174/12-29-76

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ORNL/TM-5275

A Computer Program for the Calculation of Gas-Liquid Equilibria in the KALC System CO_2-N_2-CO-O_2-Xe-Kr

R. W. Glass
R. E. Barker
J. C. Mullins

MASTER

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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy $4,50; Microfiche $3.00

ORNL/TM-5275
Dist. Category UC-77

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

THORIUM UTILIZATION PROGRAM (189a OH045)
Reprocessing Development - Task 200

A COMPUTER PROGRAM FOR THE CALCULATION OF GAS-LIQUID EQUILIBRIA IN THE KALC SYSTEM CO_2-N_2-CO-O_2-Xe-Kr

R. W. Glass, R. E. Barker, and J. C. Mullins*

Date Published: December 1976

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*Visiting professor from the Department of Chemical Engineering, Clemson University, Clemson, S.C.

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CONTENTS

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ABSTRACT

A computer program for the calculation of gas-liquid equilibria for the system CO_2-N_2-CO-O_2-Xe-Kr is presented. The thermodynamic model has been developed as part of a three-column, multicomponent, multistage model used for the study of the KALC (Krypton Absorption in Liquid CO_2) process.

1. BACKGROUND

The reprocessing of spent HTGR fuel elements as presently envisioned will require the removal of krypton in a concentrated form from other gases such as CO_2, N_2, CO, O_2, and Xe. Specifically, the reprocessing gas will consist of ppm quantities of Kr and Xe, a few percent N_2, O_2, and CO, and the remainder CO_2. The process proposed for the krypton removal step during fuel reprocessing is known as KALC (Krypton Absorption in Liquid CO_2).

Mullins and Glass[1] have modeled the basic three-column KALC system and, as a portion of that model, have provided a multicomponent, thermodynamic gas-liquid equilibria model. Selected elements have been excised

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*Visiting professor from the Department of Chemical Engineering, Clemson University, Clemson, S.C.

and combined with revised routines for Henry's constants and partial molar volumes into a concise computer procedure for calculating total system pressure and liquid mole fractions, as well as gas and liquid phase enthalpies, given system temperature and gas phase mole fractions.

A discussion of the important thermodynamic considerations is given in this report, but the interested reader is referred to the originating document[1] for details.

2. BASIC MODEL RELATIONS

Correlation and prediction of gas-liquid equilibria at moderately high pressures comprise a field in which much work is being done with a variety of approaches. The system under present consideration is a relatively simple one consisting of one heavy component (CO_2) and five light components (N_2, CO, O_2, Xe, and Kr). A survey of the available literature reveals a sufficient amount of binary data for the CO_2-x systems to provide a reasonable model over the range of interest in KALC considerations.

The following exact thermodynamic relations (unsymmetric convention) have been chosen for the present work (see Appendix E for nomenclature):

$$\bar{f}_i^G \triangleq P y_i \, \phi_i^G = \bar{f}_i^L \qquad \text{for all components } i = 1,\ldots,6 \tag{1}$$

$$\phi_1^G \, P y_1 = x_1 \, \gamma_1 \, f_1^L \qquad \text{for the solvent} \tag{2}$$

$$\phi_i^G \, P y_i = x_i \, \gamma_i^* \, H_{i,1}^{P_1^S} \qquad \text{for all solutes } i = 2,\ldots,6 \tag{3}$$

Use of the unsymmetric convention for activity coefficients provides that both γ_i^* (solutes) and γ_1 (solvent) approach unity as x_1 (solvent) approaches unity. In addition, the use of the infinite dilution convention (ideal in the sense of Henry's law) for the solutes circumvents the necessity of considering the fugacities of pure liquid solutes. Such fugacities are hypothetical quantities and are experimentally inaccessible for the present study since, in general, $T > T_{c_i}$ for the conditions of interest.

Constant-pressure coefficients must be employed in order to make use of the common-type models that describe only the composition dependence of activity coefficients (i.e., those suggested by Margules, Van Laar, Wohl, etc.). Thus the following rigorous relations are important in the overall correlation (note that the constant reference pressure selected is P = 0 atm, T = system temperature, °K, and P_1^s = saturated vapor pressure[2] of the solvent at T):

$$\gamma_i^{(0)} = \gamma_i^{(P)} \exp \int_P^0 \frac{\bar{v}_i^L}{RT}\, dP \tag{4}$$

$$f_1^{L(0)} = f_1^{L(P_1^s)} \exp \int_{P_1^s}^0 \frac{v_1^L}{RT}\, dP \tag{5}$$

$$H_{i,1}^{(0)} = H_{i,1}^{(P_1^s)} \exp \int_{P_1^s}^0 \frac{\bar{v}_{i,1}^{\infty}}{RT}\, dP \tag{6}$$

Since at saturation the fugacity of pure liquid CO_2 is equal to that of the pure saturated vapor, it may be calculated from the Redlich-Kwong equation of state (as discussed later):

$$f_1^{(P_1^s)^L} = f_1^{(P_1^s)^G} = P_1^s\, \phi_1^s \tag{7}$$

If the concentrations of the dissolved gases are not excessively high and the temperature is well below the critical temperature of CO_2 (302.2°K), the partial molar volumes of the light gases in the liquid may be assumed to be independent of concentration and equal to the partial molar volumes at infinite dilution, namely, $\overline{v}^{\infty}_{i,1}$. Likewise, the partial molar volume of liquid CO_2 may be assumed to be equal to that of pure CO_2, v_1^L, at the system temperature.

In the actual use of equations to correlate the binary system data, v_1^L has been assumed to be independent of pressure, but $\overline{v}^{\infty}_{i,1}$ has been allowed a measure of empirical pressure dependence; that is,

$$\overline{v}^{\infty}_{i,1} = \overline{v}^{\infty(P_1^s)}_{i,1} [1 - \bar{\beta}_i (P - P_1^s)] \tag{8}$$

where $\bar{\beta}$ is an empirically determined constant for each of the binary systems.

Under the noted restrictions, combination of Eqs. (2)-(8) yields the following working relations:

<u>for the solutes,</u> $i = 2,\ldots,6$

$$\frac{y_i}{x_i} = \gamma_i^{*(0)} \frac{H_{i,1}^{(P_1^s)}}{\phi_i^G P} \exp\left\{\frac{[(1 + \bar{\beta}_i P_1^s)(P - P_1^s) - \frac{1}{2}\bar{\beta}_i (P^2 - {P_1^s}^2)]\overline{v}_i^{\infty(P_1^s)}}{RT}\right\} \tag{9}$$

<u>for the solvent,</u>

$$\frac{y_1}{x_1} = \frac{\gamma_1^{(0)} P_1^s \phi_1^s}{\phi_1^G P} \exp\left\{\frac{[v_1^{L(P_1^s)} (P - P_1^s)]}{RT}\right\} \tag{10}$$

3. LIQUID PHASE

3.1 Activity Coefficients

Thermodynamic properties of the liquid phase are derived from a representation of the excess Gibbs free energy. The excess free energy is assumed to be represented by a Wohl type series expansion:[3]

$$g^{*EX} = -\alpha_{22}x_2^2 - \alpha_{33}x_3^2 - \alpha_{44}x_4^2 \cdots \tag{11}$$
$$-2\alpha_{23}x_2x_3 - 2\alpha_{24}x_2x_4 \cdots$$

where the α_{ij}'s represent deviations from ideal behavior as a result of interaction between molecules i and j. Note that neither i nor j equals one since the infinitely dilute convention is being used. It can be seen that g^{*EX} approaches zero as $x_2,\ldots,x_6$ approach zero, but not as the mole fractions approach one as in the symmetric convention. The general expression may be represented as:

$$g^{*EX} = -\sum_{i=2}^{6}\sum_{j=2}^{6} \alpha_{ij}x_ix_j \tag{12}$$

The activity coefficients are directly related by the relation

$$\left[\frac{\partial(ng^{*EX})}{\partial n_k}\right]_{T,P,n_{j\neq k}} = RT\ln\gamma_k \qquad k = 1,\ldots,6 \tag{13}$$

Substitution of Eq. (12) for g^{*EX} results in the following expressions for the activity coefficients:

$$RT \ln \gamma_k^* = \sum_{i=2}^{6} \sum_{j=2}^{6} \alpha_{ij} x_i x_j - 2 \sum_{i=2}^{6} \alpha_{ik} x_i \qquad k = 2,\ldots,6 \tag{14}$$

$$RT \ln \gamma_1 = \sum_{i=2}^{6} \sum_{j=2}^{6} \alpha_{ij} x_i x_j \tag{15}$$

The values of α_{ij} for i = j were determined by analysis of experimental data for the binary systems (i.e., CO_2-x) using a simple estimate for α_{ij}, $i \neq j$, as suggested by Muirbrook:[4]

$$\alpha_{ij} = \left[\frac{\alpha_{ii} + \alpha_{jj}}{2}\right] \tag{16}$$

3.2 Henry's Law Constants

The Valentiner equation[5]

$$\ln H_{i,1}^{(P_1^s)} = a_i + b_i \ln T + c_i/T \qquad i = 2,\ldots,6 \tag{17}$$

where a_i, b_i, and c_i have been determined from the analysis of binary systems data, is used to represent the Henry's law constants.

3.3 Partial Molar Volumes

As noted in previous discussions, the partial molar volumes for the solvent are assumed to equal the molar volumes since dilute solutions are the rule. Data[7] for liquid CO_2 density (in g/cc) have been fitted to the following equation:

$$\rho = a + b(T_c - T)^m + c(T_c - T) + d(T_c - T)^2 \tag{18}$$

where

$a = 0.4638$

$b = 1.2068 \times 10^{-1}$

$m = 0.3794$

$c = 5.1566 \times 10^{-4}$

$d = 1.2895 \times 10^{-6}$

ρ = liquid CO_2 density, g/cc

T_c = critical temperature of CO_2 = 304.15°K

T = °K .

Partial molar volumes at infinite dilution for the solutes are calculated in this work via the Redlich-Kwong relationship:[8]

$$\bar{v}_i^{\infty} = \frac{\left(\frac{RT}{v - b}\right)\left(1 + \frac{b_i}{v - b}\right) - \left[\frac{2\,a_{i1} - \frac{ab_i}{v + b}}{v(v + b)T^{1/2}}\right]}{\frac{RT}{(v - b)^2} - \frac{a}{T^{1/2}}\left[\frac{2v + b}{v^2(v + b)^2}\right]} \tag{19}$$

In this relationship, the following equations are applicable for the infinite dilution binary systems:

$$b = b_1 = \left[\frac{\Omega_b RT_c}{P_c}\right]_{\text{pure liquid } CO_2 \text{ solvent}} \tag{20}$$

$$a = \left[\frac{\Omega_a R^2 T_c^{2.5}}{P_c}\right]_{\text{pure liquid } CO_2 \text{ solvent}} \tag{21}$$

$$b_i = \left[\frac{\Omega_{b_i} RT_{c_i}}{P_{c_i}}\right] \tag{22}$$

$$a_{il} = \frac{1/4(\Omega_{a_i} + \Omega_{a_l})RT_{c_{il}}^{1.5}(v_{c_i} + v_{c_l})}{0.291 - 0.04(\omega_i + \omega_l)} \qquad (23)$$

$$v_{c_i} = (0.291 - 0.08\ \omega_i)\frac{RT_{c_i}}{P_{c_i}} \qquad (24)$$

$v = v_l^L$, the molar volume of pure liquid CO_2 at the system temperature (25)

$$T_{c_{il}} = \sqrt{T_{c_i}\ T_{c_l}}(1 - k_{il}) \qquad (26)$$

For convenience, the binary pair geometric mean correction for $T_{c_{il}}$ has been approximated by use of the Hiza-Duncan[9] ionization potential rule:

$$k_{ij} = 0.17\ (I_i - I_j)^{1/2}\ \ln\left(\frac{I_i}{I_j}\right) \qquad (27)$$

Here, the subscript i refers to the component with the larger ionization potential, I, and:

Component	I(eV)	k_{ij}
CO_2	14.4	--
Xe	12.08	0.0455
O_2	12.5	0.0332
CO	14.1	0.0020
N_2	15.51	0.0133
Kr	13.9	0.0042

Redlich-Kwong parameters Ω_a and Ω_b employed in the calculation of partial molar liquid volumes for the solute components are the "universal" values. Corresponding parameters for the solvent were obtained by fitting the Redlich-Kwong relationship to the saturated liquid.[3]

4. VAPOR PHASE

Properties of the vapor phase are calculated in this work via the Redlich-Kwong equation of state, with mixture rules and constants as given by Prausnitz.[3] This equation is also used to estimate the enthalpy departure in the gas phase as discussed later. In accordance with the Redlich-Kwong equation, the fugacity coefficients are given by:

$$\ln \phi_i^G = \ln \left(\frac{v}{v - b}\right) + \left(\frac{b_i}{v - b}\right) - \left[2 \sum_{j=1}^{6} \frac{y_j a_{ij}}{RT^{3/2} b}\right] \ln \left(\frac{v + b}{v}\right) + \frac{ab_i}{RT^{3/2}\, b^2} \left[\ln \left(\frac{v + b}{v}\right) - \frac{b}{v + b}\right] - \ln \left(\frac{Pv}{RT}\right) \tag{28}$$

where

$$b = \sum_{i=1}^{6} y_i b_i \tag{29}$$

$$b_i = \frac{\Omega_{b_i} RT_{c_i}}{P_{c_i}} \tag{30}$$

$$a = \sum_{i=1}^{6} \sum_{j=1}^{6} y_i y_j a_{ij} \qquad (a_{ij} \neq \sqrt{a_{ii} a_{jj}}) \tag{31}$$

$$a_{ii} = \frac{\Omega_{a_i} R^2 T_{c_i}^{2.5}}{P_{c_i}} \tag{32}$$

$$a_{ij} = \frac{(\Omega_{a_i} + \Omega_{a_j}) R^2 T_{c_{ij}}^{2.5}}{2P_{c_{ij}}} \tag{33}$$

$$v_{c_{ii}} = \frac{Z_{c_{ii}} RT_{c_{ii}}}{P_{c_{ii}}} \tag{34}$$

$$v_{c_{ij}}^{1/3} = 1/2 \; (v_{c_{ii}}^{1/3} + v_{c_{jj}}^{1/3}) \tag{35}$$

$$Z_{c_{ij}} = 0.291 - 0.08 \; (\frac{\omega_i + \omega_j}{2}) \tag{36}$$

$$T_{c_{ij}} = \sqrt{T_{c_i} T_{c_j}} \; (1 - k_{ij}) \tag{37}$$

In Eq. (28), v, the molar volume of the gas phase, is calculated from the Redlich-Kwong multicomponent equation of state (see Appendix C).

For calculation of the gas phase fugacity coefficients, the Redlich-Kwong parameters Ω_{a_i} and Ω_{b_i} for the solutes are taken as the "universal" values, while the values used for the solvent are those found by fitting the Redlich-Kwong equation to the saturated solvent vapor curve.[3]

5. DATA CORRELATION AND BINARY PARAMETERS

Multicomponent calculations in this work result from (1) fits of experimental binary system data to appropriate equations, and (2) mixture properties obtained by the application of mixture rules to the parameters of the binary systems.

Since only infinite dilution values of (y/x) data are known (as a function of temperature) in the case of krypton and xenon, Eq. (9) reduces to the following for these two instances:

$$\left(\frac{y_i}{x_i}\right)^{\infty} = \frac{H_{i,1}^{(P_1^s)}}{\phi_i^G P_1^s} \qquad (38)$$

By empirical optimization of the data, Eq. (38) results in three empirical constants, a, b, and c, for each binary pair, CO_2-Xe and CO_2-Kr, as required by the Henry's law constant representation [Eq. (17)].

More complete equilibria data, in particular, PTxy data, are available for O_2, CO, and N_2. Therefore, the full form of Eq. (9) has been optimized for the selected data to obtain five empirical constants for each binary pair: a_i, b_i, and c_i for Eq. (17), α_{ii} for Eq. (14), and $\bar{\beta}_i$ for Eq. (8).

Table 1 presents a summary of the empirical constants determined by optimization.

6. REPRESENTATION OF GAS AND LIQUID ENTHALPIES

The representation of enthalpy used in this work is simple but should be sufficiently accurate to provide quantitative agreement with actual system behavior. Although adequate provisions are made for nonidealities in the gas phase, no attempt is made to consider the nonideal effect of pressure on the enthalpy of the liquid phase. This neglect is of little consequence, particularly since the KALC process operates

Table 1. Optimization constants for binary pairs

Pair	Constants				
	a	b	c	α	$\beta \times 10^2$
CO_2 - Xe	29.96148	- 3.670936	-1423.981	--	--
CO_2 - O_2	108.2571	-15.98780	-3478.370	992.6501	-1.028859
CO_2 - CO	124.1770	-18.24561	-4316.308	448.3456	3.854812
CO_2 - N_2	78.20484	-11.42092	-2194.547	1817.661	-3.211558
CO_2 - Kr	36.32377	- 4.782289	-1185.152	--	--

isobarically and at low concentrations of dissolved gases. The reference temperature for the enthalpy is taken here as -40°C to conform with enthalpy tables for liquid CO_2.

Corrections for the effect of gas phase nonideality are taken into account using the Redlich-Kwong equation of state with mixture rules as given by Prausnitz.[3] (A summary of those relations is given in Appendix C.) According to the Redlich-Kwong equation of state, the difference between the molar enthalpy of a component in an ideal gas state and its partial molar enthalpy in a real gas mixture at the same temperature, pressure, and composition is:

$$h_k^o - \bar{H}_k^G = \frac{3/2}{T^{1/2}} \left\{ \frac{2}{b} \left[\sum_{i=1}^{6} y_i \, a_{ik} \right] \ln \left(\frac{v + b}{v} \right) - \frac{ab_k}{b^2} \ln \left(\frac{v + b}{v} \right) + \left(\frac{a}{b} \right) \left(\frac{vb_k - \bar{V}_k b}{v(v + b)} \right) \right\} + RT - P \bar{V}_k \tag{39}$$

This relation can, of course, be used for a pure component as well as a mixture. The partial molar volume $\bar{V}_k$ is calculated [(similar to $\bar{v}_i^{\infty}$ of Eq. (19)] from the following:[8]

$$\bar{V}_k = \frac{\dfrac{RT}{v - b} + \dfrac{RTb_k}{(v - b)^2} - \dfrac{2\sum_{i=1}^{6} y_i \, a_{ik}}{T^{1/2} \, v(v + b)} + \dfrac{ab_k}{T^{1/2} \, v(v + b)^2}}{\dfrac{RT}{(v - b)^2} - \dfrac{a}{T^{1/2}} \left[\dfrac{2 \, v + b}{v^2 (v + b)^2} \right]} \tag{40}$$

The mixture rules are the same as those for Eq. (28). The difference between the enthalpy of an ideal gas mixture and that of a real gas mixture is given by:

$$h_m^o - h_m^G = \sum_{i=1}^{6} y_i (h_i^o - \bar{H}_i^G) \tag{41}$$

The heat capacity of pure saturated liquid CO_2 is obtained from a polynomial fit by Glass[6] to the liquid enthalpy:

$$c_s^L = 279.097 - 2.20982\ T + 0.00471243\ T^2 \tag{42}$$

Integrating from T_o and neglecting the effect of pressure,

$$h_s^L = 279.097(T - T_o) - 1.10491(T^2 - T_o{}^2) + 0.00157081(T^3 - T_o{}^3) \tag{43}$$

The enthalpy of the CO_2 at any temperature in the ideal gas state is calculated from:

$$h^o = \Delta h_o^{VAP} + (h_o^o - H_o^G) + \int_{T_o}^{T} C_p^o\, dT \tag{44}$$

The heat of vaporization at T_o = -40°C is taken to be 3369.2 cal/g-mole from Perry.[7] The quantity $(h_o^o - H_o^G)$ is calculated from Eq. (39), and $C_{p_i}^o$ is represented by:

$$C_{p_i}^o = \alpha_i + \beta_i T + \gamma_i T^2 \quad i = 1,\ldots,6 \tag{45}$$

Although the reference temperature for the light gas enthalpies is also -40°C, these enthalpies are calculated relative to the partial molar enthalpy at infinite dilution in liquid CO_2 since the light gases do not exist as pure liquids at that temperature. The derivative of the Henry's law constant is used to relate this reference state to the enthalpy in the ideal gas state, as follows:

$$\frac{\partial \ln H_{i,1}^{(0)}}{\partial (1/T)} = \frac{\overline{H}_i^{\infty} - h_i^o}{R} \tag{46}$$

Since $\overline{H}_i^{\infty} = 0$ at $T_o = -40°C$, evaluation of the derivative of the Henry's law constant using the correlation developed previously yields the values of h_i^o at -40°C, i.e., $h_{o_i}^o$. Values of h_i^o at other temperatures are calculated from:

$$h_i^o = h_{o_i}^o + \int_{T_o}^{T} C_{p_i}^o \, dT \tag{47}$$

where h_i^o is the value of the enthalpy of component i in the ideal gas state at temperature T. The coefficients of $C_{p_i}^o$ in Eq. (45), along with $h_{o_i}^o$, are presented below for the light gases:

i	$h_{o_i}^o$ (cal/g-mole)	α	$\beta \times 10^5$	$\gamma \times 10^7$
1	3513.04	6.637	139.5	204.5
2	1128.74	4.968	0	0
3	- 495.138	7.011	- 81.0	28.0
4	125.278	6.962	- 9.5	3.5
5	- 930.111	6.958	- 3.5	1.5
6	139.805	4.968	0	0

The values of $\overline{H}_i^{\infty}$ at temperatures other than -40°C are readily determined from Eq. (45) after calculating the derivative of the Henry's law constant from its correlation and the value of h_i^o from Eq. (47).

Once the enthalpies of the pure components in the ideal gas state have been calculated, the enthalpy of the real gas mixture is given by:

$$h^G = \sum_{i=1}^{6} y_i \left[h_i^o - (h_i^o - \overline{H}_i^G)\right] \tag{48}$$

The enthalpy of the liquid phase is calculated by assuming that $\bar{H}_{CO_2} = h_{CO_2}$ and $\bar{H}_i = \bar{H}_i^{\infty}$ (i.e., that the solution is an ideal, infinitely dilute solution).

7. DATA SELECTION

All available data for the binary pairs of interest were considered, with the ultimate point-by-point selection being based on thermodynamic consistency tests as explained by Mullins and Glass.[1] Data considered for this work are given in Appendix D.

8. THE EQUILIBRIUM PROCEDURE

Appendix B presents the IBM 360/91 PL/I version of the basic equilibrium program. As presented, the equilibrium procedure (EQUIL) is part of a typical main or calling program (GLASS).

The EQUIL procedure is in the form of a "dew-pressure" program requiring y and T for the calculation of x and P. Other forms of the equilibrium problem can be organized from the basic elements presented.

Figure 1 illustrates the flow of information for the EQUIL procedure and affords a concise sequence for discussion of the salient features of the procedure.

Calling sequence. The equilibrium procedure is called with the following parameters:

ICALL,M,Y,TK,P,X,HG,HL,IBAD

ICALL. Input parameter. This parameter is set to 0 for the first call of EQUIL in the main program. With the first call, EQUIL initializes

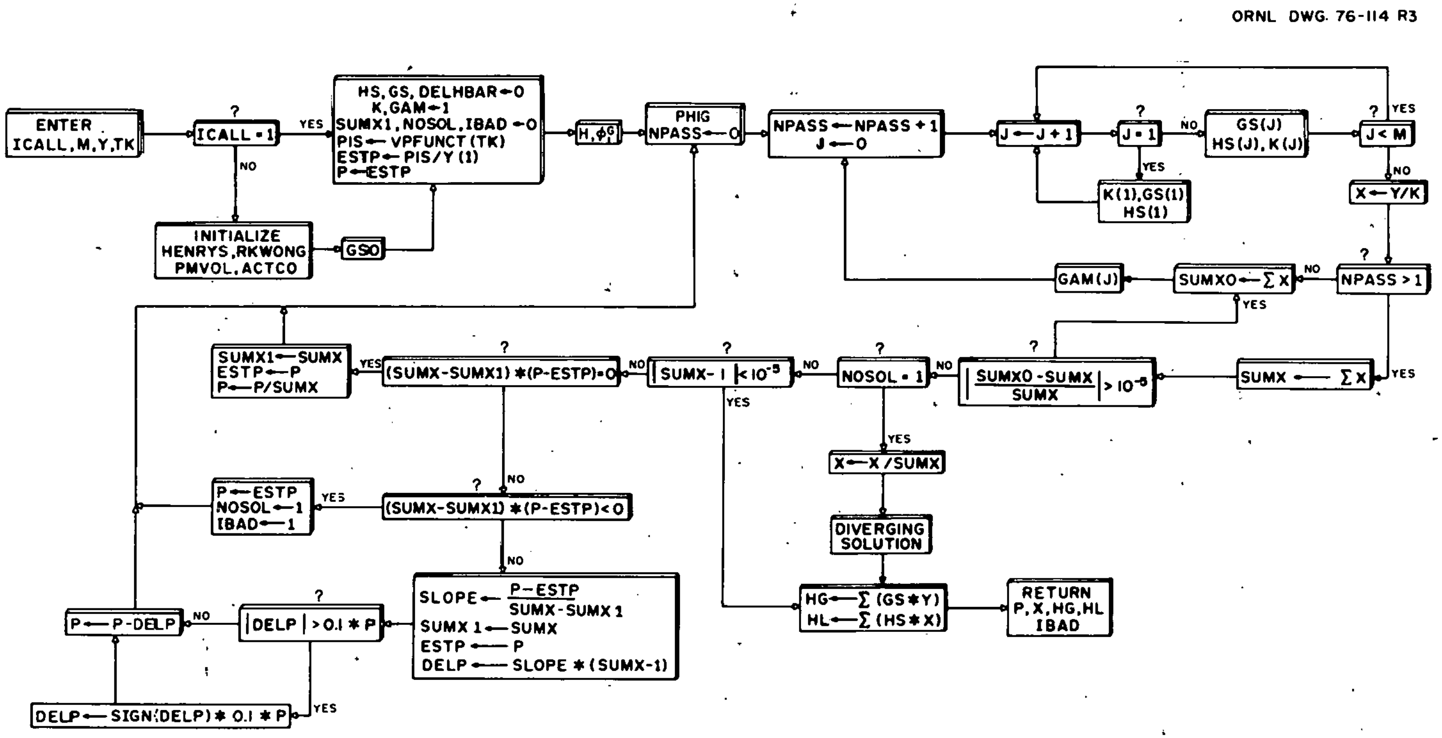

Fig. 1. Flow diagram for the equilibrium procedure.

various elements and proceeds with the equilibrium calculation. Subsequent calls to EQUIL with ICALL=1 do not require initialization, and EQUIL proceeds directly to the equilibrium calculation.

M. Input parameter. This parameter is initialized and fixed with a value of 6, which indicates the number of system components.

Y. Input parameter. Vapor mole fractions are transmitted to EQUIL through this vector of M mole fractions. Note: Mole fractions in Y must sum to unity. The component order for Y is: (1) CO_2, (2) Xe, (3) O_2, (4) CO, (5) N_2, and (6) Kr.

TK. Input parameter. The absolute system temperature, in °K, is passed to EQUIL by this parameter.

P. Returned value. The total system pressure in atm (absolute), as calculated by EQUIL based on TK and Y is returned to the calling program via this parameter.

X. Returned value. The liquid mole fractions, as calculated by EQUIL based on TK and Y, are returned via this vector. The component order for X is: (1) CO_2, (2) Xe, (3) O_2, (4) CO, (5) N_2, and (6) Kr.

HG. Returned value. Gas phase enthalpies, in cal/g-mole, referenced to pure liquid CO_2 at -40°C ($h_1^L = 0$ and $\overline{H}_i^\infty = 0$) are returned via this parameter.

HL. Returned value. Liquid phase enthalpies, in cal/g-mole, are returned via this parameter.

IBAD. Returned value. Normally this parameter retains a value of 0. In the event of a diverging solution, the value is set to 1 and the words "Diverging Solution" are printed; the values of P and X returned are, at best, only estimates of equilibrium and cannot be regarded as accurate.

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APPENDIX A: SELECTED RESULTS

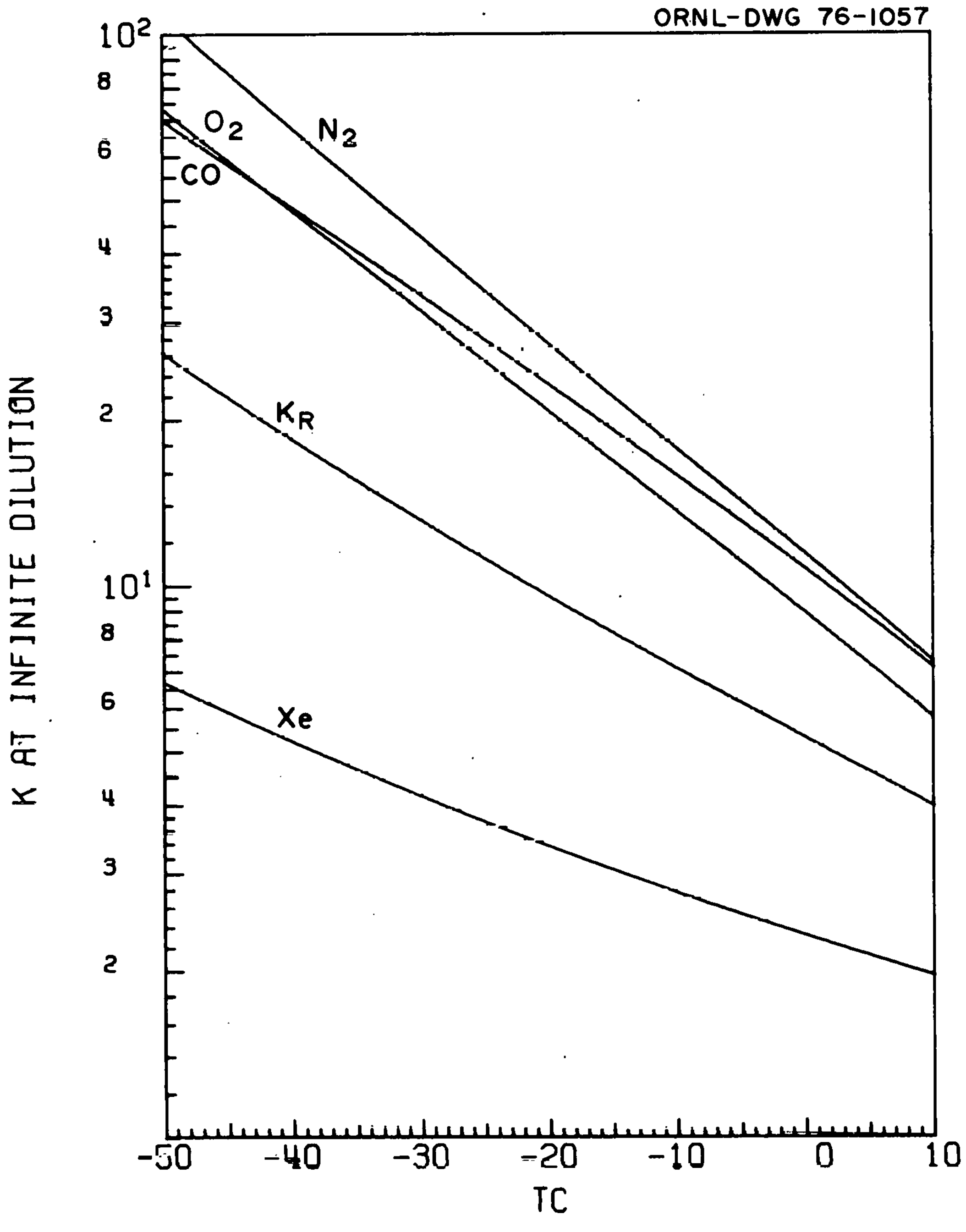

Fig. A-1. Model-predicted K values at infinite dilution.

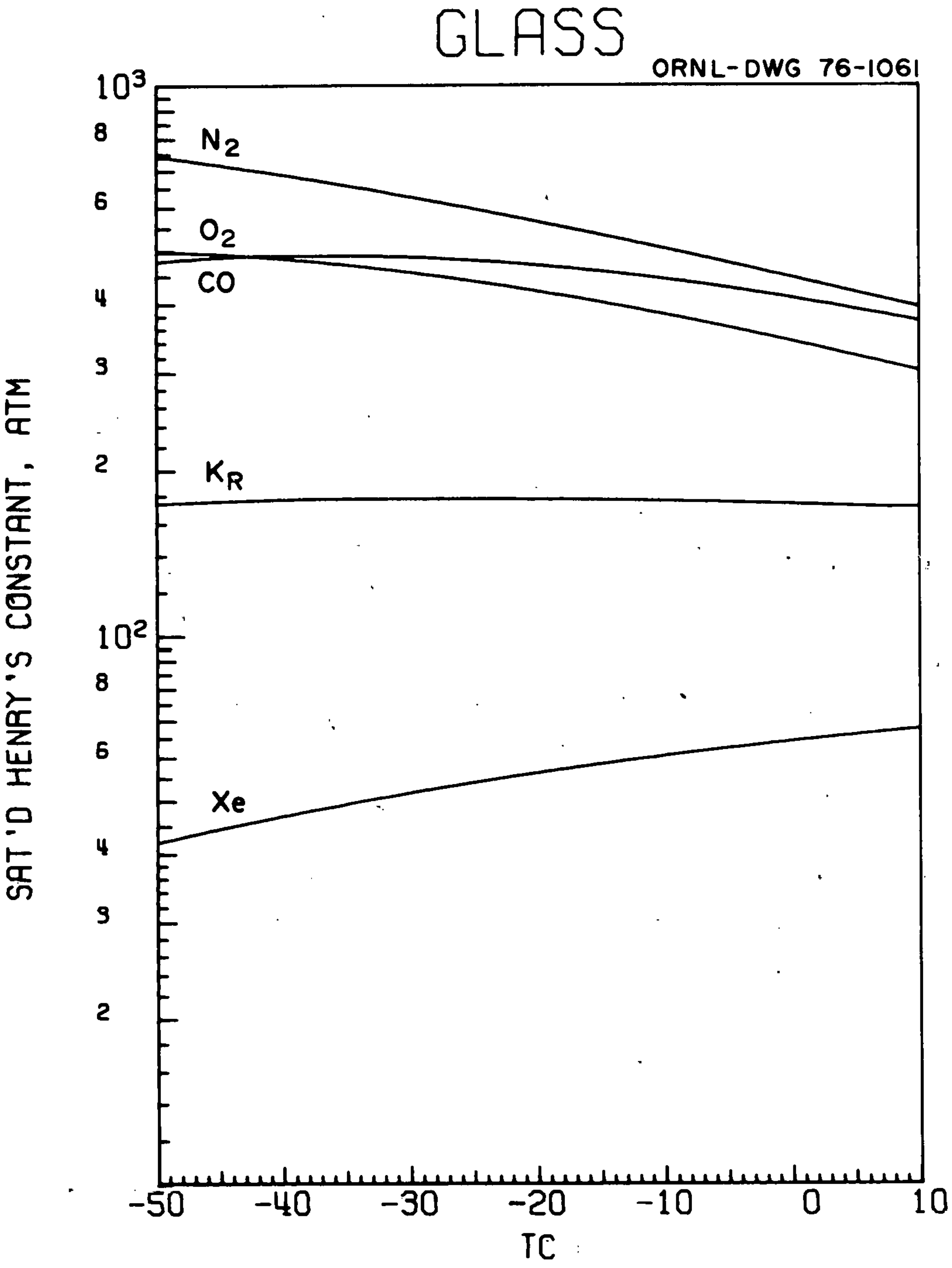

Fig. A-2. Model-predicted Henry's law constants at saturation.

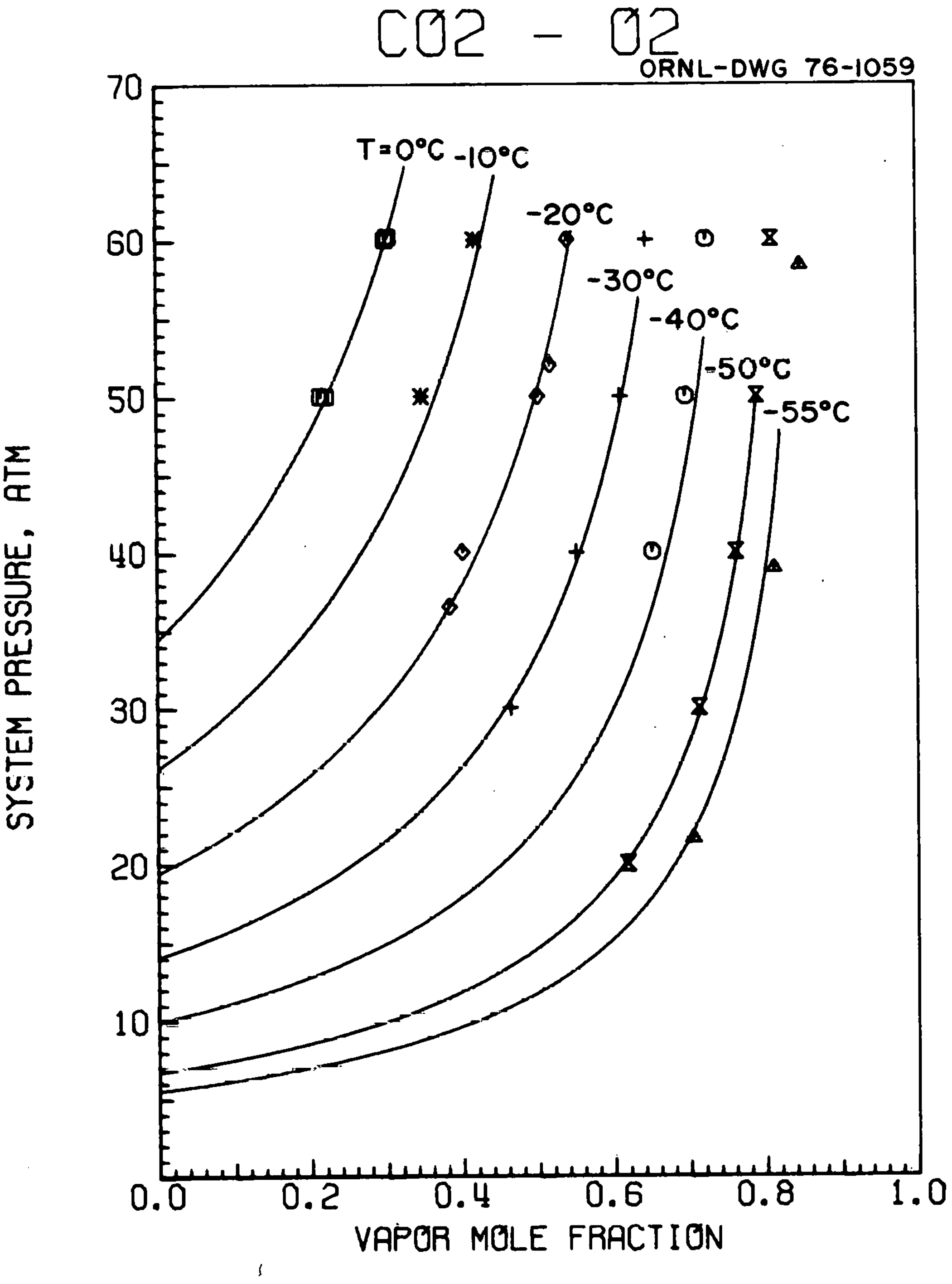

Fig. A-3. P-y diagram for CO_2-O_2.

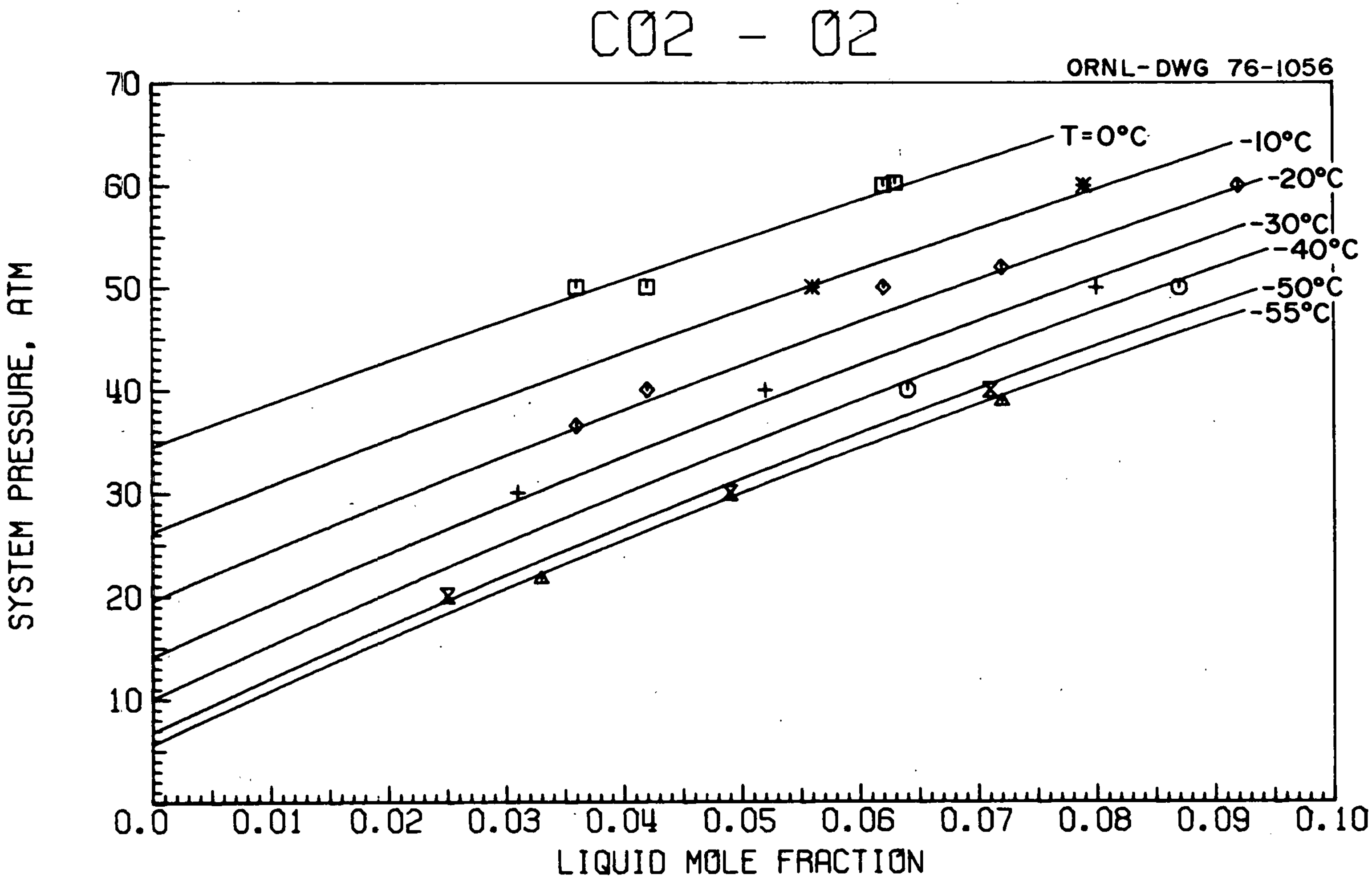

Fig. A-4. P-x diagram for CO_2-O_2.

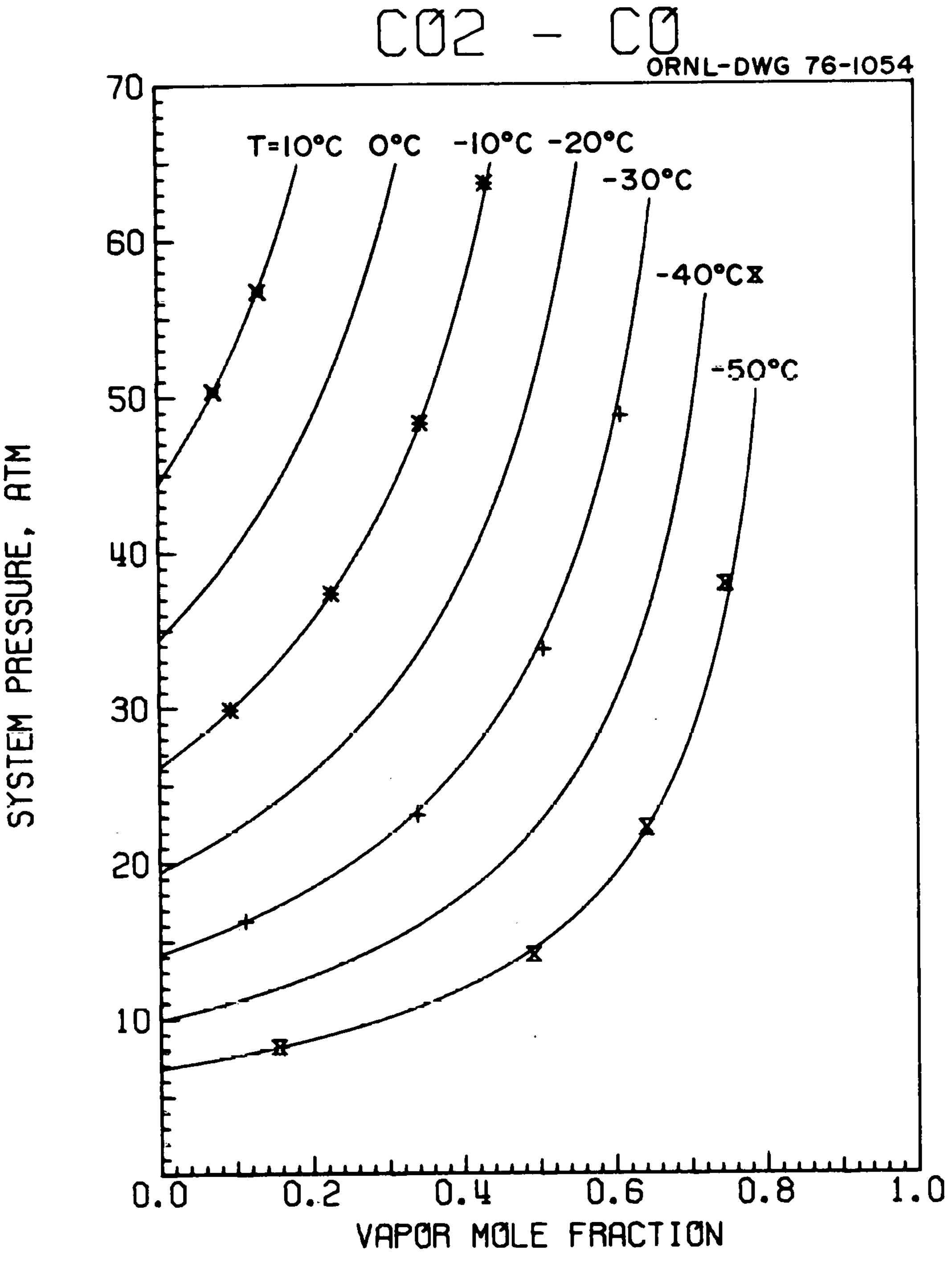

Fig. A-5. P-y diagram for CO_2-CO.

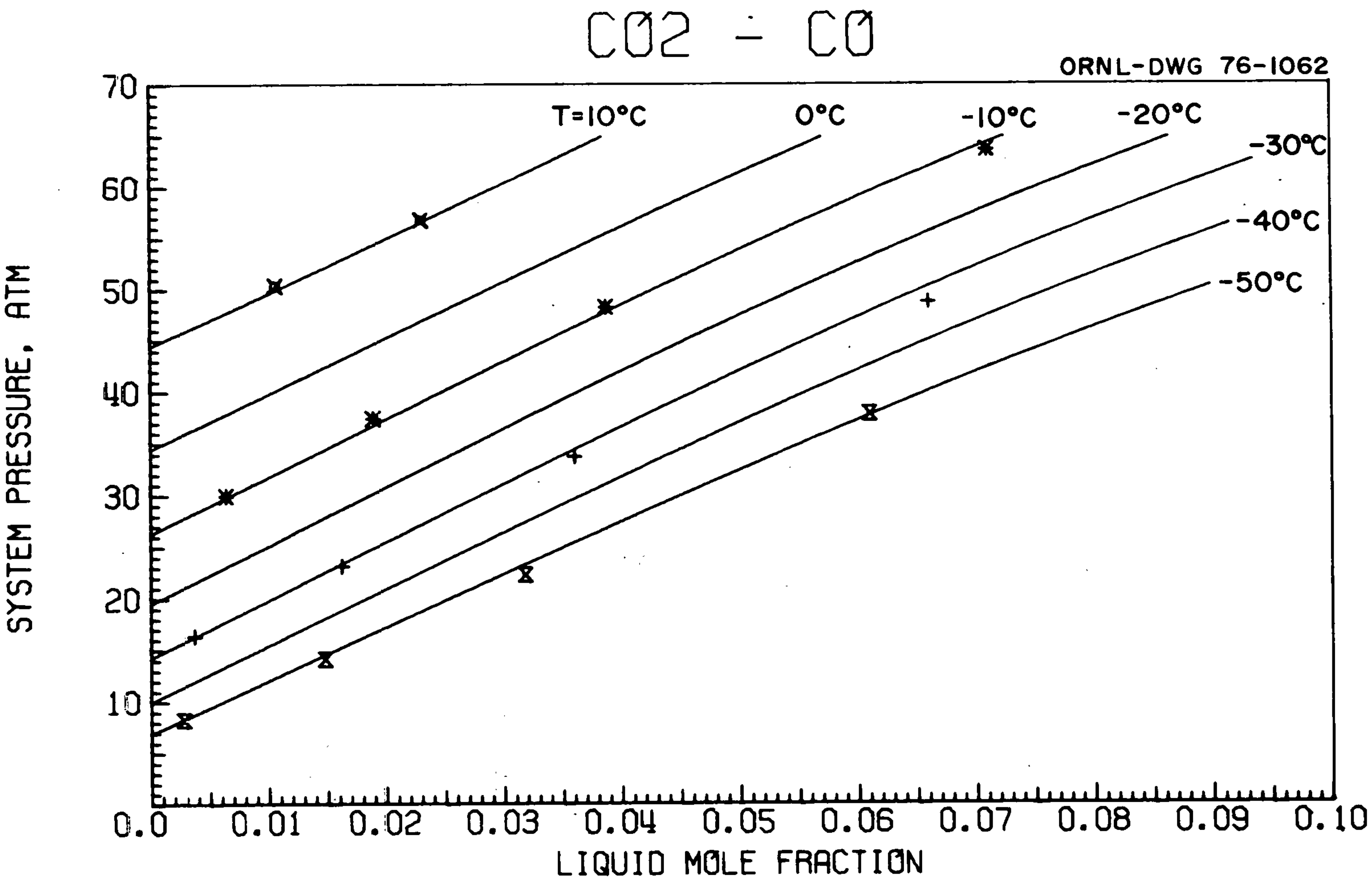

Fig. A-6. P-x diagram for CO_2-CO.

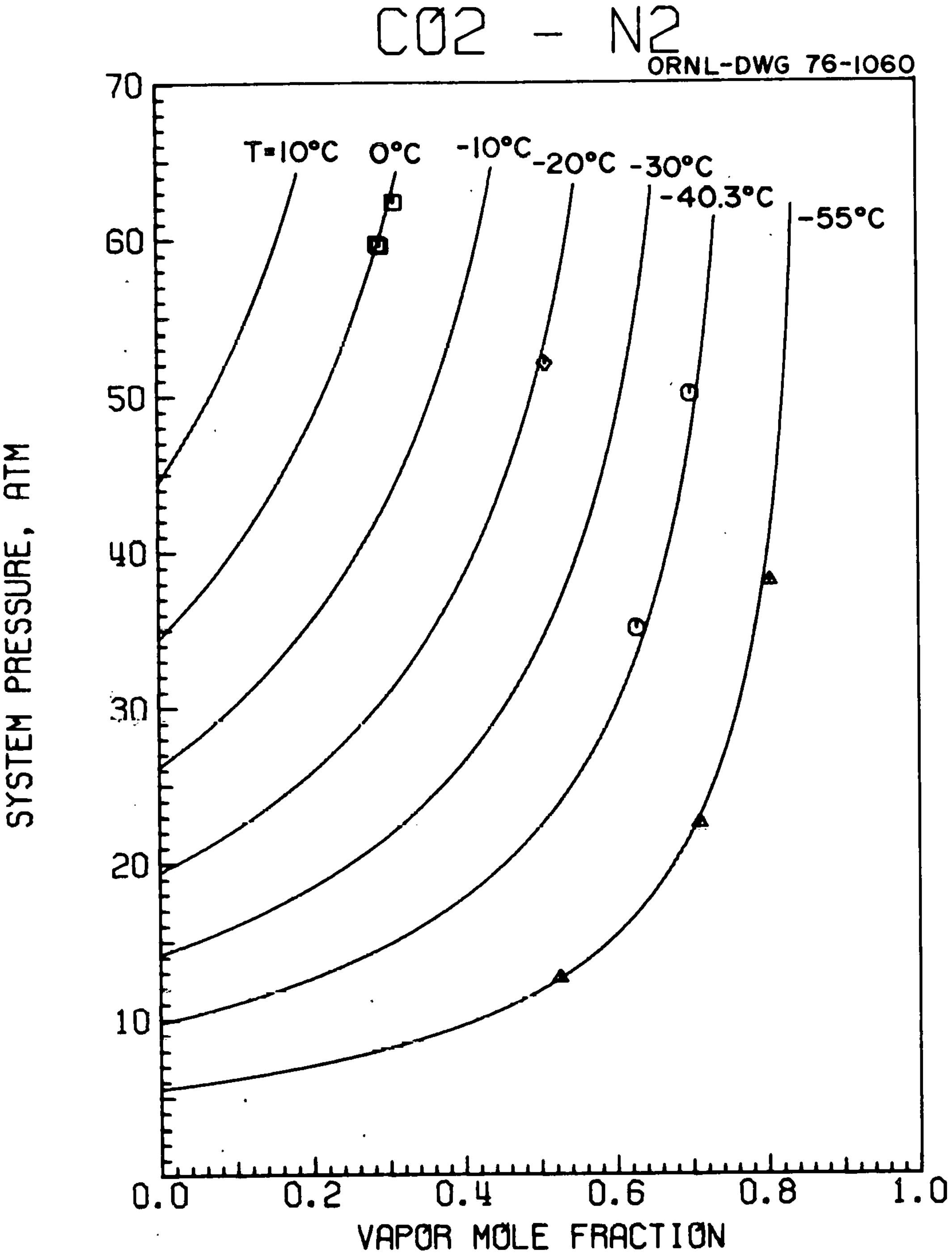

Fig. A-7. P-y diagram for CO_2-N_2.

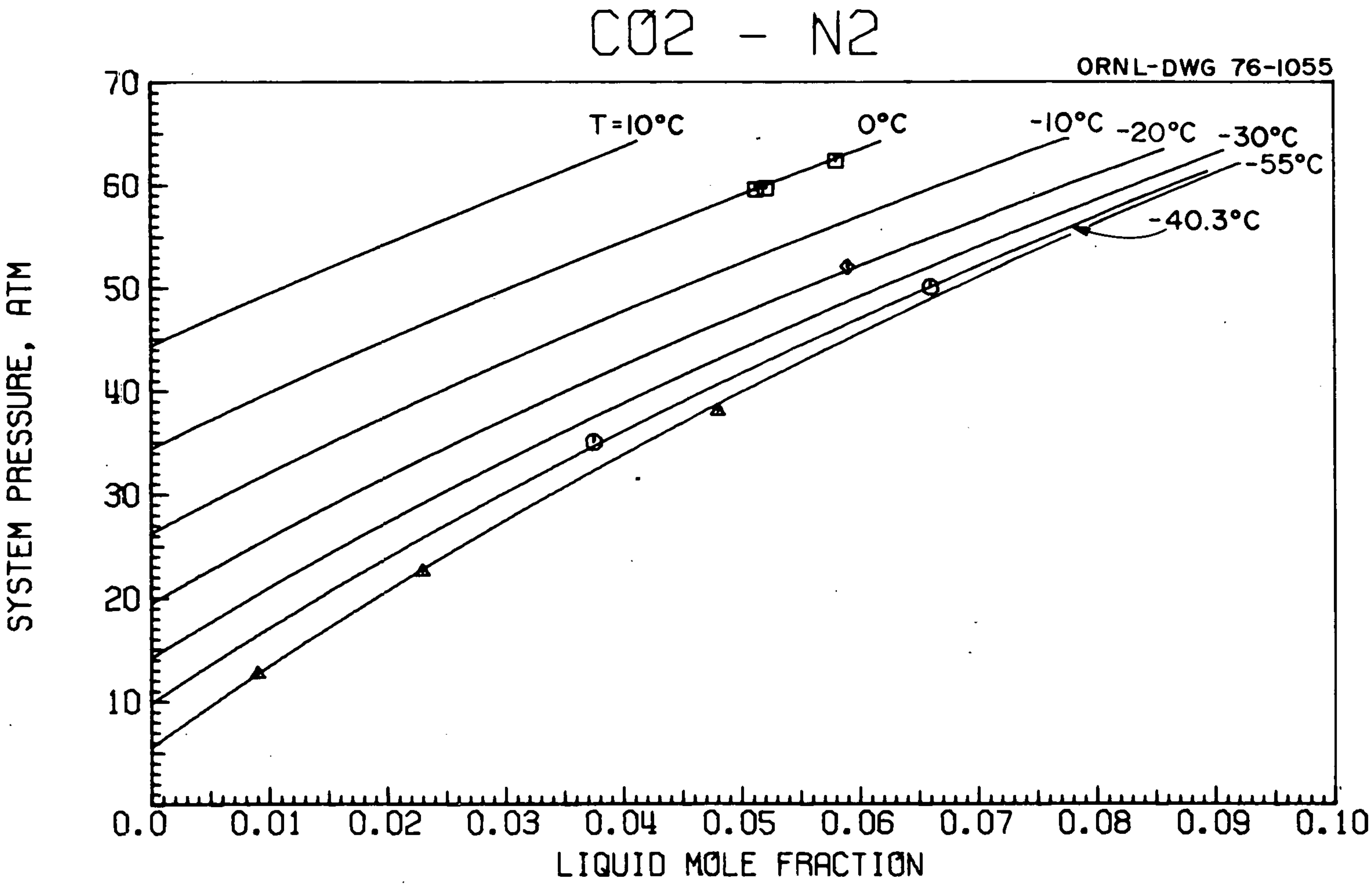

Fig. A-8. P-x diagram for CO_2-N_2.

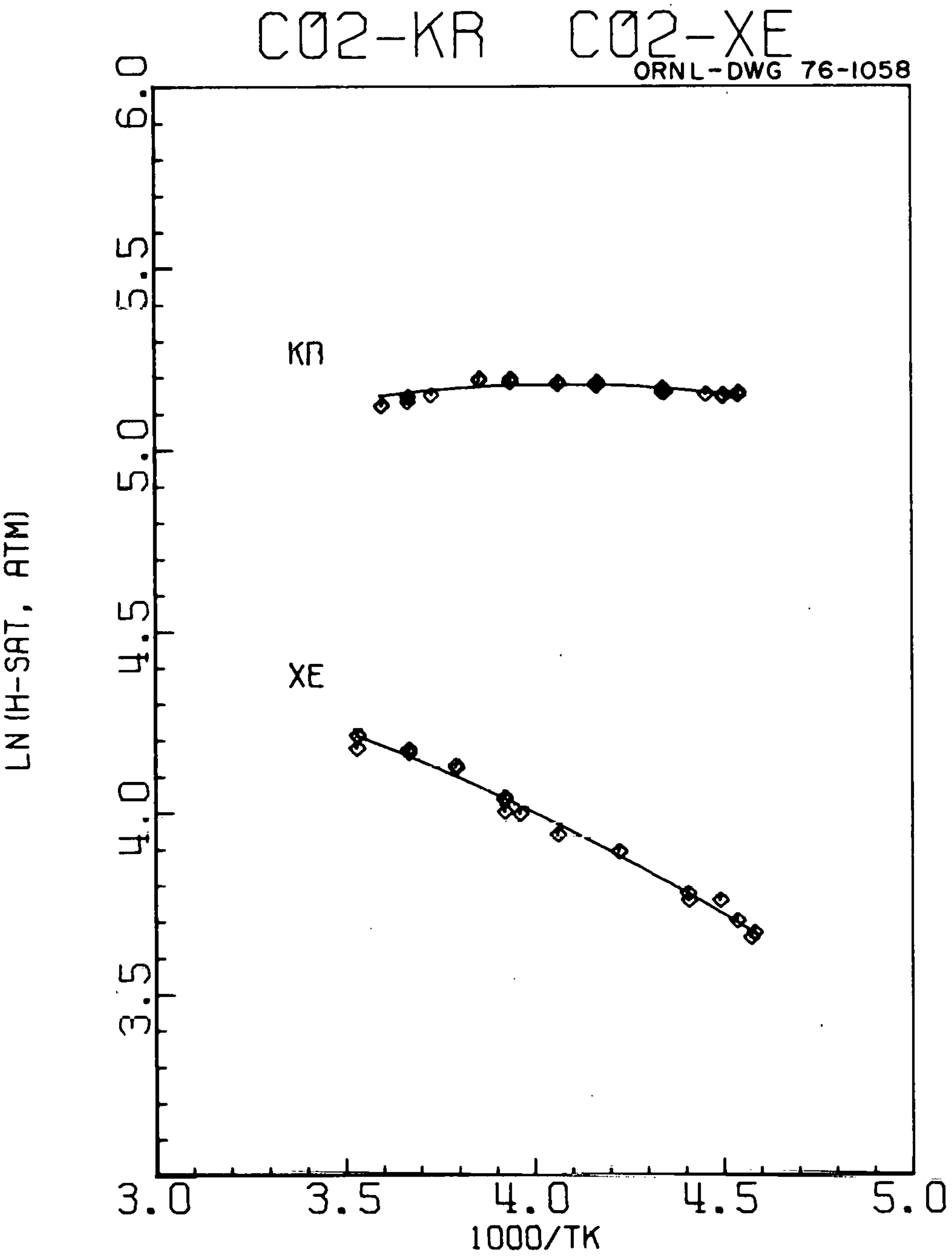

Fig. A-9. Henry's law constants for Kr and Xe in saturated CO_2.

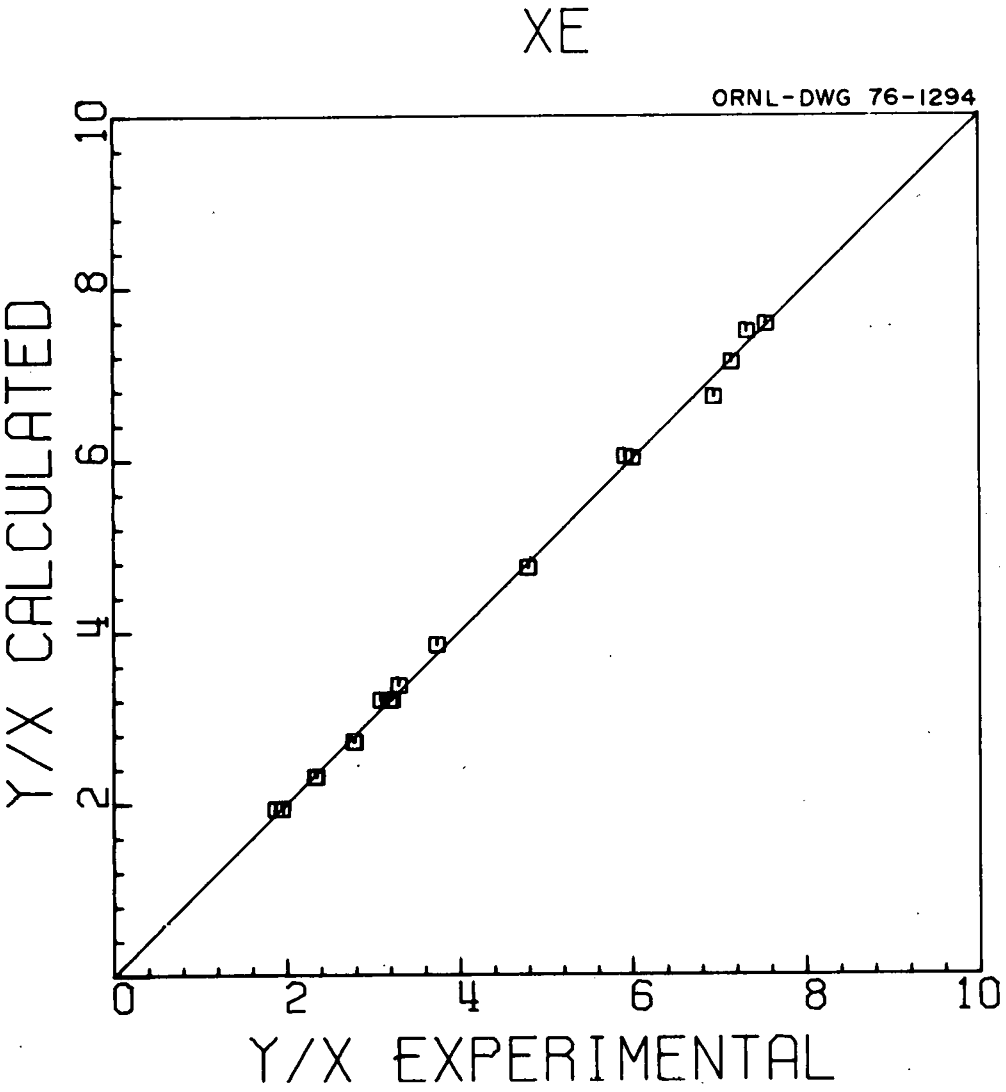

Fig. A-10. Equilibrium ratio comparisons for Xe in CO_2.

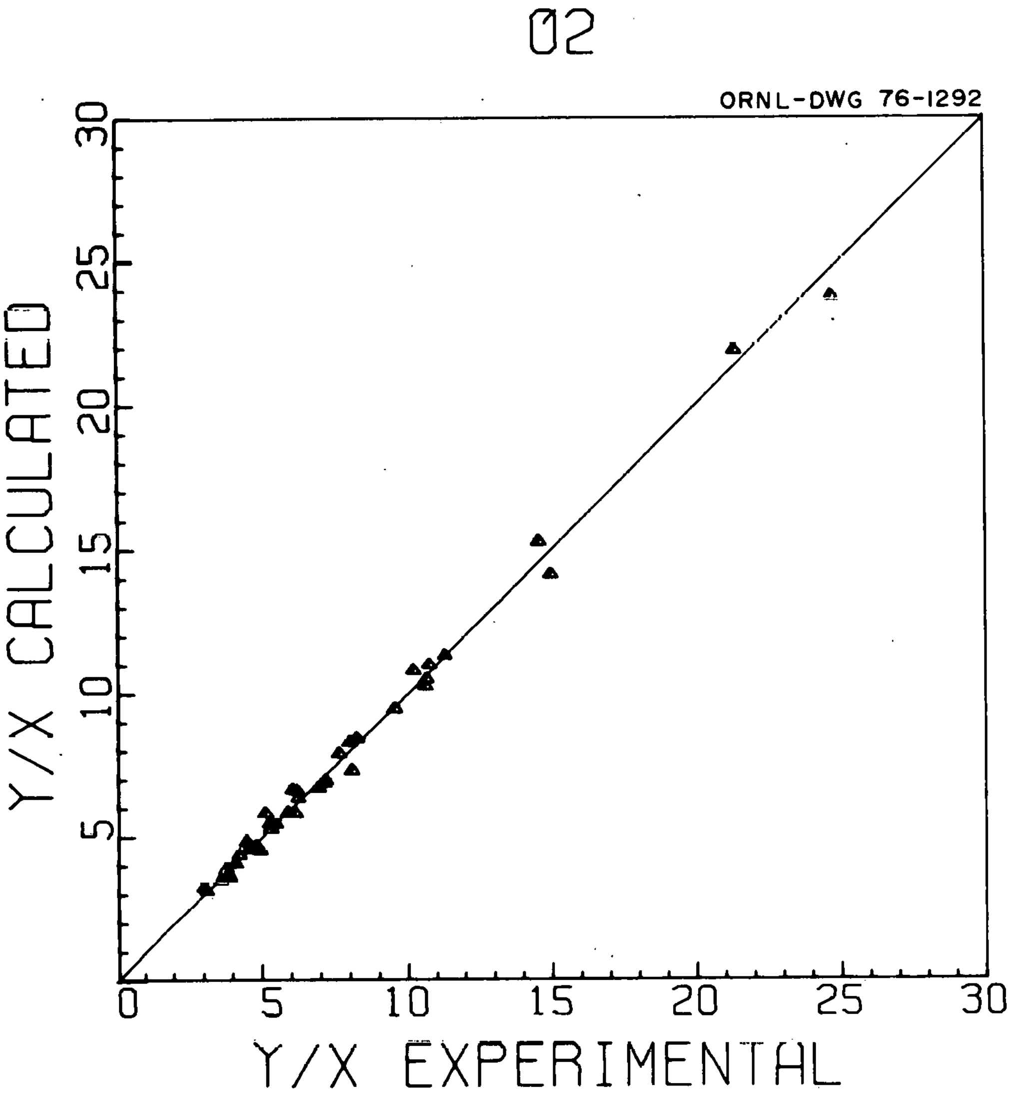

Fig. A-11. Equilibrium ratio comparisons for O_2 in CO_2.

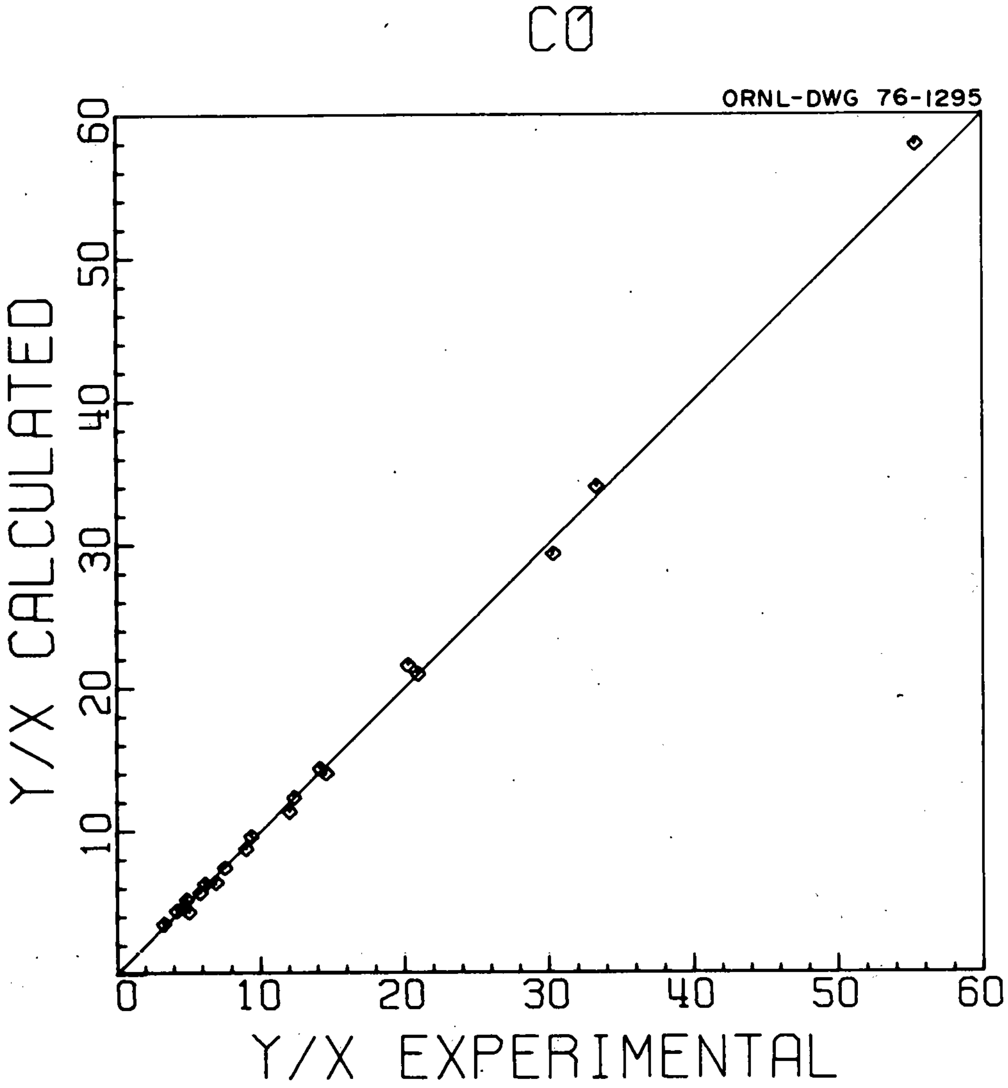

Fig. A-12. Equilibrium ratio comparisons for CO in CO_2.

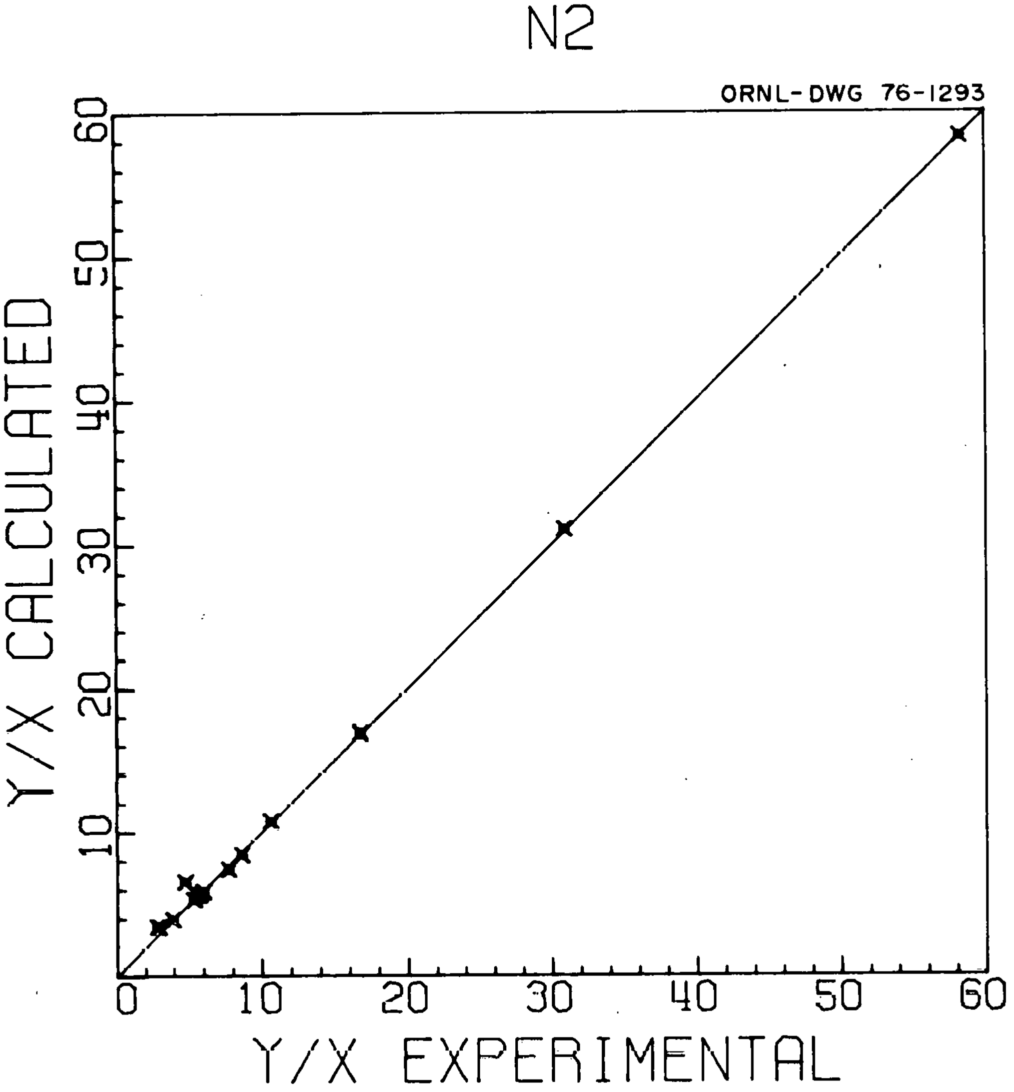

Fig. A-13. Equilibrium ratio comparisons for N_2 in CO_2.

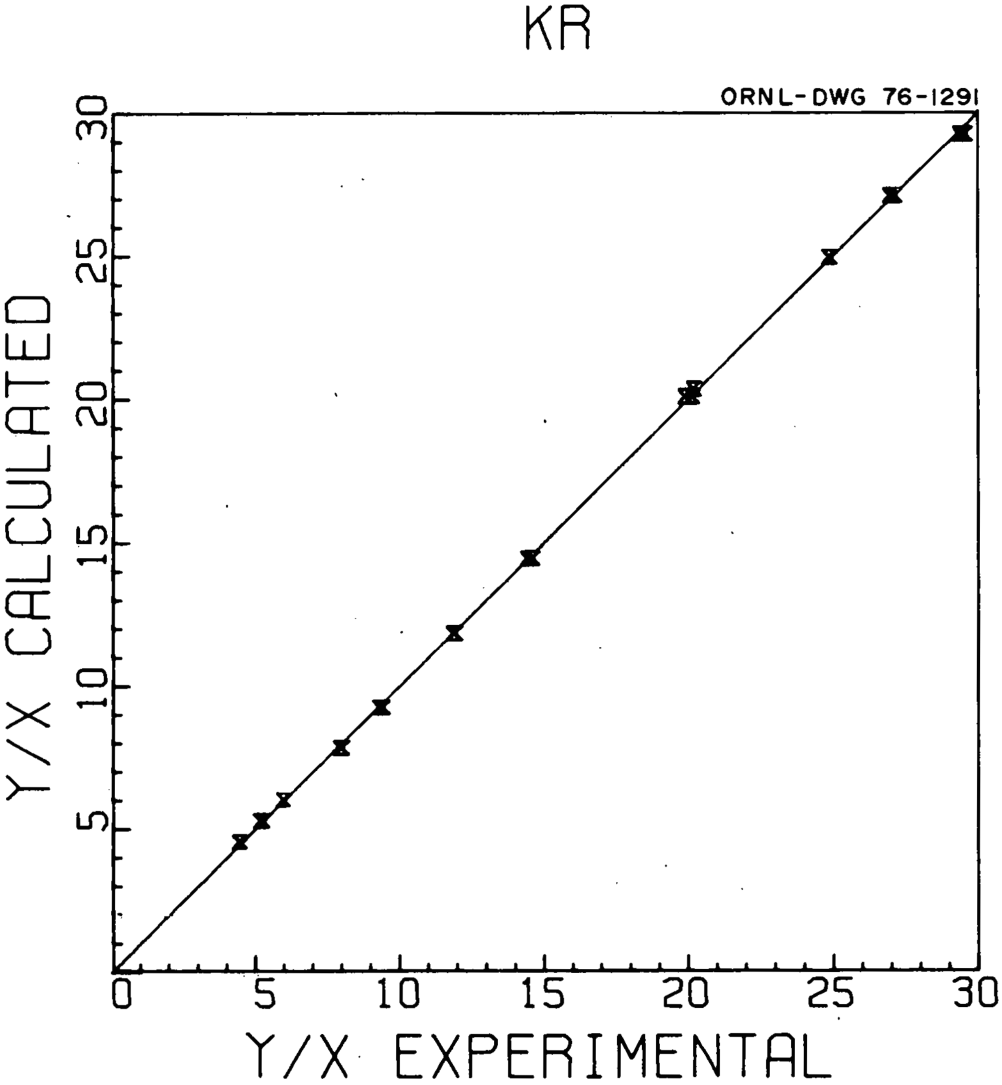

Fig. A-14. Equilibrium ratio comparisons for Kr in CO_2.

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APPENDIX B: COMPUTER PROGRAM

The following is a complete computer program provided for documentation and reference. It has been written for the IBM 360/91 (ORNL): PL/I Optimizing Compiler, Version 1 R2.2 PTF 60.

```
//XXXXXX JOB (XXXXX),'BIN X XXXXX',MSGLEVEL=1
/*ROUTE  PRINT LOCAL
//*CLASS CPU91=30S
/*ROUTE  XEQ   CPU1
// EXEC PLIXCLG,PARM.PLI='NEST',PARM.LKED='NOXREF,NOLIST',
// REGION.GO=270K
//PLI.SYSLIN DD SPACE=(80,(1700,100))
//PLI.SYSIN DD *


 THE FOLLOWING IS A TYPICAL MAIN OR CALLING PROGRAM


               /***** KALC COMPUTER STUDIES *****/
 GLASS:PROC OPTIONS(MAIN);  ON ENDFILE(SYSIN) GO TO HOUSE;
          DCL M STATIC INITIAL(6),Y(6),TC,TK,P,X(6);  ICALL=0;
 START:   GET LIST((Y(I) DO I = 2 TO 6),TC);
          TK=TC+273.15;  Y(1)=0.0;  Y(1)=1.0-SUM(Y);
          CALL EQUIL(ICALL,M,Y,TK,P,X,HG,HL,IBAD);  ICALL=1;
          PUT SKIP(2) DATA(TC,P,X,Y,HG,HL);  GO TO START;


 THE EQUIL PROCEDURE SHOULD BE INSERTED HERE


 HOUSE:  END GLASS;
/*
//GO.SYSIN DD *


 THE FOLLOWING IS A TYPICAL DATA SET


 7.2580E-06 3.9111E-01 3.5753E-02 3.1813E-02 1.7800E-05 -40.46
 3.8017E-06 1.8017E-02 1.2774E-03 1.0202E-03 4.0743E-06 -19.91
 0 .2224 0 0 0 -10
 0 .2201 0 0 0 -20
 0 .2117 0 0 0 -30
 0 .1485 0 0 0 -40


//
//
```

```
EQUIL:   PROC(ICALL,M,Y,TK,P,X,HG,HL,IBAD);
         DCL P1S,TK,TO STATIC INITIAL(233.15),P,M,ESTP,HG,HL,J,I,LL;
         DCL HE(M),HE1(M),HE2(M),Y(*),X(*),NPASS,DELH,DELP,NOSOL,SUMX1;
         DCL PHIG(M),GAM(M),DELHBAR(M),GSO(6) STATIC,SLCPE,VBAR(6),
             HS(M),VS,VS1,VCOR,GS(M),TSM(M),K(M) FLOAT,RT,SUMX,SUMX0;
         /***** IDEAL GAS HEAT CAPACITY CONSTANTS *****/
         DCL ALPHA(6) STATIC INITIAL
             (6.637,4.968,7.011,6.962,6.958,4.968);
         DCL BETA(6)  STATIC INITIAL
             (1.395E-3,0.0,-8.1E-4,-9.5E-5,-3.5E-5,0.0);
         DCL GAMMA(6) STATIC INITIAL
             (2.045E-5,0.0,2.8E-6,3.5E-7,1.5E-7,0.0);
         /***** COEFFICIENTS OF EXPANSION *****/
         DCL KAPA(6) FLOAT STATIC INITIAL
            (0,0,-1.028859E-2,3.854812E-2,-3.211558E-2,0);
         DCL IDENT(6) CHAR(6) STATIC INITIAL
             ('1= CO2','2=  XE','3=  O2','4=  CO','5=  N2','6=  KR');
         IF ICALL=1 THEN GO TO GETIT;
                      /***** INITIALIZE PROCEDURES *****/
         CALL HENRYS(1,M,VS,TK,HE);
         CALL RKWONG(1,M,Y,P,TK,PHIG,DELHBAR,DELH);
         CALL ACTCO(1,M,TK,X,GAM);
         CALL PMVOL(1,TK,VS,VBAR);
              /***** CALC IDEAL GAS ENTHALPIES AT -40 C *****/
         CALL HENRYS(2,M,VS,TO-.5,HE1);  CALL HENRYS(2,M,VS,TO+.5,HE2);
         DO I=2 TO M;
         GSO(I)=1.98726*(LOG(HE2(I))-LOG(HE1(I)))/(1/(TO-.5)-1/(TO+.5));
         END;  TSM=0;  TSM(1)=1;  P1S=VPFUNCT(TO);
         CALL RKWONG(2,M,TSM,P1S,TO,PHIG,DELHBAR,DELH);
         GSO(1)=DELH+3369.2;  /***** HEAT OF VAP FROM PERRY *****/
         PUT SKIP(2) DATA(GSO);  PUT PAGE;
          /***NOTE:  GSO(I=1,...,6) = IDEAL GAS ENTHALPIES AT -40 C***/
            /***3513.04*1128.74*-495.138*125.278*-930.111*139.805***/
GETIT:   HS,GS,DELHBAR=0;  GAM,K=1;  SUMX1=0.0;  NOSOL,IBAD=0;
         P1S=VPFUNCT(TK);  ESTP=P1S/Y(1);  P=ESTP;  RT=82.0574*TK;
         CALL HENRYS(2,M,VS,TK,HE);  TSM=0;  TSM(1)=1;
         CALL RKWONG(2,M,TSM,P1S,TK,TSM,DELHBAR,DELH);
DOPHI:   CALL RKWONG(2,M,Y,P,TK,PHIG,DELHBAR,DELH);  NPASS=0;
CPASS:   NPASS=NPASS+1;
         K(1)=GAM(1)*TSM(1)*P1S*EXP((VS*(P-P1S))/RT)/(P*PHIG(1));
         GS(1)=ALPHA(1)*(TK-TO)+BETA(1)*(TK*TK-TO*TO)/2+
              GAMMA(1)*(TK**3-TO**3)/3+GSO(1)-DELHBAR(1);
         HS(1)=279.0974416*(TK-TO)-1.104912498*(TK*TK-TO*TO)+
              1.570811188E-3*(TK**3-TO**3);
         CALL PMVOL(2,TK,VS,VBAR);  CALL HENRYS(2,M,VS1,TK+1,HE1);
         DO J=2 TO M;
            VCOR=(1+KAPA(J)*P1S)*(P-P1S)-KAPA(J)*(P*P-P1S*P1S)/2;
            VCOR=EXP(VCOR*VBAR(J)/RT);
            K(J)=(HE(J)*GAM(J)*VCOR)/(P*PHIG(J));
            GS(J)=ALPHA(J)*(TK-TO)+BETA(J)*(TK*TK-TO*TO)/2+
                 GAMMA(J)*(TK**3-TO**3)/3+GSO(J)-DELHBAR(J);
            HS(J)=DELHBAR(J)+GS(J)+1.9872*(LOG(HE1(J))-LOG(HE(J)))/
```

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                (1/(TK+1)-1/TK);  END;
         X=Y/K;  IF NPASS>1 THEN GO TO TESTX;
XVARY:   SUMX0=SUM(X);  CALL ACTCO(2,M,TK,X,GAM);  GO TO CPASS;
TESTX:   SUMX=SUM(X); IF ABS((SUMX0-SUMX)/SUMX)>1.0E-5 THEN GO TO XVARY;
         IF NOSOL=1 THEN GO TO BADEX;
         IF ABS(SUMX-1.0)<1.0E-5 THEN GO TO ENDEQ;
         IF ((SUMX-SUMX1)*(P-ESTP))=0 THEN DO;
            SUMX1=SUMX;  ESTP=P;  P=P/SUMX;  GO TO DOPHI;  END;
         IF ((SUMX-SUMX1)*(P-ESTP))<0 THEN GO TO DIVRX;
         SLOPE=(P-ESTP)/(SUMX-SUMX1);  SUMX1=SUMX;
         ESTP=P;  DELP=SLOPE*(SUMX-1);
         IF ABS(DELP)>0.1*P THEN DO;  DELP=SIGN(DELP)*0.1*P;  END;
         P=P-DELP;  GO TO DOPHI;
DIVRX:   P=ESTP;  NOSOL,IBAD=1;  GO TO DOPHI;
BADEX:   X=X/SUM(X);
         PUT SKIP EDIT('DIVERGING SOLUTION')(X(10),A);  GO TO ENDEQ;
PMVOL:   PROC(L,T,VS,VBAR);
         DCL T,RT,VS,VBAR(*),SCRAP,S(2) LABEL,J,I,VMB,VPB,L;
         DCL (A(6,6),B(6),R) STATIC;
         DCL (TC(6,6),PC(6),ZC(6),K(6,6) FLOAT,W(6),OMEGA(6),OMEGB(6),
              VC(6)) CTL;  GO TO S(L);
S(1):    ALLOCATE ZC,VC,TC,K,W INITIAL(0.225,0,0.021,0.041,0.040,0),
         PC INITIAL(72.8,57.6,49.8,34.5,33.5,54.3),
         OMEGA INITIAL(0.4184,0.4278,0.4278,0.4278,0.4278,0.4278),
         OMEGB INITIAL(0.0794,0.0867,0.0867,0.0867,0.0867,0.0867);
         TC,A,K=0;  ZC,VC=0;  R=82.0574;
         TC(1,1)=304.2;  TC(2,2)=289.7;  TC(3,3)=154.6;
         TC(4,4)=132.9;  TC(5,5)=126.2;  TC(6,6)=209.4;
          K(1,1)=     0;   K(1,2)=.0455;   K(1,3)=.0332;
          K(1,4)=.0020;    K(1,5)=.0133;   K(1,6)=.0042;
         DO I=1 TO 6;  ZC(I)=0.291-0.08*W(I);
            VC(I)=ZC(I)*R*TC(I,I)/PC(I);  B(I)=OMEGB(I)*R*TC(I,I)/PC(I);
            TC(I,1)=SQRT(TC(I,I)*TC(1,1))*(1-K(1,I));
            A(I,1)=0.25*(OMEGA(I)+OMEGA(1))*R*(TC(I,1)**1.5)*
                  (VC(I)+VC(1))/(0.291-0.04*(W(I)+W(1)));  END;
         PUT SKIP(2) DATA(A);  FREE ZC,VC,TC,PC,K;  RETURN;
S(2):    RT=R*T;  VMB=VS-B(1);  VPB=VS+B(1);
         DO I=1 TO 6;
           VBAR(I)=RT*(1+B(I)/VMB)/VMB;
           VBAR(I)=VBAR(I)-(2*A(I,1)-(A(1,1)*B(I))/VPB)/
                  (VS*VPB*SQRT(T));  SCRAP=RT/(VMB*VMB);
           SCRAP=SCRAP-A(1,1)*(2*VS+B(1))/(VS*VS*VPB*VPB*SQRT(T));
           VBAR(I)=VBAR(I)/SCRAP;  END;  END PMVOL;
VPFUNCT:PROC(T);  /*****MICHELS, PHYSICA,XVI(5),P501,1950*****/
         DCL LOGVP FLOAT,T,VP;
         LOGVP=24.61930-1353.202/T-8.142537*LOG10(T)+.006259156*T;
         VP=10.0**LOGVP;  RETURN(VP);  END VPFUNCT;
ACTCO:   PROC(L,M,T,X,GAM);  /***** EQS D3 & D4,ORNL/TM-5099 *****/
         DCL RT,GAM(*),X(*),S(2) LABEL,I,J,K;
         DCL L,M,T,SUM1,SUM2,A(6,6) STATIC;  GO TO S(L);
S(1):    A=0;  A(2,2)=0.0;  A(3,3)=992.6501;  A(4,4)=448.3456;
               A(6,6)=0.0;  A(5,5)=1817.661;
         DO I=2 TO M;  DO J=I+1 TO M;
            A(I,J)=(A(I,I)+A(J,J))/2;  A(J,I)=A(I,J);  END;  END;
         PUT SKIP(2) DATA(A);  RETURN;
S(2):    SUM1=0.0;  RT=1.98726*T;  DO J=2 TO M;  DO I=2 TO M;
         SUM1=SUM1+A(I,J)*X(I)*X(J);  END;  END;
         DO K=2 TO M;  SUM2=0.0;  DO I=2 TO M;
```

```
         SUM2=SUM2+X(I)*A(I,K);  END;
         GAM(K)=EXP((SUM1-2*SUM2)/RT);  END;
         GAM(1)=EXP(SUM1/RT);  RETURN;  END ACTCO;
HENRYS:  PROC(L,N,VS,T,H);  DCL S(2) LABEL,H(*),N,VS,T;
         DCL(A(6),B(6),C(6)) STATIC;  GO TO S(L);
S(1):    A=0;  B=0;  C=0;
         A(2)=29.96148;  B(2)=-3.670936;  C(2)=-1423.981;
         A(3)=108.2571;  B(3)=-15.98780;  C(3)=-3478.37C;
         A(4)=124.1770;  B(4)=-18.24561;  C(4)=-4316.308;
         A(5)=78.20484;  B(5)=-11.42092;  C(5)=-2194.547;
         A(6)=36.32377;  B(6)=-4.782289;  C(6)=-1185.152;  RETURN;
S(2):    CALL CDVOL(T,VS);  DO I=2 TO N;
         H(I)=A(I)+B(I)*LOG(T)+C(I)/T;  H(I)=EXP(H(I));  END;  RETURN;
CDVOL:   PROC(T,VS);  DCL T,TCMT,VS;  TCMT=304.15-T;
         VS=0.4638+1.206792E-1*TCMT**3.794458E-1+
            5.156581E-4*TCMT+1.289524E-6*TCMT*TCMT;
         VS=44.01/VS;  END CDVOL;  END HENRYS;
RKWONG:  PROC(L,M,Y,P,T,PHIG,DELHBAR,DELH);
         DCL P,RT,AM,BM,I,J,VG,EX;
         DCL R STATIC INITIAL(0.0820574),S(2) LABEL;
         DCL Y(*),PHIG(*),VBAR(M),DELHBAR(*);
         DCL (A(6,6),B(6)) STATIC;  DCL OMEGA(6) FLOAT STATIC INITIAL
            (0.4470,0.4278,0.4278,0.4278,0.4278,0.4278);
         DCL OMEGB(6) FLOAT STATIC INITIAL
            (0.0911,0.0867,0.0867,0.0867,0.0867,0.0867);
         DCL W(6) STATIC INITIAL(0.225,0.0,0.021,0.041,C.C40,0.0);
         DCL (ZC(6,6),TC(6,6),PC(6,6),VC(6,6),K(6,6) FLOAT) CONTROLLED;
         GO TO S(L);
S(1):    ALLOCATE TC,PC,VC,ZC,K;
         A=0;  ZC=0;  TC=0;  PC=0;  VC=0;  K=0;  EX=1/3;
         TC(1,1)=304.2;  TC(2,2)=289.7;  TC(3,3)=154.6;
         TC(4,4)=132.9;  TC(5,5)=126.2;  TC(6,6)=209.4;
         PC(1,1)= 72.8;  PC(2,2)= 57.6;  PC(3,3)= 49.8;
         PC(4,4)= 34.5;  PC(5,5)= 33.5;  PC(6,6)= 54.3;
         K(1,1)=0.0000;  K(1,2)=0.0455;  K(1,3)=0.0332;
         K(1,4)=0.0020;  K(1,5)=0.0133;  K(1,6)=0.0042;
         DO I=1 TO M;  DO J=I TO M;
            ZC(I,J)=0.291-0.04*(W(I)+W(J));  END;  END;
         DO I=1 TO M;  VC(I,I)=ZC(I,I)*R*TC(I,I)/PC(I,I);
            B(I)=OMEGB(I)*R*TC(I,I)/PC(I,I);  END;
         DO I=1 TO M;  DO J=I+1 TO M;
            VC(I,J)=((VC(I,I)**EX+VC(J,J)**EX)/2)**3;
            TC(I,J)=SQRT(TC(I,I)*TC(J,J))*(1-K(I,J));
            PC(I,J)=ZC(I,J)*R*TC(I,J)/VC(I,J);
            VC(J,I)=VC(I,J);  TC(J,I)=TC(I,J);  PC(J,I)=PC(I,J);  END;  END;
         DO I=1 TO M;  DO J=I TO M;
            A(I,J)=(OMEGA(I)+OMEGA(J))*R*R*(TC(I,J)**2.5)/(2*PC(I,J));
            A(J,I)=A(I,J);  END;  END;  PUT PAGE DATA(A);
         FREE ZC,TC,PC,VC,K;  RETURN;
S(2):    AM=0;  RT=R*T;  BM=0;  DO I=1 TO M;  BM=BM+Y(I)*B(I);
         DO J=1 TO M;  AM=AM+Y(I)*Y(J)*A(I,J);  END;  END;  CALL VOLG;
         DELH=RT*(1.5*AM/(BM*RT*T**0.5)*LOG((VG+BM)/VG)+1-P*VG/RT);
         DELH=(1.98726/0.0820574)*DELH;
         DO I=1 TO M;  PHIG(I)=FUNCT(I);
            VBAR(I)=VFUNCT(I);  DELHBAR(I)=HFUNCT(I);  END;
FUNCT:   PROC(I);  /***** EQ B11, ORNL/TM-5099 *****/  DCL X;
         X=0;  DO J=1 TO M;  X=X+Y(J)*A(J,I);  END;
         X=((-2*X)/(R*BM*T**1.5))*LOG((VG+BM)/VG)+LOG(VG/(VG-BM))+
```

```
           B(I)/(VG-BM)+AM*B(I)*(LOG((VG+BM)/VG)-BM/(VG+BM))/
           (R*T**1.5*BM*BM)-LOG(P*VG/(R*T));  X=EXP(X);  RETURN(X);
         END FUNCT;
VFUNCT:  PROC(I);  /***** EQ B14, ORNL/TM-5099 *****/  DCL X,XX,J,T12;
         T12=SQRT(T);  X=0;  DO J=1 TO M;  X=X+Y(J)*A(J,I);  END;
         X=-2*X/(T12*VG*(VG+BM));  X=X+(RT/(VG-BM))*(1+B(I)/(VG-BM));
         X=X+AM*B(I)/(T12*VG*(VG+BM)**2);  XX=RT/(VG-BM)**2;
         XX=XX-(AM/T12)*(2*VG+BM)/(VG*VG*(VG+BM)**2);
         X=X/XX;  RETURN(X);  END VFUNCT;
HFUNCT:  PROC(I);  /***** EQ B13, ORNL/TM-5099 *****/  DCL X,J;
         X=0;  DO J=1 TO M;  X=X+Y(J)*A(J,I);  END;
         X=(2*X-AM*B(I)/BM)/BM;  X=X*LOG((VG+BM)/VG);
         X=X+(AM/BM)*(VG*B(I)-VBAR(I)*BM)/(VG*(VG+BM));
         X=1.5*X/SQRT(T)+RT-P*VBAR(I);
         X=X*1.98726/R;  RETURN(X);  END HFUNCT;
VOLG:    PROC;  /***** SOLVES R-K USING CUBIC SOLUTION  *****/
         DCL A,B,C(4),D(4),PHI,VGAS(3),A3,B3,L,M,MM,RR,K,T12;
         L=2;  M=3;  T12=SQRT(T);  C(1)=1;  C(2)=-RT/P;
         C(3)=-BM**2-RT*BM/P+AM/(T12*P);  C(4)=-AM*BM/(P*T12);
         D(1)=1;  D(2)=0;  D(3)=(3*C(3)-C(2)**L)/3;
         D(4)=(27*C(4)-9*C(2)*C(3)+2*C(2)**M)/27;
         RR=(D(3)/3)**M+(D(4)/2)**L;  IF RR<0 THEN DO;  MM=1;
         PHI=ATAND(SQRT(-(D(3)**M/27+D(4)**L/4)/(D(4)**L/4)));
         DO K=0 TO 2;  VGAS(K+1)=2*SQRT(-D(3)/3)*COSD(PHI/3+120*K);
            VGAS(K+1)=VGAS(K+1)-C(2)/3;  END;
         VG=MAX(VGAS(1),VGAS(2),VGAS(3));  END;
         ELSE DO;  MM=0;  A3=(-D(4)/2+SQRT(RR));  B3=(-D(4)/2-SQRT(RR));
         A=ABS(A3)**(1/3);
         IF A3<0 THEN A=-A;  B=ABS(B3)**(1/3);  IF B3<0 THEN B=-B;
         VG=A+B-C(2)/3;  END;  RETURN;  END VOLG;
         END RKWONG;  ENDEQ:  HG=SUM(GS*Y);  HL=SUM(HS*X);  END EQUIL;
```

APPENDIX C: CORRELATION AND EQUATIONS

Redlich-Kwong Equation of State:[3]

$$\frac{Pv}{RT} = \frac{v}{v - b} - \frac{a}{RT^{3/2}(v + b)} \qquad \text{(C-1)}$$

where, for pure components,

$$a = \frac{\Omega_a R^2 T_c^{2.5}}{P_c} \qquad \text{(C-2)}$$

and

$$b = \frac{\Omega_b R T_c}{P_c} \qquad \text{(C-3)}$$

If the equation is fitted such that the first and second partial derivatives of pressure with respect to volume are zero at the critical point, $\Omega_a = 0.4278$ and $\Omega_b = 0.0867$. For CO_2 fitted to the saturated vapor curve, $\Omega_a = 0.4470$ and $\Omega_b = 0.0911$; and for CO_2 fitted to the saturated liquid curve, $\Omega_a = 0.4184$ and $\Omega_b = 0.0794$.

Mixture rules given by Eqs. (29) - (37) are used for multicomponent gas phase calculations. Mixture rules given by Eqs. (20) - (26) are used for dilute liquid phase calculations.

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APPENDIX D: DATA

Data considered for inclusion into the model formulation are listed and referenced in this appendix.

Table D-1. Summary of gas-liquid equilibrium data considered for CO_2-x systems

System	Temperature range (°C)	Pressure range (atm)	Reference	Investigator
CO_2-Xe	-54.8 to 10.4	$P^s_{CO_2}$	10	Notz et al. (1973)
CO_2-O_2	0	41 to 116	11	Muirbrook and Prausnitz (1965)
	-55 to 0	31 to 146	12	Zenner and Dana (1963)
	-40 to 25	36 to 126	13	Kaminishi and Toriumi (1966)
	-50 to 10	10 to 130	14	Fredenslund and Sather (1970)
	-49.4 to -4	7 to 142	15	Fredenslund et al. (1972)
CO_2-CO	-50 to 10	10 to 130	16	Kaminishi et al. (1968)
	-50 to 10	8 to 140	17	Christiansen et al. (1974)
CO_2-N_2	0	48 to 116	11	Muirbrook and Prausnitz (1965)
	-55 to 0	12 to 137	12	Zenner and Dana (1963)
	-40 to 25	50 to 125	13	Kaminishi and Toriumi (1966)
	0 to 25	0 to 181	18	Abdullaev (1939)
	-55 to 0	41 to 155	19	Pollitzer and Strebel (1924)
CO_2-Kr	-53 to 22	$P^s_{CO_2}$	10	Notz et al. (1973)

APPENDIX E: NOMENCLATURE

a	Mixture constant for the Redlich-Kwong equation
a_{ij}	Interaction constant in the Redlich-Kwong equation
b	Mixture constant for the Redlich-Kwong equation
b_i	Pure component constant for the Redlich-Kwong equation
C_p^o	Ideal gas heat capacity, cal/g-mole·°K
C_s^L	Heat capacity of saturated liquid CO_2, cal/g-mole·°K
f	Fugacity, atm: $\bar{f}_i^G$, gas phase component i; $f_1^{(P_1^s)}$, pure liquid CO_2 at saturation pressure P_1^s; $f_1^{(0)}$, pure liquid CO_2 at zero pressure
g^{*EX}	Excess molar Gibbs free energy based on ideal dilute solution, cal/g-mole
h	Enthalpy, cal/g-mole: h_i^o, component i in ideal gas state; $h_{i_o}^o$, component i in ideal gas state at reference temperature; h_m^o, mixture in ideal gas state; h_o^G, real gas at reference temperature; h^L, liquid
$H_{i,1}^{(P_1^s)}$	Henry's law constant for component i in pure solvent at its saturated vapor pressure and temperature, atm
$\bar{H}_i^G$	Partial molar enthalpy of mixture component i in the gas state, cal/g-mole; $\bar{H}_i^\infty$, partial molar enthalpy of component i at infinite dilution in liquid CO_2, cal/g-mole
Δh_o^{VAP}	Heat of vaporization at reference temperature of -40°C, cal/g-mole

M	Number of system components (6)
n	Total number of moles; n_i moles of component i
P	Pressure, atm: P_1^s, saturated CO_2 vapor pressure
R	Gas constant
T	Temperature, °K unless otherwise noted; T_o, reference temperature of -40°C
$\bar{V}$	Partial molar volume, cc/g-mole: $\bar{V}_i$, component i; $\bar{V}_i^\infty$, component i at infinite dilution; $\bar{V}_{i_o}^\infty$, component i at infinite dilution and reference temperature of -40°C
v	Molar volume of gas mixture in the Redlich-Kwong equation
v_1^L	Molar volume of pure liquid CO_2, cc/g-mole; $v_{1_o}^L$, at reference temperature of -40°C
x	Liquid phase mole fraction
y	Vapor phase mole fraction
α_{ij}	Coefficient in expansion of excess free energy representing interaction of components i and j
α,β,γ	Coefficients in heat capacity equation for ideal gas
$\bar{\beta}_i$	Average coefficient of expansion of partial molar volume for component i
γ	Activity coefficient: $\gamma_i^{*(0)}$, component $i \neq 1$, corrected to zero reference pressure, unsymmetric convention; $\gamma_1^{(0)}$, pure CO_2 corrected to zero reference pressure
ϕ	Fugacity coefficient: ϕ_i^G, gas phase component i

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