measured at temperatures above 600°C. but were estimated by Equation (2) of reference *1*, which was based upon low-temperature equilibrium measurements. Extrapolation of the equilibrium U(IV) fractions to chlorine partial pressures less than 1 atm. was equally unsuccessful, as evidenced by the deviations of the data for gas mixtures from those of pure chlorine in Figure 5 of reference *1*. The inability to extend the equilibrium data beyond the range in which measurements were made suggests that the extrapolation method, which was based upon the assumption that the reaction is that given by Equation (1) of reference *1*, is in error. This conclusion is substantiated by the observation (for which we are indebted to Leo Brewer) that the measured reaction entropy of 6.2 entropy units (eu) is much larger than the entropy change for the standard state reaction (—31.3 eu). Since the difference of 37.5 eu is far in excess of what would be expected from excess entropies of solution of uranium tetrachloride and uranium hexachloride, it appears that the increase in the uranium valency observed in the equilibrium experiments cannot be attributed to a simple chlorination reaction. Several possible sources of this discrepancy are discussed in reference 2.

According to the development in the Appendix of reference *1*, the preceding analysis of the kinetic results does not require detailed knowledge of the nature of the products involved in the reaction. Even if impurities such as oxygen or water vapor participated as gaseous reactants, the analysis would remain valid. All that is required is that an equilibrium U(IV) concentration be maintained at the gas–liquid surface on the rod, and that this concentration be the same as that measured in the equilibrium experiments. This condition is satisfied if the composition of the gas phase which generates the equilibrium distribution among the different oxidation states of the uranium in solution is the same in both the equilibrium and kinetic measurements.

ACKNOWLEDGMENT

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NOTATION

a = rod radius, cm.
$\bar{C}_4/C_0$ = U(IV) fraction in outlet salt
C_{40}/C_0 = U(IV) fraction in feed salt
$(C_4/C_0)_{eq}$ = U(IV) fraction in salt at equilibrium
$\bar{C}^*$ = $[(\bar{C}_4/C_0) - (C_4/C_0)_{eq}]/[(C_{40}/C_0) - (C_4/C_0)_{eq}]$
D_l = diffusivity of U(IV) in salt, sq.cm./sec.
L = length of rod, cm.
Q = salt flow rate down rod, cc./sec.
ν = kinematic viscosity of salt, sq.cm./sec.

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A Modified Redlich-Kwong Equation for Helium from 30° to 1,473° K.

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The original Redlich-Kwong equation is modified for helium by setting $B = 0.06372\ T_c/P_cT$ for $30° \lesssim T \lesssim 1.473°K$. This modified equation represents the compressibility factors of each of seventy-six isotherms tested in this temperature range to less than 1% average deviation.

Numerous investigators (*3, 11, 14 to 16, 20, 21, 23* to *25*) have used the virial equation of state to represent the experimental compressibility factors for helium. Mann (*12*) used a seventeen-constant, modified Benedict-Webb-Rubin equation. McCarty and Stewart (*13*) developed a six-constant equation explicit in volume. Dodge (*4*) used special reduced conditions for fitting the helium data on a generalized compressibility chart. Redlich (*18*) suggested the use of the pseudocritical values, $T_c = 12.2°K.$ and $P_c = 7.8$ atm., in conjunction with a recent work (*17*).

The original Redlich-Kwong (*19*) equation of state is

$$P = RT/(V-b) - a/T^{1/2}V(V+b) \qquad (1)$$

or

$$Z = 1/(1-h) - (A^2/B)h/(1+h) \qquad (2)$$

where

$$Z = PV/RT \qquad (3)$$

$$A^2 = a/R^2T^{2.5} = 0.4278\ T_c^{2.5}/P_cT^{2.5} \qquad (4)$$

$$B = b/RT = 0.0867\ T_c/P_cT \qquad (5)$$

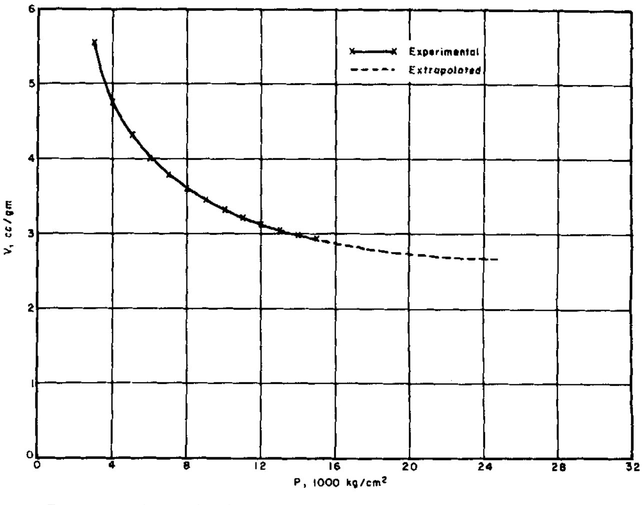

Fig. 1. Bridgman's (*1*) data extrapolated to constant volume.

$$h = b/V = BP/Z \qquad (6)$$

In this investigation the experimental critical values of helium, that is, $T_c = 5.2°K.$, $P_c = 2.26$ atm., were used.

This paper concerns the adjustment of the coefficient 0.0867 in Equation (5) to produce good agreement between the experimental compressibility factors for helium and those calculated by Equation (2), which can be solved by successive approximations in Z.

This work was prompted by a statement in the original Redlich-Kwong (*19*) paper which says that *b* represents the limiting volume of a gas at high pressure. They selected an average value of 0.26 V_c for the limiting volume for use in their equation. A specific value for helium was determined as follows.

DETERMINATION OF THE LIMITING VOLUME

To determine a specific value for the limiting volume of helium, a plot of *V* vs. *P* was made using Bridgman's (*1*) data, which goes to 14,500 atm. A curve (Figure 1) was drawn through these points and extrapolated until it was parallel to the pressure axis. A point of 2.68 cc./g. at 23,200 atm., which is equivalent to 0.186 V_c and a *B* coefficient of 0.062, was selected.

The effect of molecular attractive forces on the pressure is corrected for by the second (*a*) term of Equation (1). These forces are minimized at high temperatures and low pressures, that is, when the molecules are far apart. The five lowest pressure data points on Michels and Wouters' (*14*) 323°K. isotherm were arbitrarily selected as a basis for optimizing the *B* coefficient. These points were at 10.8, 13.3, 16.6, 20.9, and 25.8 atm. At these conditions, it was assumed that any deviation between the true value of the attractive forces correction and the value determined by Redlich and Kwong would have little or no effect on obtaining a better value for the *B* coefficient.

Using a digital computer and Equation (2), while holding A^2 constant, we looked for a *B* coefficient near 0.062 which minimized the standard error of estimate for the five data points mentioned above. This coefficient was found to be 0.06372, which corresponds to a limiting volume of 0.191 V_c or 2.75 cc./g.

If we assume that the molecules are arrayed as closely packed spheres, the intermolecular distance equivalent to this volume is 2.956 Å.

DISCUSSION OF RESULTS

This modified Redlich-Kwong equation was used to calculate compressibility factors at the same experimental pressures and temperatures reported by Michels and Wouters (*14*), Miller et al. (*15*), White et al. (*21*), Canfield (*3*), Wiebe et al. (*22*), and Hill and Lounasmaa (*5*). Calculated compressibility factors were also compared with those generated from the virial coefficients of Holborn and Otto (*6, 7*) and Yntema and Schneider (*25*), as well as those calculated by Johnson and Stewart (*8*) from Keesom's (*9*) virials. The range of pressures and temperatures where the equation has been tested is shown in Figure 2, along with the accuracy which can be expected at specified conditions. The graph also shows the area where the original Redlich-Kwong equation represents the data to 1%. The blank areas of the graph represent conditions where no PVT data are available for testing, with one exception: the data of Buchman (*2*) (13° to 18°K. and 200 to 1,550 atm.) which lie below the range of usefulness of the equation.

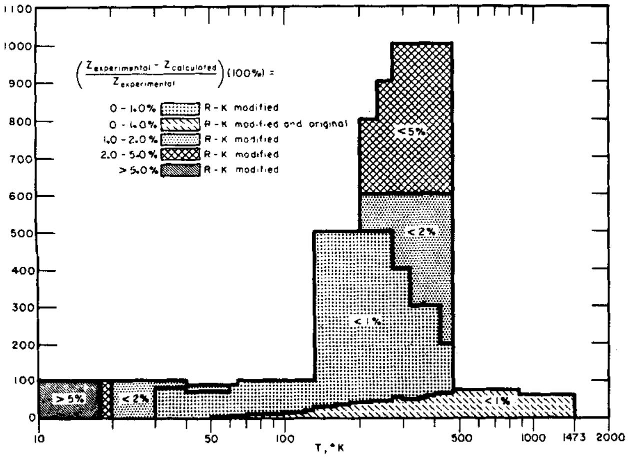

Fig. 2. Percent difference between experimental and calculated Z's as a function of temperature and pressure.

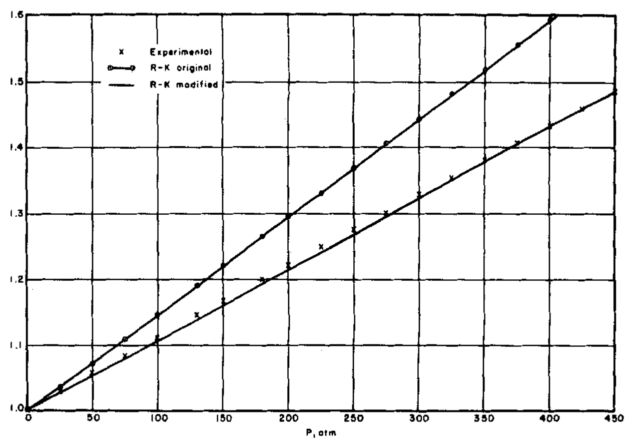

Fig. 3. *Z* vs. *P* (*3*), 133.15°, R-K original, R-K modified.

With the exception of the data of Wiebe et al. (*22*), the mean deviation for each isotherm from 60° to 1,473°K. was less than 0.34%, with a maximum deviation of less than 1% for any given point. For Wiebe et al., between 203° and 473°K. and pressures above 200 atm., this maximum is exceeded (see Figure 2). From 30° to 60°K. the mean deviation is less than 1% with a maximum of 1.38% for any given point. Below 30°K. it was not possible to achieve this degree of precision.

A separate comparison was made between the performance of this modified Redlich-Kwong equation and the virial equations of those who also published their experimental data, with the exception of Wiebe et al. (high pressure) and Holborn and Otto (nonisothermal). For the data of Michels and Wouters, Miller et al., White et al., and Canfield, the virial equations have an average deviation in Z of 0.009%. The modified Redlich-Kwong equation has an average deviation of 0.141%. Therefore, the justification for this modified equation does not lie in the fact that it is superior to the 121 virial coefficients contained in 39 virial equations, but that it summarizes, with an acceptable level of accuracy, all these data and coefficients into an equation of state containing only two constants. This equation can be used at any temperature in its range of applicability without interpolation. It can also be used to predict the compressibility factors of mixtures. As such, the suggested single equation should be much more acceptable for chemical engineering process calculations than are the 76 virial equations in the range from 30° to 1,473°K.

The modified two-constant Redlich-Kwong equation proposed here also offers advantages over the equations proposed for helium by Mann and by Stewart and McCarty, namely, simplicity and large temperature range. Use of the original Redlich-Kwong equation with the pseudocritical values, T_c = 12.2°K. and P_c = 7.8 atm., as suggested by Redlich (*18*), was investigated. The percentage deviations were found to be less for the modified equation.

A Z vs. *P* plot is shown in Figure 3 for Canfield's (*3*) 133.15°K. experimental data. Compressibility factors cal-

TABLE 1. COMPARISON OF HELIUM FUGACITIES

Investigator	T, °K.	P, atm.	f, atm. Graphical	 Original R-K	 This modification
Michels and Wouters (*14*)	323.15	115.82	121.88	124.32	121.99
Holborn and Otto (*7*)	90.17	41.1	43.67	44.77	43.69

culated by the original Redlich-Kwong equation and by the modified version are also shown.

A detailed comparison of experimental compressibility factors with those calculated by the original and modified Redlich-Kwong equations will be included in a forthcoming Bureau of Mines Report of Investigations.

FUGACITY

The fugacity of helium was determined at two conditions using the original Redlich-Kwong equation, this modification, and graphical integration of PVT data. The results are given in Table 1.

The improvement in the fugacities is consonant with the improved compressibility factors. Kharakhorin (*10*) calculated a fugacity of 43.72 at 90.1° and 41.1 atm. with the Beattie-Bridgman equation of state.

SUMMARY

A modified, two-constant Redlich-Kwong (*19*) equation for helium has been presented which will calculate compressibility factors for 1,073 data points in the range from 30° to 1,473°K., with a mean deviation of 0.18% from the experimental data.

NOTATION

A = parameter of Redlich-Kwong equation
a = parameter of Redlich-Kwong equation
B = parameter of Redlich-Kwong equation
b = parameter of Redlich-Kwong equation
f = fugacity
h = BP/Z
K = Kelvin temperature
P = pressure
P_c = critical pressure
R = universal gas constant
R-K = Redlich-Kwong
T = temperature
T_c = critical temperature
V = molal volume
V_c = critical molal volume
Z = compressibility factor, PV/RT

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A New Method to Measure Reaction Rates for Highly Reactive Catalysts: Heat and Mass Transfer on Catalytic Surfaces

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In case of gaseous reactions catalyzed by solid particles, the reactants diffuse from the ambient gas stream to the surface of the catalyst. On the other hand, the products and also the heat of reaction are transferred from the surface to the ambient gas stream. As a result, there exist the differences of the concentrations of the reactants and of the products, and also the differences of the temperature between the ambient gas stream and the catalytic surface (*1*). Especially for a highly reactive catalyst, these differences are considerably large. For example, as shown later in the experimental results, this temperature difference becomes as much as 200°C.

The experiments of kinetic analyses of reactions catalyzed by solid particles have usually been performed by using differential reactors of packed beds. The rate of reaction has generally been determined from the gas anal-