(larger $\alpha = 2.5$), the comparison is still good, but for high reaction rates ($\alpha = 25$), large deviations begin to occur. These results are more or less as expected from the discussion above, but now give more quantitative criteria. It is seen that over a rather wide practical range of the parameters, the axial dispersion model provides a good approximation to the more exact, but more complicated, three-dimensional equations. Since laminar flow is an extreme example of sharp velocity profile, the use of the axial dispersion model for other cases, such as turbulent flow with a more flat velocity profile, should be satisfactory.

TABLE 1.

$\alpha = 0.25$

$z_L{}^+$	$\overline{C_L{}^+}$	C_L'	N_{Pe}	R_1
0.2	0.906	0.907	4.8	0.1
0.4	0.821	0.822	9.6	0.2
0.6	0.744	0.745	14.4	0.3
0.8	0.675	0.676	19.2	0.4
1.0	0.612	0.612	24.0	0.5
$\alpha = 2.5$				
0.2	0.405	0.417	4.8	1.0
0.6	0.073	0.076	14.4	3.0
1.0	0.0135	0.0140	24.0	5.0
$\alpha = 25$				
0.02	0.421	0.455	0.48	1.0
0.05	0.144	0.218	1.2	2.5
0.10	0.028	0.064	2.4	5.0

Recently, Horn and Parish (*15*) have presented a theoretical justification of the use of the axial dispersion model similar to the analysis of Taylor and Aris, but actual numerical criteria were not given.

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NOTATION

a = parameter = $\sqrt{1 + 4R_1/Bo} = \sqrt{1 + \alpha/3}$
A_n = constant in eigenvalue expansion, Equation (8)
C = concentration
C_o = feed concentration
C^+ = dimensionless concentration = C/C_o
$\overline{C_L{}^+}$ = cross section flow mean concentration at reactor exit, defined by Equation (3)
C' = dimensionless mean concentration found from axial dispersion model
$\mathcal{D}$ = molecular diffusivity
D_L = axial dispersion coefficient
k = reaction rate coefficient
N_n = constant in mean concentration expansion, Equation (8)
N_{Pe} = dimensionless Peclet number = vz_L/D_L
r = radial coordinate
r^+ = dimensionless radial coordinate = r/R
R = tube radius
R_1 = rate group = kz_L/v
v = mean velocity
z = axial coordinate
z_L = reactor length
$z_L{}^+$ = dimensionless reactor length = $2\mathcal{D}z_L/vR^2 = N_{Pe}/24$
α = parameter = $kR^2/4\mathcal{D}$
ω_n = eigenvalue

Superscripts

$+$ = dimensionless variable
= refers to axial dispersion model concentration

Subscript

L = refers to value at end of reactor

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Methods of Predicting the Occurrence and Type of Fluid-Fluid Equilibria in Binary Systems

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In a recent paper (*1*) I presented a semiempirical method (the D^2 method) by which gas-gas equilibrium (limited mutual solubility of gases at temperatures above the critical temperature of the least volatile component) could be predicted for binary systems on the basis of critical data and experimental gas-gas equilibria results on systems not necessarily containing either of the components of the system whose behavior is in question.

The types of gas-gas equilibrium are designated as type I or II, depending on whether the $p(T)$ critical curve, starting from the critical point of the least volatile component, has a positive or negative slope. Figure 1 shows the difference between these two types and usual critical curve behavior. The one shortcoming of the D^2 method is that it does not predict what type of gas-gas equilibrium will occur. Another simple method that is in good agreement

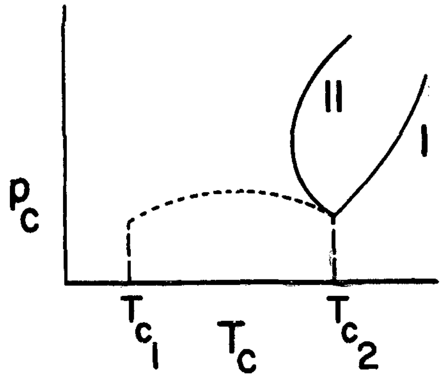

Fig. 1. $p(T)$ critical curves in binary systems. *I* signifies type *I* gas-gas equilibrium; *II* signifies type *II* gas-gas equilibrium; and the dashed curve signifies usual critical behavior.

with the available data eliminates this restriction.

Before presenting this method I will clarify one point relating to my original paper (*1*) and show how successfully my method has predicted systems tested since it was devised, as well as how it relates to Schneider's (*2* to *5*) theoretical consideration of the phenomenon.

Originally, my definition of gas-gas equilibrium restricted the prediction method to temperatures above the temperature of the least volatile component. I listed four systems (Water-nitrogen (*6*), water-carbon dioxide (*7*), nitrogen-sulfur dioxide (*8*), and ammonia-methane (*9*). Water-*n*-butane (*10*) has now joined these systems for a reason to be explained later) in Table 3 (*1*) as having experimentally shown gas-gas equilibria on the tacit assumption that they would do so, even though their $p(T)$ critical curves were not investigated at temperatures above the critical temperature of the least volatile component. They were, however, investigated above the double homogeneous point, DHP in Figure 2.

At temperatures between T_{DHP} and T_{c2} and at pressures between p_{I} and p_{DHP} (see Figure 2), liquid-gas equilibrium occurs. At temperatures between T_{DHP} and T_{c2} and at pressures at or between p_{DHP} and p_{II}, a phenomenon loosely called *type II* gas-gas equilibrium occurs; and at temperatures above T_{c2}, type II gas-gas equilibrium occurs, as I have defined it.

It would now be clear to define as fluid-fluid equilibrium the phenomenon that begins at the pressure of the double homogeneous point, p_{DHP}, in type II systems or at the pressure corresponding to $T_{c\mathrm{LVC}}$ in type I systems, extends to higher pressures, and continues at least as long as the unbroken $p(T)$ critical curve maintains a positive slope in type I or type II systems.

Further experimentation will confirm that these five systems do indeed show gas-gas equilibrium at sufficiently high temperatures and pressures unless the critical curve, at pressures above p_{DHP} but below p_{II}, is interrupted by the formulation of a solid phase or bends backward toward the critical temperature of the most volatile component. This latter possibility is unlikely.

Whether fluid-fluid equilibria (gas-gas equilibria plus those conditions represented by the crossed curve in Figure 2) can be predicted in a manner similar to that for gas-gas equilibria is uncertain without more experimental data [Kreglewski's (*11*) rule, however, is also applicable to fluid-fluid equilibria]; but it is probable that the equilibria can be so predicted for systems possessing the usual type of double homogeneous point, which occurs when the liquid-liquid critical curve intersects the gas-liquid critical curve before the latter has passed over a pressure maximum (refer to curve 2 in Figure 3), and on gas-gas equilibria systems (with the possibility that a negative prediction may in reality signify an unusual double homogeneous point fluid-fluid equilibrium system).

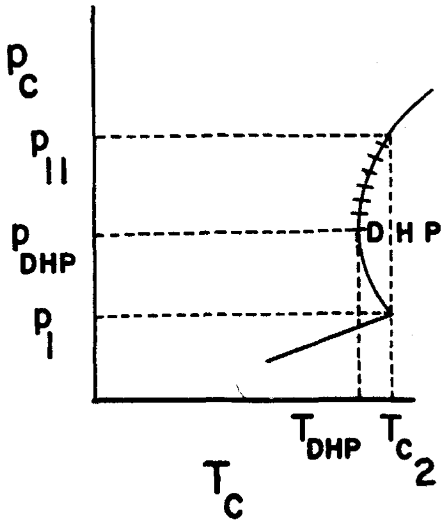

Fig. 2. $p(T)$ critical curve for a type *II* system.

This restriction is made since all the Y experimental data in Table 3 (*1*), from which gas-gas, [assuming that water-carbon dioxide and nitrogen-sulfur dioxide do show gas-gas equilibria, such behavior being predicted for ammonia-methane, water-nitrogen, and water-*n*-butane by the D^2 method, as a consequence of the results on ammonia-argon (*12*) and water-argon (*13*)] or fluid-fluid equilibria predictions can be made, are for systems of type I or II, but show a usual double homogeneous point. In the light of Schneider's (*2* to *5*) theory, which shows that a system with an unusual double homogeneous point is a borderline system, between usual critical curve behavior and fluid-fluid equilibrium behavior and the inexactness of the D^2 method (See later discussion), it is preferable to so restrict the fluid-fluid equilibria predictions.

Fourteen systems [water-argon (*13*), helium-acetylene (*14*), helium-ethane (*14*), water-ethane (*15*), helium-nitrous oxide (*16*), water-benzene (*5*, *17*), water-toluene (*17*), water-*n*-heptane (*17*), water-*n*-pentane (*17*), water-isohexane (*17*), helium-nitrogen (*18*), helium-argon (*19*), carbon dioxide-*n*-tridacane (*4*), and carbon dioxide-*n*-hexadecane (*4*)] have been experimentally found to show fluid-fluid equilibria since my original article was written. Three systems showed an unusual double homogeneous point [water-benzene (*5*), carbon dioxide-*n*-tridacane (*4*), and carbon dioxide-*n*-hexadecane (*4*)], and fluid-fluid

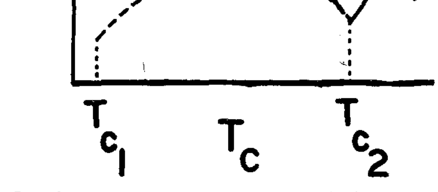

Fig. 3. $p(T)$ critical curves. The dashed curve is the usual liquid-gas critical curve. The solid curves represent the critical curves near the intersections of the liquid-gas and liquid-liquid critical curves.

equilibrium was predicted in each of the twelve permissible cases [water-benzene (*5*) is a permissible case, since it was predicted to show fluid-fluid equilibrium]. In the first five cases the predicted gas-gas equilibria also have been confirmed.

Other evidence favoring the method is that twenty tested systems (*4, 20* to *22*) do not show fluid-fluid equilibria. Fifty-six systems are now known to conform to the D^2 trend.

Also, Schneider's (*4*) data on carbon dioxide-*n*. alkane systems show that the larger the alkane, the more probable is the occurrence of fluid-fluid equilibria in such systems. These results are in agreement with the D^2 trend.

It should be noted that predictions are not made for systems such as E-W on the basis of a prediction or result on a system such as E-K, where W has a D^2 value greater than that of E and K has a D^2 value less than that of E or vice versa, since such predictions are apparently less reliable than the type made in (*1*). Thus the criticism which Tsiklis and Prokhorov (*13*) made of Kreglewski's (*11*) method, "... the value of D^2 for water is very large, so that according to Kreglewski separation into layers should always be observed in aqueous systems, which is extremely doubtful," does not apply to mine, since no predictions can be made at present for a number of water systems, that is, those for which the other component has a D^2 value greater than 396 atm. [for example, ammonia, which does not show fluid-fluid equilibrium with water (*23*)].

TABLE 1. TYPE OF FLUID-FLUID EQUILIBRIA IN HELIUM SYSTEMS (*1, 14, 16, 19*). (II? INDICATES THAT IF FLUID-FLUID EQUILIBRIUM EXISTS, IT IS OF TYPE II.)

Element or compound	He	H_2	Ne	C_6H_{14}	N_2	C_4H_{10}	C_3H_8	Ar	C_2H_6	C_6H_6	C_2H_4	Xe	C_2H_2	CO_2	N_2O	SO_2	CH_3OH	NH_3
D^2 value, atm.	11	63	131	170	173	205	228	244	254	266	280	314	337	396	397	436	535	688
Type occurring	—	II?	II?	I	II	I	I	II	I	I	I	I	I	I	I	I	I	I

Schneider (*2* to *5*) has suggested that fluid-fluid equilibrium is merely liquid-liquid equilibrium displaced to higher temperatures and pressures. He states that "... with systems with limited miscibility in the liquid phase, the $p(T)$ critical curve for liquid-liquid equilibrium ... (can be) displaced to so high a temperature that it lies in the region of the liquid-gas critical phenomenon; ... (then) the critical curve for the liquid-gas equilibrium ... no longer needs to proceed to the critical temperature of pure component I (that of the more volatile component), but can inflect and continuously go over to the critical curve for liquid-liquid equilibrium" (*3*).

Schneider's theory explains why fluid-fluid equilibrium occurs even in simple systems such as helium-xenon (*24*) and why the $p(T)$ critical curve which starts from the critical temperature of the least volatile component has never been observed to bend backward toward the critical temperature of the most volatile component after it attains a positive slope, even at pressures up to 15,000 kg./sq. cm. (*10*).

Experimental data on carbon dioxide-*n*. alkane systems (*2* to *4*) and on the water-benzene system (*5*) support Schneider's theory, but more experimental data are necessary before it can be accepted. The theory, however, seems promising.

Both Schneider's theory and Kreglewski's result, upon which my prediction method is based, are derived from liquid-liquid behavior, in particular liquid-liquid immiscibility. Indeed, Kreglewski's result is based on Hildebrand and Scott's (*25*) means of determining liquid-liquid immiscibility. Therefore, it is of interest to determine whether the D^2 method can be used to predict type I or type II behavior as well as to check the agreement between the D^2 method and Schneider's theory.

According to Schneider's theory, the less the miscibility of the components in the liquid phase (hence, to a first approximation, the greater the difference in the D^2 values of the components when one component is kept constant), the more probable is the occurrence of fluid-fluid equilibrium. As the miscibility becomes progressively less, and the D^2 difference correspondingly greater, fluid-fluid equilibria of type II and, in the extreme, type I are predicted.

In Table 1 helium systems are used as examples. Despite some anomalies in the lower range of D^2 values, the trend, in agreement with Schneider, is from type II to type I behavior as the D^2 difference increases. Due to the approximation made, complete agreement could not be expected; however, lack of an orderly change from type II to type I behavior indicates that the D^2 method, even though it has been shown to be correct in each of its tested predictions (with the exception of the two carbon dioxide systems which show unusual double homogeneous points), fails to consider important aspects of the phenomenon.

There have been only a few previous attempts to predict the type of gas-gas or fluid-fluid equilibria that occurs in binary systems. Rott's (*26*) method predicts only whether or not type I behavior will occur, predicting this behavior for H_2O-*n*-C_4H_{10}, H_2O-C_6H_{10}, H_2O-C_6H_{14} and H_2O-C_8H_{18} and predicting that it would not occur for water-nitrogen, water-carbon dioxide, water-argon (*13*), or water-ethylene. Jones (*27*) predicted the course of the critical curve, correctly predicting type I behavior for the helium-*n*-butane system but erroneously expecting all helium systems that show gas-gas equilibrium to be of type I. Zanderbergen, Knaap, and Beenakker (*28*) predicted type I behavior for helium-xenon and helium-krypton, but incorrectly predicted no fluid-fluid equilibrium for helium-argon.

Since all systems that show fluid-fluid equilibria other than helium systems are of type II, a method of predicting merely whether helium systems will show type I or type II behavior is required.

[Tsiklis and Maslennikova (*10*) reported that the water-*n*-butane system shows type I gas-gas equilbrium; however Danneil (*15, 29*) showed that this system is indeed of type II, having a 351°C. temperature at the double homogeneous point. Danneil's measurements are accepted on the basis of Connolly's (*17*) type II results for water-*n*-pentane and water-*n*-heptane, Danneil's own type II results for water-ethane, and the trend of other fluid-fluid equilibria results.

If Danneil's measurements are accepted, Rott's (*26*) prediction for this system would not be correct, and thus the D^2 method is left as the only one which has so far proved correct in each of its (permissible) tested predictions.

Lentz (*29*) observed type I gas-gas equilibrium for the water-argon system; however Tsiklis and Prokhorov (*13*) had found this system to be of type II in agreement with Rott's prediction.]

If other than helium systems are found to show type I behavior [as was suggested by Danneil, Todheide, and Franck (*29*) for *n*-alkane-water systems from undecane up and indicated by the measurements of Lentz (*29*)], a prediction method similar to that devised for helium systems could be formulated for them. The suggestion of Danneil, et al. would be in agreement with the critical temperature trend stated below if such behavior begins with, or after *n*-dodecane, rather than with *n*-undecane.

Table 2 indicates the importance of the critical temperature in determining the type of fluid-fluid equilibrium behavior shown, as was suggested by Streett (*30*). If the component other than helium has a critical temperature greater than 191°K., the critical temperature of methane, type I behavior is shown and if it has a critical temperature less than 191°K., type II behavior is shown. In general, the greater the difference between the critical temperatures of the components, when one component is kept constant, the greater is the probability that type I gas-gas equilibrium will occur.

The only helium systems that have experimentally failed to confirm the method are those which contain complex molecules which are, perhaps by chance, fluorine compounds: sulfur hexafluoride (*14*), chlorotrifluoromethane, trifluoromethane, d,d-difluoroethylene, and $CH_2 = CF_2$ (*16*). With the exception of these fluorine systems, the predicted and observed behavior agrees in each of the fifteen cases for which data are available. By using this method in conjunction with the D^2 method will make possible the prediction of first, whether fluid-fluid equilibrium or, in particular, gas-gas equilibrium will occur and, second, of what type it will be.

TABLE 2. PREDICTED AND OBSERVED TYPES OF FLUID-FLUID EQUILIBRIA IN HELIUM SYSTEMS (*3, 14, 16, 18, 19, 24, 27*). (II? INDICATES THAT IF FLUID-FLUID EQUILIBRIUM EXISTS, IT IS OF TYPE II.)

Component other than helium	T_{cLVC}, °K.	Type predicted	Type found experimentally
N_2	126	II	II
Ar	151	II	II
C_2H_4	283	I	I
Xe	290	I	I
CO_2	304	I	I
C_2H_6	306	I	I
C_2H_2	309	I	I
N_2O	309	I	I
C_3H_8	370	I	I
NH_3	406	I	I
n.C_4H_{10}	425	I	I
SO_2	431	I	I
n.C_6H_{14}	508	I	I
CH_3OH	513	I	I
C_6H_6	562	I	I
H_2	33	II	II?
Ne	45	II	II?
O_2	155	II	
Kr	210	I*	
n.C_5H_{12}	470	I	
C_7H_8	594	I	
H_2O	647	I	

* This type agrees with that predicted by Zandbergen, Knaap, and Beenakker (*28*).

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NOTATION

D = solubility parameter at the critical point
DHP = double homogeneous point
p = pressure
p_I = critical pressure corresponding to the critical temperature of the least volatile component at a pressure below that of the double homogeneous point
p_{II} = critical pressure corresponding to the critical temperature of the least volatile component at a pressure above that of the double homogeneous point
T = temperature
T_{c1} = critical temperature of the most volatile component
T_{c2} = critical temperature of the least volatile component

Subscripts

c = at the critical point
LVC = least volatile component

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