for pseudoreduced isotherms of 0.9, 0.95, 1.0, 1.05, and 1.1. The pseudoreduced isotherms for saturated liquid mixtures show the same general configuration as the curves given by Watson and Smith for pure gases. The 1.0 T_r curve from their generalized chart is a satisfactory representation of the liquid data along the same reduced isotherm. Above 1.0 T_r the same displacement of the reduced isotherms that was noted for saturated vapors is also apparent in the liquid phase. The data for saturated vapors overlapped the liquid compressibility factors, and the curves representing the liquid data are extensions of those previously established for the vapor phase. The compressibility factors show their greatest sensitivity in this range and a relatively small error in estimating the pseudocritical properties of the mixture might well account for the differences between the curves for pure gases and the data for mixtures.

Figure 4 demonstrates that it is possible to estimate the compressibility factors for saturated liquid mixtures from a generalized correlation extending over the entire two-phase region. The precision of the correlation for the liquid phase appears to be as good as if not better than that for the vapor phase.

SUMMARY AND CONCLUSIONS

A study of the compressibility factors for pure substances under saturated conditions indicated that a unique saturation curve can be expressed as a function of reduced pressure for compounds with the same critical compressibility factor. Saturation curves for various values of Z_c are presented in Figure 2.

TABLE 3. EFFECT OF Z_c ON THE COMPRESSIBILITY FACTORS OF PURE SATURATED VAPORS AND LIQUIDS

	Vapor phase			Liquid phase			
Z_c	0.290	0.275	0.220	0.290	0.275	0.245	0.220
	Z, Compressibility factor						
P_R							
0.02	—	—	—	0.00374	0.00329	0.00270	0.00223
0.04	0.947	0.940	0.922	0.00725	0.00636	0.00534	0.00451
0.07	0.920	0.915	0.886	0.0123	0.0109	0.00920	0.00793
0.10	0.898	0.892	0.856	0.0173	0.0152	0.0131	0.0113
0.20	0.838	0.830	0.785	0.0332	0.0299	0.0256	0.0226
0.30	0.786	0.780	0.734	0.0492	0.0450	0.0388	0.0341
0.40	0.746	0.730	0.683	0.0660	0.0613	0.0527	0.0459
0.50	0.688	0.680	0.633	0.0835	0.0780	0.0677	0.0585
0.70	0.591	0.582	0.529	0.118	0.116	0.102	0.0883
0.80	0.536	0.526	0.478	0.148	0.140	0.123	0.109
0.90	0.469	0.453	0.406	0.182	0.175	0.149	0.138
0.95	0.416	0.405	0.344	0.216	0.202	0.176	0.163
1.00	0.290	0.275	0.220	0.290	0.275	0.245	0.220

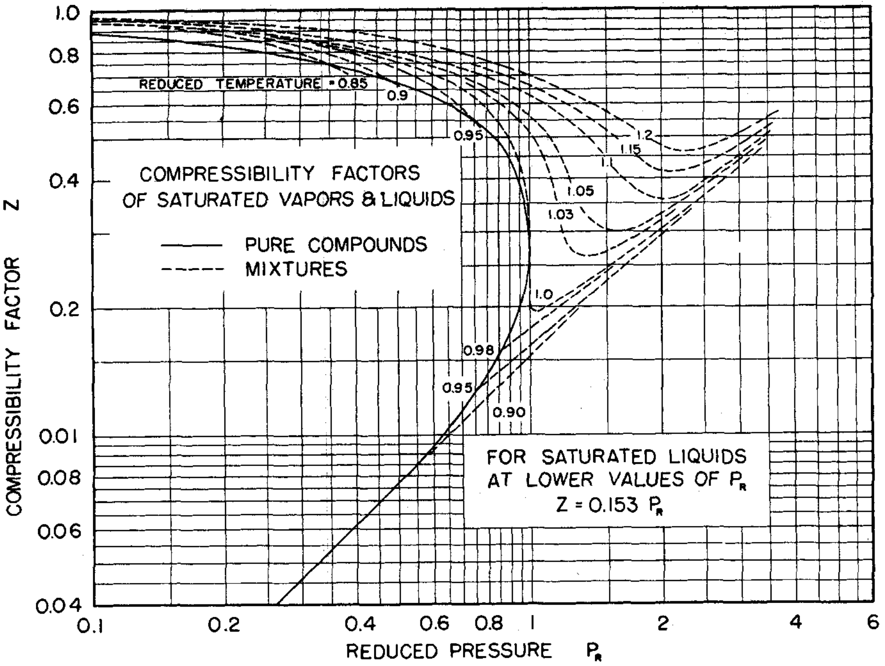

Fig. 5. Compressibility factors for saturated liquids and vapors of pure compounds and of mixtures based upon pseudoreduced properties estimated by Kay's method (*14*).

Compressibility factors for saturated mixtures in both the vapor and liquid phases were correlated over the entire two-phase region by means of pseudoreduced variables based upon Kay's pseudocritical concept (*14*). These data were then compared with Watson and Smith's (*41*) average-compressibility-factor chart for pure gases and with a saturation curve applicable to pure substances with a critical compressibility factor of 0.27. The comparisons are presented in Figures 3 and 4. The pseudoreduced isotherms for mixtures provide excellent correlation above 1.0 T_r, but fall below the corresponding isotherms for pure gases. The agreement between the vapor and liquid compressibility factors along a given pseudoreduced isotherm is also excellent.

Figure 5 summarizes the results of the study on mixtures and provides a graphical presentation of the pseudoreduced equations of state for both saturated vapors and liquids. Figure 5 applies specifically to Kay's method for estimating the pseudocritical properties of the mixture and differs from the average-generalized-compressibility-factor chart for pure gases. It is reasonable to assume that a more accurate method of determining the pseudocritical properties might produce better agreement. In view of the simplicity of Kay's method, however, the new relationships presented in Figure 5 would seem to be justified. Although this procedure may not be the most satisfactory one from the technical standpoint, it offers a practical method for estimating the compressibility factors of multicomponent hydrocarbon systems with a reasonable degree of precision. The absolute errors resulting from the use of Figure 5 are reported in Table 4 for a number of systems.

TABLE 4. REPRESENTATIVE ERRORS RESULTING FROM THE USE OF FIGURE 5 FOR ESTIMATING COMPRESSIBILITY FACTORS OF SATURATED MIXTURES

System	Range of compositions, mole %	Number of mixtures	Number of datum points	Average absolute error, %	Maximum error, %
		Saturated liquids			
Methane—normal butane	20.0 -60.0 methane	3	14	3.4	6.7
Ethane—normal butane	17.49-94.72 ethane	5	39	2.2	5.9
Ethane—normal heptane	26.54-96.85 ethane	4	41	2.7	10.0
Carbon dioxide—methane	33.3 -82.7 methane	4	12	15.0	27.0
Methane—normal pentane	10.0 -60.0 methane	3	12	3.7	14.9
Hydrogen sulfide—methane	10.0 -40.0 methane	3	8	10.7	21.8
Propane—benzene	12.1 -81.0 propane	4	20	2.4	10.9
		Saturated vapors			
Methane—normal butane	17.49-82.18 methane	2	9	4.0	8.2
Ethane—normal heptane	58.7 -88.71 ethane	2	14	6.3	10.6
Ethylene—normal heptane	28.57-89.31 ethane	3	12	2.6	6.8
Methane—normal pentane	20.0 -90.0 methane	6	20	4.3	9.8
Propane—normal pentane	14.68-85.50 *n*-pentane	5	24	2.7	4.3

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Presented at A.I.Ch.E. Detroit meeting

Turbulent Exchange of Mass and Momentum with a Boundary

THOMAS J. HANRATTY

University of Illinois, Urbana, Illinois

Visual observations by Fage and Townend of the behavior of a turbulent-flow stream near a boundary and experimental data by Lin, Moulton, and Putnam of concentration profiles near a boundary contradict the commonly held concept of the "laminar sublayer." A model developed by Higbie and Danckwerts which is consistent with the visual observations of Fage and Townend is used to describe the exchange of mass and heat between a turbulent fluid and a solid surface. It is postulated that masses of fluid are continuously moving to and from the wall. The exchange process then depends on the average contact time of these fluid masses with the wall.

The agreement of the concentration profile predicted on the basis of the proposed model with experimental mass transfer data where the exchange process is rate controlling lends support to the usefulness of the model. No equivalent data are available for velocity profiles. Velocity data represent a condition where the transport process within the fluid is playing an important role; however, in the immediate vicinity of the wall the proposed model might serve as a rough approximation of the profile. Such an approximation is made in this paper, and the agreement obtained is much better than should be expected.

That rates of momentum, heat, and mass transfer in a turbulent field are very much smaller in the vicinity of a surface than in the main body of a fluid has been recognized for a long time. In order to explain this phenomenon it has been postulated that there exists a thin nonturbulent layer of fluid adjacent to the wall. In this "laminar sublayer" momentum, heat, and mass are transported by random motion of the molecules rather than motion of macroscopic masses. As would be predicted by such a model, velocity-profile data extrapolate to a linear relationship between the velocity and distance in the vicinity of the wall. If, as is commonly assumed, the edge of the laminar sublayer is at the point where the velocity data deviate from linearity, its thickness may be calculated from the following empirical equation:

$$\frac{\delta_b}{d} = \frac{5}{Re}\sqrt{\frac{8}{f}} \qquad (1)$$

Fage and Townend (*1*) studied the behavior of fluid in the immediate vicinity of the wall by examining under the ultramicroscope the motion of dust particles in turbulently flowing water. The conditions of their experiments were such that the laminar-sublayer thickness as calculated by Equation (1) was about 0.03 in. Their experiments gave no evidence of the existence of a region possessing rectilinear motion. The following is a description of the flow very near the boundary given by Fage and Townend:

> With this magnification particles with a distance of 0.001 inch (0.0023s) from the surface were in focus. The view obtained showed a large number of particles moving in sinuous paths, and a few very slow particles which in the absence of a hairline in the eyepiece appeared to be moving in rectilinear paths.... The slowest particles seen were therefore moving with a mean velocity of about 0.006 feet per second, and since the gradient $\partial(V/V_0)/\partial(n/s)$ at the surface was roughly 14, the distance of these particles from the surface was of the order of 1/40,000 inch. Attention could therefore be confined to the motion of particles at this distance from the boundary.
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> It was first thought that these particles were moving in rectilinear paths, but it was noticed that their axial motions were frequently jerky (u, comparable with V, see later), and that sometimes they almost came to rest. A hairline was then inserted in the eyepiece of the microscope, and it subsequently appeared that all such particles moving near the hairline usually crossed and recrossed it several times. A considerable time was spent in observing these particles and the impression formed was that no particle was ever seen about which it could be said with conviction that its motion was rectilinear. In addition to these very slowly moving particles other faster particles could be observed at the same time on account of the finite thickness of fluid (0.001 inch) within the focus of the microscope. It occasionally happened that a group of