UCRL-11645

University of California

Ernest O. Lawrence Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

USE OF THE PROGRAM "EQUATION OF STATE 1964" (FORTRAN II)

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Research and Development

UCRL-11645
UC-4 Chemistry
TID-4500 (29th Ed.)

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

USE OF THE PROGRAM "EQUATION OF STATE 1964" (FORTRAN II)

Otto Redlich, F. J. Ackerman, R. D. Gunn
M. Jacobson, S. Low

September 1964

Printed in USA. Price 50 cents. Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D.C.

USE OF THE PROGRAM "EQUATION OF STATE 1964" (FORTRAN II)

General Information

Identification

ES64 - Equation of State 1964 - August 20, 1964.

Purpose

Calculation of the compressibility factor, the heat content, the entropy and the fugacity coefficient for a pure substance, the same mean quantities and the individual fugacity coefficients for a mixture from an empirical equation of state.

Subroutines

The special subroutines FDM, FDML, FTEM, FTEML, FFC, DEV, ZLQ, FUGAM, ANGLE, VAP are included in the main deck. Also included is the subroutine VIETA-MODIFICATION 3. This subroutine can be replaced by the following subroutines: VIETA (SHARE GCF0001) and the subroutines CUBERTF, ASINF, ACOSF. On the other hand, VIETA-MOD 3 requires ATANF.

The subroutines SQRTF, LOGF, EXPF, COSF, MAX1F, MIN1F, ABSF are supposed to be available.

The read-in, read-out and punch commands used in the program are

WRITE INPUT TAPE 2, (from cards)

WRITE OUTPUT TAPE 3, (print)

WRITE OUTPUT TAPE 14, (punch cards).

The program handles up to 999 points (sets of temperature, pressure and composition) in a single series. It is self-restoring and a new problem can be started without interruption.

Scope

The program ES64 is based on the equation of state proposed by Redlich and Kwong.* This equation has been improved by the addition of a deviation function for gases and one for liquids.

The program ES64 can be used for the computation of the compressibility factor Z = PV/RT and derived thermodynamic quantities for a pure substance or a mixture (up to 7 components). The data required for the computation are the critical temperature and pressure, and Pitzer's acentric factor** for each component.

The introduction of interaction coefficients for mixtures is optional for the calculation of Z and the mean quantities. They cannot be used for the calculation of individual fugacity coefficients.

Experimental data (compressibility factors, data for PV, volume or density) may be read in. The program converts the data to Z (if the input is different from Z) and prints the experimental values of Z and the difference between observed and calculated values.

The program allows a variety of prescriptions for schedules of temperatures and pressures, and for output options.

The temperature schedule provides for sets consisting of a starting temperature TL and an arbitrary number of higher temperatures TL + DT, TL + 2DT, TL + 3DT, ... at equal intervals.

---

* O. Redlich and J. N. S. Kwong, Chem. Revs., 44, 233 (1949).

** Lewis-Randall-Pitzer-Brewer, "Thermodynamics," McGraw-Hill Book Co., New York, 1961. See Appendix 1.

Also: W. C. Edmister, Petrol. Refiner, 37, No. 4, 173 (1958).

The pressure schedule may follow one of three schemes: (1) starting pressure PL and any number of higher pressures PL + DP, PL + 2DP, PL + 3DP, . . . at equal intervals, (2) starting pressure PL and any number of pressures of the amounts 2PL, 5PL, 10PL, etc., (3) starting pressure plus any number of additional pressures as read in as part of the data.

After a T-P schedule for a pure substance (NOS = 1) a new T-P schedule may be provided. The total number of points (sum of the products NOT . NOP) must not exceed 999. If no other T-P schedule is desired, a blank card is inserted. Now an entirely new problem can be prescribed to the computer, beginning with a new Title-Card and the whole input as described. If no new problem is to be submitted, a second blank is inserted. The calculation will then be terminated.

After a T-P schedule for a mixture (NOS > 1) the compositions for which the computation is to be carried out must be provided for. The number of such mixtures NOM has been prescribed in the Title-Card and is fixed for a whole problem. A new T-P schedule may follow. But the same number NOM of compositions must be provided for after each T-P schedule. The total number of points (sum of the products NOT . NOP . NOM) must not exceed 999. If no new T-P schedule is desired, a blank and a new problem (Title-Card and so on) may be put in. Two blank cards will terminate the computation.

For the various schedules, the following outputs are available: (1) only the compressibility factor Z, (2) only the compressibility factor and the mean fugacity coefficient ϕ, (3) option 2 plus a mean heat content function H/RT and a mean entropy expressed as S/R, and (4) option 3 plus individual fugacity coefficients ϕ_i. These options are controlled by the control quantity ECL.

The calculation of the terms H/RT and S/R requires a differentiation with respect to the temperature. Since the mixing rule used depends on a pseudo critical temperature, the calculation of the individual fugacity coefficients also involves a differentiation with respect to the temperature. The derivatives from the term of Redlich and Kwong are easily obtained algebraically but such a calculation would be unnecessarily involved for the additional correction terms. The derivatives of these terms are therefore obtained by computation of the difference quotient in the interval T and T + EE. The temperature interval EE should be small enough to allow replacement of the derivative by the difference quotient, and large enough so that the difference of the function values at T and T + EE furnishes about four significant figures (the function itself being expressed by eight significant figures). Usually EE = 0.1 is a satisfactory choice if the temperature is expressed in °K or °R. Other choices can be prescribed in accord with EE = 0.1/ECL/ by appropriate prescription of ECL.

If the control quantity KCL = 1, the intermediate quantities FDT and $FPC_i = \partial \ln \phi_{AG}/\partial y_i$ will be printed out. The control quantity NPC = 1 may be used to punch the normal output.

The program can also be used for computations starting from the reduced variables T_r and P_r. In this case, one sets $T_c = 1$, $P_c = 1$ and introduces T_r and P_r wherever T and P are prescribed. If heat content, entropy, and individual fugacity coefficients are desired, the absolute value of ECL in the Title Card should be 0.01. This makes EE = 0.001. The lower numerical values of T_r necessitate a lower value of EE for the differentiation with respect to T.

The same (arbitrary) units must be used for the whole input. The output is given in the same units or in dimensionless quantities such as T_r, P_r, Z, H/RT, S/R, ϕ. The quantity S/R contains ln P_r as an additive term. The selection of P_r rather than P makes the value of S/R independent of the choice of the pressure unit.

Various Degrees of Usefulness

An equation of state must strike a compromise between general applicability and accuracy. The reliability of the results is different in various parts of the field T_r-P_r of the reduced variables, and it is different for different classes of substances.

In general, the prediction of the program is quite good in the range $0.8 < T_r < 4$ and $P_r < 10$. Inside this field somewhat larger deviations may occur for $0.95 < T_r < 1.15$ and $1 < P_r < 6$, especially for mixtures. The extension to higher temperatures ($T_r > 10$) and pressures ($P_r > 20$) may entail appreciable deviations. The usefulness of the equation of state is questionable when both T_r and P_r are high. In this case the values given by the old equation of Redlich and Kwong (also printed out by the program) are more reliable.

Results for liquids, especially for very high and very low pressures, are less reliable than for gases. A subroutine VAP for the computation of vapor pressure of pure liquids, based on Maxwell's criterion, is included in the program but the results have not been satisfactory.

The results are best for the lower hydrocarbons, less good for heavy hydrocarbons and for polar substances. Water is not well represented. For hydrogen and helium quite good results are obtained with the fictitious values

	H_2	He
T_c(°K)	40.0	12.2
P_c(atm)	28.0	7.8

for the critical constants. For hydrogen, the improved equation (ZAG, FAG) is to be used with an acentric factor W = 0. For helium, the values 12.2°K and 7.8 atm. furnish quite satisfactory results up to T_r = 30 and P_r = 130 with the old equation of Redlich and Kwong while the improved equation is not at all satisfactory at these high values of the reduced variables.

Input

1. Title Card

Column	
1-54	Title of the problem
55-56	KCL: Print intermediate quantities: 0 no print 1 print
57	MCL: Experimental data: 0 no data 1, 2 data If MCL = 1, data are given as Z, but if MCL = 2, data are given as PV, or volume, or density. An Experimental Data Control Card must follow if MCL = 2.
58	NOS: Number of Components (1-7, never zero)
59	NOM: Number of Mixtures (1-9)
60	NPC: Punch normal output: 0 no punch 1 punch
61	NRC: Interaction coefficients are to be read in if NRC = 1
62-72 (4 dec.)	ECL: Output option and increment EE in the differentiation with respect to temperature.

ECL = 0: Compute only Z

ECL = 99.0: Compute Z and the mean fugacity coefficient ϕ

ECL < 0: Compute Z, ϕ, H/RT, S/R

EE = -0.1 ECL

ECL > 0(but≠99.0): Compute Z, ϕ, H/RT, S/R, ϕ_i

EE = 0.1 ECL

2. Experimental Data Control (only if MCL = 2)

This card contains RR (= 1/R), WOM (molal weight MW) and MVD (-1 for volume, 0 for PV, + 1 for density)

Units			R	RR col. 1-12 (6dec)	WOM col. 13-24 (6dec)	MVD col. 29-30
for P	for T	for volume or density				
atm.	°K	amagat	-	-1	0	0
atm.	°K	cm^3/g	82.0567	0.012187	MW	-1
atm.	°K	g/cm^3	82.0567	0.012187	MW	1
atm.	°K	lit/mole	0.820544	12.1871	0	-1
atm.	°K	moles/lit	0.820544	12.1871	0	1
mm Hg	°K	lit/mole	62.3613	0.016037	0	-1
PSIA	°R	cuft/lb	10.7315	0.093184	MW	-1
PSIA	°R	lb/cuft	10.7315	0.093184	MW	1
PSIA	°R	cuft/lb-mole	10.7315	0.093184	0	-1
PSIA	°R	lb-mole/cuft	10.7315	0.093184	0	1

3. Experimental Data (only if MCL = 1 or 2)

Insert any number of cards up to 999.

Column

1-10 (4 dec.) Z_E: Experimental value of Z or PV or volume or density. No card with Z_E = 0 is allowed.

The last card is followed by a blank card.

4. Substance Cards

NOS cards, one for each substance (NOS < 8)

Column	
1-24	Name of substance
25-36 (6 dec)	TC(JS) Critical temperature in any units.
37-48 (6 dec)	PC(JS) Critical pressure in any units.
49-60 (6 dec)	WS(JS) Acentric factor

5. Interaction Coefficients (only if NRC = 1)

NOS cards. The input consists of a symmetric matrix of order NOS with 1.0 in the diagonal.

Column		
1-12 (4 dec)	R(1, JR)	(JR = 1, 2, ... NOS)
13-22 (4 dec)	R(2, JR)	
.....		
63-72 (4 dec)	R(7, JR)	

6. T-P Schedule

Column	
1-12 (6 dec)	TL lowest temperature to be introduced, in same unit as TC(JS).
13-24 (6dec)	PL lowest pressure to be introduced, in same units as PC(JS). A negative value of PL leads to the calculation of the vapor pressure.
29-30	NOT number of temperatures to be introduced.
31-42	NOP number of pressures to be introduced. If the computation of the vapor pressure is desired, put NOP = 0.

49-60 (6 dec)	DT temperature increment in same units as TL.
61-72 (6 dec)	DP = -1: pressure schedule is PL, 2PL, 5PL, 10PL, etc. for NOP pressures. DP = 0: schedule given by PL and the following NOP-1 additional pressure cards. DP > 0: pressure increment for NOP pressures (same units as PL).

7. Additional Pressure Cards

(NOP-1 cards only if DP = 0.)

Column	
13-24 (6 dec)	pressure (same units as PL)

8. Composition Cards

(Only if NOS > 1, NOM cards for the preceding T-P schedule, one for each mixture)

Column	
1-12 (4 dec)	Y(1) mole fraction of first component (described in the first substance card)
13-22 (4 dec)	Y(2) mole fraction of second component (described in the second substance card)
23-32 (4 dec)	Y(3) mole fraction of third component (described in third substance card)
33-42 (4 dec)	Y(4) mole fraction of fourth component (described in the fourth substance card)
43-52 (4 dec)	Y(5) mole fraction of fifth component (described in the fifth substance card)
53-62 (4 dec)	Y(6) mole fraction of sixth component (described in the sixth substance card)

63-72 (4 dec) Y(7) mole fraction of seventh component (described in the seventh substance card)

9. New T-P schedule (insert additional pressure cards if prescribed by DP and NOP, and insert NOM composition cards if NOS > 1.) Not more than 999 points may be prescribed up to this stage.

A blank card starts a new problem (insert a full set of cards, types 1-8).

A new count of points (up to 999) starts.

A second blank card (0 in column 58) means end of calculation.

Output

The first line of every problem reproduces the Title Card. If an Experimental Data Control Card has been read in, it is given in the following line. The Substance Cards are printed then. For mixtures, the composition (mole fractions) follows.

The main output is arranged in tables for each temperature (and the corresponding set of pressures). Each table starts with the following heading:

ZRK	Z computed by the old equation of Redlich and Kwong
ZAG	Z computed by the improved equation by Ackerman and Gunn)
ZEX	Z as given by or computed from the experimental value read in as part of the data
DZ	ZEX-ZAG
LOG FRK	$\text{Log}_{10}\ \phi_K$ (fugacity coefficient of the old equation)
LOG FAG	$\text{Log}_{10}\ \phi_{AG}$ (fugacity coefficient of the improved equation)
FAG	ϕ_{AG}

MZ	Number of the point
Q	Kind of the printed line (or punched card)
C	Number of the component
P	Number of the phase

Below this heading, the temperature (in the same units as the input) and the reduced temperature are printed. This line is characterized by a 1 in the column headed Q.

For each point, the first line gives pressure, reduced pressure, the heat content (divided by RT) H/RT, and the entropy (divided by R) S/R. For this line the running number MZ is given and we have Q = 2. The following line furnishes the values ZRK and so on as prescribed in the heading. The point number MZ is given, for Q the value 3 is printed, and the number 1 or 2 of the phase is indicated.

For mixtures, if individual fugacity coefficients are prescribed, one more line follows for each component. It is distinguished by Q = 4 and the proper number C of the component. It contains the fugacity of the component and the individual values of the component for log ϕ_K, log ϕ_{AG} and ϕ_{AG} as prescribed by the general heading of the table.

The index MZQCP has been added for easier reading of the output and especially for convenience in the use of punched output cards. It contains the running number MZ (same for two phases at the same T and P), the kind of card Q as mentioned before, the component number C for individual cards and the number of the phase.

Two Phases

Since the old equation of state is of third order, it may furnish one or three real solutions for Z. The addition of the deviation function does

not change the order in Z since it depends explicity only on the reduced temperature and pressure. The multiplicity of the solutions is therefore the same.

If the equation of Redlich and Kwong furnishes three positive solutions for Z, the program interprets the highest value of Z as the value for the gaseous phase and the lowest value as that for the liquid phase. All further calculations are carried out separately for both phases. The intermediate value is discarded as a value for an unstable phase.

The computer does not directly indicate the stability of either phase. For a pure substance the stable phase is given by Maxwell's criterion. Since the fugacity coefficients of both phases are referred to the same standard state (gas at low pressure), the criterion is expressed directly by the magnitude of the fugacity coefficients: The stable phase is the one with the lower fugacity coefficients, the other is metastable. Vapor-liquid equilibrium exists if the fugacity coefficients are equal.

For mixtures, no simple stability criterion exists. The computer prints fugacities of the components if the calculation of individual coefficients is prescribed (pressure units as prescribed for the computation). Vapor-liquid equilibrium exists if the fugacities of two mixtures at the same temperature and pressure are correspondingly equal. The stability of either phase of a mixture can be discussed only if computations have been carried out for a sufficient range of composition at the given temperature and pressure. So far, no attempt has been made to solve the general problem of stability of mixtures by appropriate extension of the program.

Extraneous Solutions

The equation of Redlich and Kwong furnishes three real solutions at some temperatures above the Boyle temperature. In addition to the

desired positive value, there appear also two negative solutions for Z, corresponding with negative values of the volume. The program ignores these solutions.

The equation furnishes also one metastable and one unstable negative value for Z if a negative value for the pressure is prescribed. A positive value of Z (third real solution), associated with a negative pressure, corresponds with a negative volume. The program is not designed to handle negative pressures.

Irregularity of the Deviation Function

The deviation function has been constructed in such a manner that it vanishes at infinite temperature or at infinite pressure. But it may behave irregularly if both T_r and P_r assume very high values (above 20).

In addition, the deviation function behaves somewhat irregularly if

$$T_r > 2.4$$

$$D - 3.5 < P_r < D + 4$$

$$D = (T_r - 1.00122)/(0.0112141 + 0.0495574\ T_r).$$

If results are desired in this irregularity interval, the computer calculates the deviation function for the ends of the pressure interval and interpolates it linearly. The terms of Redlich and Kwong are not affected.

For extreme values of T_r and P_r the old equation may furnish better estimates than the improved equation. The results for both equations are printed.

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Research and Development

UCRL-11645
UC- 4 Chemistry
TID-4500 (29th Ed.)

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

USE OF THE PROGRAM "EQUATION OF STATE 1964" (FORTRAN II)

Otto Redlich, F. J. Ackerman, R. D. Gunn
M. Jacobson, S. Low

September 1964

USE OF THE PROGRAM "EQUATION OF STATE 1964" (FORTRAN II)

General Information

Identification

ES64 - Equation of State 1964 - August 20, 1964.

Purpose

Calculation of the compressibility factor, the heat content, the entropy and the fugacity coefficient for a pure substance, the same mean quantities and the individual fugacity coefficients for a mixture from an empirical equation of state.

Subroutines

The special subroutines FDM, FDML, FTEM, FTEML, FFC, DEV, ZLQ, FUGAM, ANGLE, VAP are included in the main deck. Also included is the subroutine VIETA-MODIFICATION 3. This subroutine can be replaced by the following subroutines: VIETA (SHARE GCF0001) and the subroutines CUBERTF, ASINF, ACOSF. On the other hand, VIETA-MOD 3 requires ATANF.

The subroutines SQRTF, LOGF, EXPF, COSF, MAX1F, MIN1F, ABSF are supposed to be available.

The read-in, read-out and punch commands used in the program are

WRITE INPUT TAPE 2, (from cards)

WRITE OUTPUT TAPE 3, (print)

WRITE OUTPUT TAPE 14, (punch cards).

The program handles up to 999 points (sets of temperature, pressure and composition) in a single series. It is self-restoring and a new problem can be started without interruption.

Scope

The program ES64 is based on the equation of state proposed by Redlich and Kwong.* This equation has been improved by the addition of a deviation function for gases and one for liquids.

The program ES64 can be used for the computation of the compressibility factor Z = PV/RT and derived thermodynamic quantities for a pure substance or a mixture (up to 7 components). The data required for the computation are the critical temperature and pressure, and Pitzer's acentric factor** for each component.

The introduction of interaction coefficients for mixtures is optional for the calculation of Z and the mean quantities. They cannot be used for the calculation of individual fugacity coefficients.

Experimental data (compressibility factors, data for PV, volume or density) may be read in. The program converts the data to Z (if the input is different from Z) and prints the experimental values of Z and the difference between observed and calculated values.

The program allows a variety of prescriptions for schedules of temperatures and pressures, and for output options.

The temperature schedule provides for sets consisting of a starting temperature TL and an arbitrary number of higher temperatures TL + DT, TL + 2DT, TL + 3DT, ... at equal intervals.

---

* O. Redlich and J. N. S. Kwong, Chem. Revs., 44, 233 (1949).

** Lewis-Randall-Pitzer-Brewer, "Thermodynamics," McGraw-Hill Book Co., New York, 1961. See Appendix 1.

Also: W. C. Edmister, Petrol. Refiner, 37, No. 4, 173 (1958).

The pressure schedule may follow one of three schemes: (1) starting pressure PL and any number of higher pressures PL + DP, PL + 2DP, PL + 3DP, ... at equal intervals, (2) starting pressure PL and any number of pressures of the amounts 2PL, 5PL, 10PL, etc., (3) starting pressure plus any number of additional pressures as read in as part of the data.

After a T-P schedule for a pure substance (NOS = 1) a new T-P schedule may be provided. The total number of points (sum of the products NOT . NOP) must not exceed 999. If no other T-P schedule is desired, a blank card is inserted. Now an entirely new problem can be prescribed to the computer, beginning with a new Title-Card and the whole input as described. If no new problem is to be submitted, a second blank is inserted. The calculation will then be terminated.

After a T-P schedule for a mixture (NOS > 1) the compositions for which the computation is to be carried out must be provided for. The number of such mixtures NOM has been prescribed in the Title-Card and is fixed for a whole problem. A new T-P schedule may follow. But the same number NOM of compositions must be provided for after each T-P schedule. The total number of points (sum of the products NOT . NOP . NOM) must not exceed 999. If no new T-P schedule is desired, a blank and a new problem (Title-Card and so on) may be put in. Two blank cards will terminate the computation.

For the various schedules, the following outputs are available: (1) only the compressibility factor Z, (2) only the compressibility factor and the mean fugacity coefficient ϕ, (3) option 2 plus a mean heat content function H/RT and a mean entropy expressed as S/R, and (4) option 3 plus individual fugacity coefficients ϕ_i. These options are controlled by the control quantity ECL.

The calculation of the terms H/RT and S/R requires a differentiation with respect to the temperature. Since the mixing rule used depends on a pseudo critical temperature, the calculation of the individual fugacity coefficients also involves a differentiation with respect to the temperature. The derivatives from the term of Redlich and Kwong are easily obtained algebraically but such a calculation would be unnecessarily involved for the additional correction terms. The derivatives of these terms are therefore obtained by computation of the difference quotient in the interval T and T + EE. The temperature interval EE should be small enough to allow replacement of the derivative by the difference quotient, and large enough so that the difference of the function values at T and T + EE furnishes about four significant figures (the function itself being expressed by eight significant figures). Usually EE = 0.1 is a satisfactory choice if the temperature is expressed in °K or °R. Other choices can be prescribed in accord with EE = 0.1/ECL/ by appropriate prescription of ECL.

If the control quantity KCL = 1, the intermediate quantities FDT and $FPC_i = \partial \ln \phi_{AG}/\partial y_i$ will be printed out. The control quantity NPC = 1 may be used to punch the normal output.

The program can also be used for computations starting from the reduced variables T_r and P_r. In this case, one sets $T_c = 1$, $P_c = 1$ and introduces T_r and P_r wherever T and P are prescribed. If heat content, entropy, and individual fugacity coefficients are desired, the absolute value of ECL in the Title Card should be 0.01. This makes EE = 0.001. The lower numerical values of T_r necessitate a lower value of EE for the differentiation with respect to T.

The same (arbitrary) units must be used for the whole input. The output is given in the same units or in dimensionless quantities such as T_r, P_r, Z, H/RT, S/R, ϕ. The quantity S/R contains ln P_r as an additive term. The selection of P_r rather than P makes the value of S/R independent of the choice of the pressure unit.

Various Degrees of Usefulness

An equation of state must strike a compromise between general applicability and accuracy. The reliability of the results is different in various parts of the field T_r-P_r of the reduced variables, and it is different for different classes of substances.

In general, the prediction of the program is quite good in the range $0.8 < T_r < 4$ and $P_r < 10$. Inside this field somewhat larger deviations may occur for $0.95 < T_r < 1.15$ and $1 < P_r < 6$, especially for mixtures. The extension to higher temperatures ($T_r > 10$) and pressures ($P_r > 20$) may entail appreciable deviations. The usefulness of the equation of state is questionable when both T_r and P_r are high. In this case the values given by the old equation of Redlich and Kwong (also printed out by the program) are more reliable.

Results for liquids, especially for very high and very low pressures, are less reliable than for gases. A subroutine VAP for the computation of vapor pressure of pure liquids, based on Maxwell's criterion, is included in the program but the results have not been satisfactory.

The results are best for the lower hydrocarbons, less good for heavy hydrocarbons and for polar substances. Water is not well represented. For hydrogen and helium quite good results are obtained with the fictitious values

	H_2	He
T_c (°K)	40.0	12.2
P_c (atm)	28.0	7.8

for the critical constants. For hydrogen, the improved equation (ZAG, FAG) is to be used with an acentric factor W = 0. For helium, the values 12.2°K and 7.8 atm. furnish quite satisfactory results up to T_r = 30 and P_r = 130 with the old equation of Redlich and Kwong while the improved equation is not at all satisfactory at these high values of the reduced variables.

Input

1. Title Card

Column	
1-54	Title of the problem
55-56	KCL: Print intermediate quantities: 0 no print 1 print
57	MCL: Experimental data: 0 no data 1, 2 data If MCL = 1, data are given as Z, but if MCL = 2, data are given as PV, or volume, or density. An Experimental Data Control Card must follow if MCL = 2.
58	NOS: Number of Components (1-7, never zero)
59	NOM: Number of Mixtures (1-9)
60	NPC: Punch normal output: 0 no punch 1 punch
61	NRC: Interaction coefficients are to be read in if NRC = 1
62-72 (4 dec.)	ECL: Output option and increment EE in the differentiation with respect to temperature.

ECL = 0: Compute only Z

ECL = 99.0: Compute Z and the mean fugacity coefficient ϕ

ECL < 0: Compute Z, ϕ, H/RT, S/R

EE = -0.1 ECL

ECL > 0(but≠99.0): Compute Z, ϕ, H/RT, S/R, ϕ_i

EE = 0.1 ECL

2. Experimental Data Control (only if MCL = 2)

This card contains RR (= 1/R), WOM (molal weight MW) and MVD (-1 for volume, 0 for PV, + 1 for density)

Units			R	RR col. 1-12 (6dec)	WOM col. 13-24 (6dec)	MVD col. 29-30
for P	for T	for volume or density				
atm.	°K	amagat	-	-1	0	0
atm.	°K	cm^3/g	82.0567	0.012187	MW	-1
atm.	°K	g/cm^3	82.0567	0.012187	MW	1
atm.	°K	lit/mole	0.820544	12.1871	0	-1
atm.	°K	moles/lit	0.820544	12.1871	0	1
mm Hg	°K	lit/mole	62.3613	0.016037	0	-1
PSIA	°R	cuft/lb	10.7315	0.093184	MW	-1
PSIA	°R	lb/cuft	10.7315	0.093184	MW	1
PSIA	°R	cuft/lb-mole	10.7315	0.093184	0	-1
PSIA	°R	lb-mole/cuft	10.7315	0.093184	0	1

3. Experimental Data (only if MCL = 1 or 2)

Insert any number of cards up to 999.

Column

1-10 (4 dec.) Z_E: Experimental value of Z or PV or volume or density. No card with Z_E = 0 is allowed.

The last card is followed by a blank card.

4. Substance Cards

NOS cards, one for each substance (NOS < 8)

Column	
1-24	Name of substance
25-36 (6 dec)	TC(JS) Critical temperature in any units.
37-48 (6 dec)	PC(JS) Critical pressure in any units.
49-60 (6 dec)	WS(JS) Acentric factor

5. Interaction Coefficients (only if NRC = 1)

NOS cards. The input consists of a symmetric matrix of order NOS with 1.0 in the diagonal.

Column		
1-12 (4 dec)	R(1, JR)	(JR = 1, 2, ... NOS)
13-22 (4 dec)	R(2, JR)	
.....		
63-72 (4 dec)	R(7, JR)	

6. T-P Schedule

Column	
1-12 (6 dec)	TL lowest temperature to be introduced, in same unit as TC(JS).
13-24 (6dec)	PL lowest pressure to be introduced, in same units as PC(JS). A negative value of PL leads to the calculation of the vapor pressure.
29-30	NOT number of temperatures to be introduced.
31-42	NOP number of pressures to be introduced. If the computation of the vapor pressure is desired, put NOP = 0.

49-60 (6 dec)	DT temperature increment in same units as TL.
61-72 (6 dec)	DP = -1: pressure schedule is PL, 2PL, 5PL, 10PL, etc. for NOP pressures. DP = 0: schedule given by PL and the following NOP-1 additional pressure cards. DP > 0: pressure increment for NOP pressures (same units as PL).

7. Additional Pressure Cards

(NOP-1 cards only if DP = 0.)

Column	
13-24 (6 dec)	pressure (same units as PL)

8. Composition Cards

(Only if NOS > 1, NOM cards for the preceding T-P schedule, one for each mixture).

Column	
1-12 (4 dec)	Y(1) mole fraction of first component (described in the first substance card)
13-22 (4 dec)	Y(2) mole fraction of second component (described in the second substance card)
23-32 (4 dec)	Y(3) mole fraction of third component (described in third substance card)
33-42 (4 dec)	Y(4) mole fraction of fourth component (described in the fourth substance card)
43-52 (4 dec)	Y(5) mole fraction of fifth component (described in the fifth substance card)
53-62 (4 dec)	Y(6) mole fraction of sixth component (described in the sixth substance card)

63-72 (4 dec) Y(7) mole fraction of seventh component (described in the seventh substance card)

9. New T-P schedule (insert additional pressure cards if prescribed by DP and NOP, and insert NOM composition cards if NOS > 1.) Not more than 999 points may be prescribed up to this stage.

A blank card starts a new problem (insert a full set of cards, types 1-8).

A new count of points (up to 999) starts.

A second blank card (0 in column 58) means end of calculation.

Output

The first line of every problem reproduces the Title Card. If an Experimental Data Control Card has been read in, it is given in the following line. The Substance Cards are printed then. For mixtures, the composition (mole fractions) follows.

The main output is arranged in tables for each temperature (and the corresponding set of pressures). Each table starts with the following heading:

ZRK	Z computed by the old equation of Redlich and Kwong
ZAG	Z computed by the improved equation by Ackerman and Gunn)
ZEX	Z as given by or computed from the experimental value read in as part of the data
DZ	ZEX-ZAG
LOG FRK	$\text{Log}_{10}\ \phi_K$ (fugacity coefficient of the old equation)
LOG FAG	$\text{Log}_{10}\ \phi_{AG}$ (fugacity coefficient of the improved equation)
FAG	ϕ_{AG}

MZ	Number of the point
Q	Kind of the printed line (or punched card)
C	Number of the component
P	Number of the phase

Below this heading, the temperature (in the same units as the input) and the reduced temperature are printed. This line is characterized by a 1 in the column headed Q.

For each point, the first line gives pressure, reduced pressure, the heat content (divided by RT) H/RT, and the entropy (divided by R) S/R. For this line the running number MZ is given and we have Q = 2. The following line furnishes the values ZRK and so on as prescribed in the heading. The point number MZ is given, for Q the value 3 is printed, and the number 1 or 2 of the phase is indicated.

For mixtures, if individual fugacity coefficients are prescribed, one more line follows for each component. It is distinguished by Q = 4 and the proper number C of the component. It contains the fugacity of the component and the individual values of the component for log ϕ_K, log ϕ_{AG} and ϕ_{AG} as prescribed by the general heading of the table.

The index MZQCP has been added for easier reading of the output and especially for convenience in the use of punched output cards. It contains the running number MZ (same for two phases at the same T and P), the kind of card Q as mentioned before, the component number C for individual cards and the number of the phase.

Two Phases

Since the old equation of state is of third order, it may furnish one or three real solutions for Z. The addition of the deviation function does

not change the order in Z since it depends explicity only on the reduced temperature and pressure. The multiplicity of the solutions is therefore the same.

If the equation of Redlich and Kwong furnishes three positive solutions for Z, the program interprets the highest value of Z as the value for the gaseous phase and the lowest value as that for the liquid phase. All further calculations are carried out separately for both phases. The intermediate value is discarded as a value for an unstable phase.

The computer does not directly indicate the stability of either phase. For a pure substance the stable phase is given by Maxwell's criterion. Since the fugacity coefficients of both phases are referred to the same standard state (gas at low pressure), the criterion is expressed directly by the magnitude of the fugacity coefficients: The stable phase is the one with the lower fugacity coefficients, the other is metastable. Vapor-liquid equilibrium exists if the fugacity coefficients are equal.

For mixtures, no simple stability criterion exists. The computer prints fugacities of the components if the calculation of individual coefficients is prescribed (pressure units as prescribed for the computation). Vapor-liquid equilibrium exists if the fugacities of two mixtures at the same temperature and pressure are correspondingly equal. The stability of either phase of a mixture can be discussed only if computations have been carried out for a sufficient range of composition at the given temperature and pressure. So far, no attempt has been made to solve the general problem of stability of mixtures by appropriate extension of the program.

Extraneous Solutions

The equation of Redlich and Kwong furnishes three real solutions at some temperatures above the Boyle temperature. In addition to the

desired positive value, there appear also two negative solutions for Z, corresponding with negative values of the volume. The program ignores these solutions.

The equation furnishes also one metastable and one unstable negative value for Z if a negative value for the pressure is prescribed. A positive value of Z (third real solution), associated with a negative pressure, corresponds with a negative volume. The program is not designed to handle negative pressures.

Irregularity of the Deviation Function

The deviation function has been constructed in such a manner that it vanishes at infinite temperature or at infinite pressure. But it may behave irregularly if both T_r and P_r assume very high values (above 20).

In addition, the deviation function behaves somewhat irregularly if

$$T_r > 2.4$$

$$D - 3.5 < P_r < D + 4$$

$$D = (T_r - 1.00122)/(0.0112141 + 0.0495574\ T_r).$$

If results are desired in this irregularity interval, the computer calculates the deviation function for the ends of the pressure interval and interpolates it linearly. The terms of Redlich and Kwong are not affected.

For extreme values of T_r and P_r the old equation may furnish better estimates than the improved equation. The results for both equations are printed.

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.