D-468

ORNL-5122

The Distribution of Xenon Between Gaseous and Liquid CO.

R. D. Ackley
K. J. Notz

BLANK PAGE

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 \$4.00, Microfilm \$2.25

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Energy Research and Development Administration/United States Nuclear Regulatory Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or 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.

ORNL-5122
Dist. Category UC-77

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

THORIUM UTILIZATION PROGRAM (189a OR945)

Reprocessing Development
Task 200

THE DISTRIBUTION OF XENON BETWEEN GASEOUS AND LIQUID CO₂

R. D. Ackley
K. J. Notz

Date Published: October 1976

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or 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.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

MASTER

TABLE OF CONTENTS

ABSTRACT.	1
1. INTRODUCTION	1
2. APPARATUS AND PROCEDURES	3
2.1 Group I (Isothermal) Y_{Xe}/X_{Xe} Measurements	3
2.1.1 Apparatus	3
2.1.2 Procedures	7
2.2 Group II (Nonisothermal) Y_{Xe}/X_{Xe} Measurements	12
2.2.1 Apparatus	12
2.2.2 Procedures	15
3. RESULTS AND DISCUSSION	20
3.1 Group I Y_{Xe}/X_{Xe} Values and Related Results	20
3.1.1 Y_{Xe}/X_{Xe} Values	20
3.1.2 Henry's Law Constants	24
3.1.3 Bunsen and Ostwald Coefficients	26
3.1.4 Heat of Solution	26
3.2 Group II Y_{Xe}/X_{Xe} Values	29
4. ACKNOWLEDGEMENTS	29
5. REFERENCES	32
6. APPENDIX A	34

THE DISTRIBUTION OF XENON BETWEEN GASEOUS AND LIQUID CO₂

R. D. Ackley

K. J. Notz

ABSTRACT

The distribution of xenon at low concentrations between gaseous and liquid CO₂ was measured over essentially the entire liquid range of CO₂. These measurements involved using a collimated radiation-detection cell to determine the relative quantities of ¹³³Xe-traced xenon in the separate phases contained in a vertical cylinder under isothermal conditions. The results are expressed in terms of a distribution ratio (mole fraction of xenon in the gaseous phase divided by mole fraction of xenon in the liquid phase) which decreased from 7.53 at -54.8°C to 1.10 at 30.5°C. These data were used to calculate various other solubility-related quantities.

1. INTRODUCTION

The method being developed for reprocessing spent fuel from high-temperature gas-cooled reactors (HTGRs) involves burning the graphite fuel blocks and recovering uranium and thorium from the residue. The burner off-gas, predominantly CO₂, will be contaminated with various radioactive species of which ³H, ⁸⁵Kr, ¹²⁹I, ¹³¹I, and ²²⁰Rn are considered the more significant. As presently planned, the ³H (as H₂O), the ^{129,131}I (as I₂), and ²²⁰Rn are to be removed from the off-gas by using solid sorbents. Following compression and partial liquefaction of the CO₂, the ⁸⁵Kr is to be removed by the KALC process.¹⁻⁴ The acronym KALC is derived from the first step of the process, Krypton Absorption in Liquid CO₂; subsequent steps are fractionation, stripping, and concentration. The projected operating conditions are about 20 atm, and -40 to -15°C.⁵

In order to provide a basis for KALC process design calculations, a laboratory method was developed for determining the distribution of krypton between gaseous and liquid CO₂, and a detailed set of measurements were made which covered the temperature range of -52.8 to +29.1°C.⁶

Triple point and critical temperature values for CO_2 are -56.59 and 31.05°C , respectively.⁷ The results were expressed in terms of a distribution ratio $Y_{\text{Kr}}/X_{\text{Kr}}$, which is defined as the ratio of the mole fraction of krypton in the gaseous phase to the mole fraction of krypton in the liquid phase, and which decreases as the temperature increases.

The burner off-gas will also contain fission-product xenon. However, the behavior and disposition of xenon in a KALC-type system should be far less crucial than that of ^{85}Kr . This is because HTGR fuel-cooling times of at least 5 months are anticipated, and all radioactive xenon isotopes of significance here have relatively short half-lives. On the other hand, there would be a very small amount of xenon radioactivity (mainly due to $^{131\text{m}}\text{Xe}$). Also, the atomic concentration of xenon would be roughly four times that of krypton.⁵ As a related consideration, xenon is more volatile than CO_2 but less volatile than krypton. Although information concerning the relative volatilities is either known or can be estimated, actual Xe- CO_2 distribution data are desired for a more dependable calculation of the apportionment of xenon between the krypton-enriched and krypton-depleted streams. Accordingly, equilibrium measurements have been made for the Xe- CO_2 system. The temperature range over which these results were obtained was -54.8 to $+30.5^\circ\text{C}$. This range, as well as that for the Kr- CO_2 system, is more extensive than needed for present KALC design purposes.

Experimentally, these distribution ratio results were obtained by gamma counting of the saturated vapor and liquid phases in a vertical cylinder containing CO_2 and ^{133}Xe -labeled xenon. The cylinder was maintained under isothermal conditions, and the liquid level was usually near the midpoint of the cylinder. The possibility of bias in the xenon (and krypton) equilibrium values, as determined by this experimental method, was considered with regard to the following postulated situations: (1) a significant film of condensed CO_2 on the wall of the cylinder above the liquid level, and (2) an appreciable amount of mist in the vapor. Either of these situations would have resulted in an exaggerated counting rate for the vapor phase, since the concentration of ^{133}Xe (or ^{85}Kr) would have been higher in the film or in the mist than in the

vapor phase itself. Therefore, an additional group of Xe-CO₂ distribution ratio measurements were made in which a portion of the vapor phase at a temperature about 10°C higher than that of the liquid phase was gamma counted. Any film or mist effects previously encountered should have been virtually eliminated by this modification in technique. These results can also be applied to the Kr-CO₂ system because these effects are governed by the CO₂ properties. Since the solubility of xenon in liquid CO₂ is greater than that of krypton, xenon provides the greater sensitivity for delineating film and mist effects.

2. APPARATUS AND PROCEDURES

Basically, the distribution of xenon between gaseous and liquid CO₂ was determined by using an in situ counting technique with ¹³³Xe as the tracer. For the most part, the equipment and procedures that were used and/or developed in the earlier Kr-CO₂ investigation were also applied in the Xe-CO₂ studies.

The various Xe-CO₂ distribution measurements that were made may be divided into two main groups: (I) the CO₂ cylinder containing the two separate phases was maintained at isothermal conditions throughout its length; and (II) a portion of the region in the cylinder corresponding to the vapor phase was maintained at a temperature about 10°C higher than that of the region corresponding to the liquid phase.

2.1 Group I (Isothermal) Y_{Xe}/X_{Xe} Measurements

2.1.1 Apparatus

A schematic diagram of the apparatus used for these measurements is shown in Fig. 1. Cylinder A was fabricated from a section of stainless steel tubing of approximately 0.069-in. wall thickness. The length of the principal cylindrical section was almost 11 in., and the internal volume of the cylinder was about 100 cm³. A photograph of cylinder A and cylinder B, which is to be described later, is shown in Fig. 2.

Provisions for maintaining constant temperatures in the bath over the range of -60 to +40°C included a sensitive thermoregulator, an immersion heater connected to an electronic relay for intermittently

ORNL DWG 76-1392

Fig. 1. Schematic diagram of apparatus used for determination of Xe-CO₂ distribution ratios.

PHOTO 2535-75A

Fig. 2. Photograph of cylinders A and B.

actuating the heater as required, an auxiliary cold bath (at $\sim -80^{\circ}\text{C}$), and a circulation pump. The latter served two purposes: (1) to circulate the fluid (trichloroethylen e) of the main bath through a heat exchanger (coil of copper tubing) in the auxiliary bath and back to the main bath; and (2) to promote good mixing in the main bath, particularly in the zone about cylinder A.

Bath temperatures were measured using a four-junction, copper-constantan thermopile calibrated to $\pm 0.01^{\circ}\text{C}$ by the Instrumentation and Controls Division (ORNL); the reference junctions were maintained at 0°C with a water-ice bath. The thermopile was encased in a thin-walled metal tube, and the junctions were located adjacent to cylinder A at about the location indicated in Fig. 1. The corresponding emf was generally measured with a potentiometer of a type which resulted in an estimated temperature accuracy of about 0.05°C . A less sensitive potentiometer used during the initial stages of this work gave an estimated temperature accuracy of only about 0.2°C . A few measurements made with the junctions adjacent to the part of cylinder A that contained the vapor indicated no significant vertical temperature gradients.

A single-channel analyzer was used for the ^{85}Kr counting and for the ^{133}Xe counting in the earlier stages of the present work. Two modes of ^{133}Xe counting with this analyzer were employed: (1) over the photon energy range $> 10\text{ keV}$, and (2) over a section of the 81-keV photopeak. The number of counts accumulated during an appropriate clock-time period were read off a decade scaler. According to counting data obtained in the earlier Kr- CO_2 investigation,⁶ the dead-time corrections for the counting-rate range in the present investigation (and for this analyzer) were negligible and were not applied.

The majority of the results presented in this report correspond to the use of a multichannel analyzer, which replaced the single-channel analyzer. The newer analyzer (Technical Measurement Corporation Model 401 B6, 400 channels) was operated in conjunction with a resolver-integrator and printer which enabled either manual or automatic totaling of the counts in a selected group of channels. For present purposes, the channels comprising the 81-keV photopeak were utilized. With the multichannel analyzer, counting rates were obtained on a live-time basis (as opposed to clock time); therefore, no dead-time correction was required.

The detector used with both analyzers was a 1-7/8-in. diam, 1-in. thick, NaI (Tl-doped)-scintillation crystal. It was located within a 2-in. lead shield. The horizontal collimation slit was 2 x 2 x 1/4 in.

2.1.2 Procedures

Charging of cylinder A. Prior to performing a group of determinations, a predetermined quantity of CO_2 was added to cylinder A by using a pressure-vacuum manifold and a liquid nitrogen or dry ice--trichloroethylene bath. The quantity added was such that the liquid level would be fairly near the midpoint of the cylinder during the determinations. Following transfer of a suitable amount from a commercial cylinder into an auxiliary pressure vessel, the CO_2 was prepurified by condensing it at the temperature of dry ice--trichloroethylene slush and then flashing off the vapors to vacuum. Available information indicated that the CO_2 in the commercial cylinder was 99.5% pure and had a dew point of -40°C .

The ^{133}Xe -labeled xenon was added either before or after the CO_2 . In the latter case, cylinder A was immersed in liquid nitrogen to reduce the pressure to practically zero so that the xenon could be transferred. The practice of using liquid nitrogen for either CO_2 or Xe transfers was, however, eventually discontinued because of the possibility that the thermal shocks might result in sufficient metal fatigue to cause failure of cylinder A. The ^{133}Xe -labeled xenon, which was obtained from the ORNL Isotopes Development Center, was used without further treatment. In addition to ^{133}Xe , it typically consists of ^{131}Xe , ^{132}Xe , ^{134}Xe , ^{136}Xe , and extraneous substances such as H_2 , CO_2 , and N_2 , which, at the concentrations involved, are not pertinent to this work. Considering both phases as a whole, the xenon to CO_2 molar ratio varied over an estimated range of 0.5×10^{-6} to 1.5×10^{-6} .

Obtaining counting data for determining $Y_{\text{Xe}}/X_{\text{Xe}}$. In performing a Y/X determination, cylinder A was first placed in a horizontal position in the bath with one end on a pivot and the other end attached to an oscillating device by a wire. The latter end was then successively raised and lowered about 15° above and below the horizontal position, which allowed the liquid CO_2 to flow in alternate directions periodically and hastened the attainment of equilibrium. This operation was continued for at least 30 min and usually for at least 45 min after the bath

temperature had become stabilized at a constant value; 45 min had been found adequate in the earlier work.⁶ An extension rod was then attached to cylinder A, which was next positioned as shown in Fig. 1, taking care to avoid having any part of the cylinder emerge from the bath fluid. The distance from the external edge of the collimation slit to the center of the positioned cylinder A was about 2-1/8 in.

Following the positioning of cylinder A, a brief period was allowed to elapse for drainage of CO₂ from the upper section of the cylinder. Gamma counting of either the liquid or vapor phase was then initiated, with the collimated slit being directed toward a central section of the respective zone. Depending on the amount and distribution of ¹³³Xe in the cylinder, counting periods varied from 1 to 15 min. For any given Y/X determination, however, the counting-time periods were uniform. In general, at least two counting rates were measured for each of the two phases, and background counting rates for the corresponding detector locations were obtained in conjunction with these X/Y determinations.

Evaluation of attenuation factors for CO₂. In calculating the Y/X values, correction was made for background and decay (for 5.27-day half-life). In addition, correction was made for the varying ¹³³Xe-photon attenuation encountered because the CO₂ density varied with temperature and two phases were involved. In the case of these isothermal measurements, no attenuation correction was made relative to the variation in trichloroethylene density with temperature since, for each temperature, this density was the same in both the upper and the lower regions of the bath. The CO₂ attenuation correction was made in terms of an attenuation factor, U, which is defined as the fractional attenuation in CO₂ at a density of 1 g/cm³ of either the > 10 keV or the 81 (and 80)-keV photons under the geometrical situation that pertained. A linear relationship between the degree of attenuation and density was assumed.

Data for evaluating the attenuation factor for the 81-keV results were obtained as follows:

- (1) Cylinder A was evacuated and about 0.02 cm³ (STP) of ¹³³Xe-labeled xenon was added.
- (2) Counting data (corresponding to 81-keV photopeak) were obtained for both gas- and liquid-counting positions at +28.1,

-20.6, and -54.4°C. The background- and decay-corrected counting rates decreased moderately with decreasing temperature due to the increased attenuation that resulted from the increase in trichloroethylene density with decreasing temperature.

- (3) Carbon dioxide was added to yield only gas phase with a density of 0.22 g/cm^3 at 28.1°C; care was taken to avoid any loss of ^{133}Xe .
- (4) Counting data were obtained for both gas- and liquid-counting positions at 28.1°C.
- (5) Additional CO_2 was added to provide a suitable liquid level for counting both liquid and gas at low temperatures.
- (6) Counting data were obtained for both counting positions at -20.6 and -54.4°C.

The 28.1°C data of steps (2) and (4) enabled a direct U evaluation of $0.122 \text{ cm}^3/\text{g}$. Cylinder A was weighed frequently during this series of operations and no untoward weight changes were observed. The -20.6 and -54.4°C data of steps (2) and (6) enabled two less direct evaluations of U. This involved a counts-balance method in which the weight of CO_2 and the cylinder volume were used to calculate the relative volumes of gas and liquid. The -20.6°C data yielded a U value of $0.080 \text{ cm}^3/\text{g}$, and the -54.4°C data yielded a U value of $0.071 \text{ cm}^3/\text{g}$. The average of the three values, $0.091 \text{ cm}^3/\text{g}$, was used in calculating the 81-keV Y/X values.

Essentially the same procedure had been used earlier to obtain the U value of $0.060 \text{ cm}^3/\text{g}$ that was used to calculate the > 10-keV Y/X's. The earlier procedure had also been employed to obtain a U value for 81 keV of $0.092 \text{ cm}^3/\text{g}$; this is in excellent agreement with the value that was adopted for final use. The > 10-keV U value probably should be at least as high as the 81-keV U value considering the photon energies involved and published attenuation coefficient vs energy curves;⁸ however, because the > 10 keV counting mode was discontinued and, in each case, 81-keV data had also been obtained, this apparent discrepancy has not been pursued. An error in U results in more error in Y/X at a lower temperature than at a higher temperature. For example,

for the lowest pertaining temperature (-54.8°C), an error in U of $0.01 \text{ cm}^3/\text{g}$ corresponds to an error in Y/X of 1.3%.

Development of vertical alignment correction factors. Another source of error was associated with an indicated gradual or possibly sudden shift in the vertical alignment of cylinder A at some time during the course of the following measurements: (1) the earlier evaluations of U ; and (2) the determination of the Y/X values (shown in Table 1, p. 21) exclusive of those at temperatures of -54.4 , -20.6 , and $\geq 27.0^{\circ}\text{C}$. Initially, for the case of no liquid phase present, the ratio of the counting rate for the liquid position to that for the gas position was 1.011 for the $> 10\text{-keV}$ mode and 1.020 for the 81-keV mode. At the conclusion of the specified measurements, the ratio for the 81-keV mode was 1.060. For purposes of calculation, an alignment correction factor L was used which was assumed to change linearly with time, from 1.011 to 1.060 for the $> 10\text{-keV}$ mode or from 1.020 to 1.060 for the 81-keV mode.

For the Y/X determinations at -54.4 , -20.6 , and $\geq 27.0^{\circ}\text{C}$, and for the later evaluation of U , the vertical positioning of cylinder A was realigned so that L was in the range of 1.005 to 1.011, depending on temperature. The possible and slight variation of L with temperature was ignored in calculating the earlier U 's and $Y_{\text{Xe}}/X_{\text{Xe}}$'s.

Calculation of Group I distribution ratios or $Y_{\text{Xe}}/X_{\text{Xe}}$'s. Following the approach used previously,⁶ the relative volatility⁹ (RV) for these systems is defined as

$$\text{RV} = \frac{Y_1/Y_{\text{CO}_2}}{X_1/X_{\text{CO}_2}}, \quad (1)$$

where

Y_1 = mole fraction of krypton or xenon in the gas phase,

X_1 = mole fraction of krypton or xenon in the liquid phase,

Y_{CO_2} = mole fraction of CO_2 in the gas phase, and

X_{CO_2} = mole fraction of CO_2 in the liquid phase.

The right side of Eq. (1) may also be referred to as a separation factor,¹⁰ and this terminology has been used on a number of occasions in connection with this work.

At very low concentrations of krypton or xenon, Y_{CO_2} and X_{CO_2} are essentially unity, and Eq. (1) simplifies to

$$RV \sim Y_i/X_i. \quad (2)$$

In this and in the preceding report,⁶ the quotient Y_i/X_i is termed a distribution ratio.

Considering the experimental situation and xenon only, Eq. (2) may be extended as follows:

$$Y_{Xe}/X_{Xe} = \frac{n_{Xe,g}/(n_{Xe,g} + n_{CO_2,g})}{n_{Xe,l}/(n_{Xe,l} + n_{CO_2,l})}, \quad (3)$$

where

$n_{i,j}$ = number of roles of component i in the counted volume of phase j , with the counted gas volume being equal to the counted liquid volume.

The quantities $n_{Xe,g}$ and $n_{Xe,l}$ were negligible relative to the respective quantities, $n_{CO_2,g}$ and $n_{CO_2,l}$. The ratio $n_{Xe,g}/n_{Xe,l}$ is equal to the experimentally determined counting-rate ratio (gas/liquid) after appropriate correction, and the ratio $n_{CO_2,g}/n_{CO_2,l}$ is equal to the corresponding CO_2 density ratio (saturated vapor/liquid) at the temperature of the measurement. Accordingly, the following equation was used for calculating the Group I Y_{Xe}/X_{Xe} values:

$$Y_{Xe}/X_{Xe} = \frac{LC/\rho_g(1 - U\rho_g)}{C_g/\rho_l(1 - U\rho_l)}, \quad (4)$$

where

L = alignment correction factor;

C_g, C_l = background- and decay-corrected counting rates for gas and liquid phases, respectively;

ρ_g, ρ_l = density of saturated CO_2 vapor and corresponding CO_2 liquid, respectively, at the temperature of the Y/X measurement (g/cm^3); and

U = attenuation factor (cm^3/g).

The CO_2 densities were based on those tabulated by Vukalovich and Altunin for the liquid/vapor equilibrium line.¹¹

Determination of counting rate vs counting position profiles. In general, counting rates were measured for only the usual gas-counting and liquid-counting positions that were at or near 6 cm, and 21 cm above the base of cylinder A.* Its principal cylindrical section was 27.8 cm long. On occasion, more detailed counting was performed, and, in two cases, highly detailed counting rate vs counting position profiles were obtained. These are shown in Figs. 3 and 4 and indicate that satisfactory counting-rate plateaus existed in the vicinity of the usual counting positions. However, in the case of the 22.0°C data, a slightly different selection of counting positions was employed because of an indicated higher liquid level in the cylinder, as confirmed by calculation. (The liquid level is calculated by using the cylinder height and volume, the weight of CO₂, and the gas and liquid densities at the temperature of the measurement.)

2.2 Group II (Nonisothermal) Y_{Xe}/X_{Xe} Measurements

2.2.1 Apparatus

A new cylinder, cylinder B, was fabricated for use in this phase of the investigation and is shown in Fig. 2. The principal cylindrical sections of both A and B were practically identical, but cylinder B was equipped with two thermocouples (Chromel-Alumel, grounded junction, 12 in. long, 1/16 in. OD) which extended into the cylinder such a distance that their tips were 7.1 cm from the top of the cylinder. (In this and subsequent references to lengths from the top of cylinder B, the length is measured from the top of the principal cylindrical section.) One thermocouple junction was located near the axis of the cylinder, and the other was at the wall. Their locations corresponded to a counting position (for the gas) of 20.75 cm. The previous liquid-counting position, near 6 cm, was used again, and the bath temperature was measured with the four-junction, copper-constantan thermopile. The Chromel-Alumel thermocouples were calibrated against this thermopile, and the three emf's were measured, via a switch box, using the more sensitive potentiometer referred to earlier. While the bath temperatures were probably still accurate to about 0.05°C, the gas temperatures obtained with the single-junction thermocouples were probably only accurate to about 0.2°C. Otherwise, the equipment was the same or similar to that used in the

*Excluding the lower positioning extension.

ORNL DWG 76-1409

Fig. 3. Counting rate - counting position data at -52.6°C.

Fig. 4. Counting rate - counting position data at 22.0°C.

Group I measurements, including the main bath, the auxiliary bath, the detector and shield, and the multichannel analyzer.

2.2.2 Procedures

Charging of cylinder B. No important changes were made in charging procedures and related details from those described previously; however, research grade xenon was added with the ^{133}Xe -labeled xenon for some of the subsequent measurements.

Arrangement of bath and liquid CO_2 levels. In these measurements, an experimental objective was to maintain the upper cylinder and gas phase, in the gas-counting zone, at a temperature (or temperatures) moderately higher than the bath or liquid CO_2 temperature. This was accomplished, to the extent of $\sim 10^\circ\text{C}$, by maintaining the bath at a level about 5-1/8 in. below the top of cylinder B. The amount of CO_2 added for the Y/X measurements was such that the CO_2 liquid levels should have been 6-15/16 to 7-1/16 in. below the top of cylinder B, depending on the temperature of the measurement.

Determination of counting-rate ratio in the absence of CO_2 Because the trichloroethylene level was below the zone used for gas counting, but above that used for liquid counting, the counting rate for the gas was less affected by attenuation than was that for the liquid. Accordingly, a number of measurements were made to determine the ratio of gas counting rate/liquid counting rate as a function of temperature over the range $+10$ to -20°C for the case in which no CO_2 is present. Such measurements were made both before and after the Group II Y/X determinations and with xenon at low pressures (roughly 0.1 or 0.2 torr) and at a higher pressure (about 1 atm). Where necessary, carrier xenon was added to the ^{133}Xe -labeled xenon to obtain the desired pressure.

In treating these data, correction was made by means of the ideal gas law for the variation in density that resulted from the upper zone being at the higher temperature, so that each of the calculated ratios corresponded to a uniform density. The values obtained for the density-corrected counting-rate ratio, which is designated $R_{t/b}$, are shown as a function of the bath temperature in Fig. 5. The indicated decrease in $R_{t/b}$ with increasing bath temperature is ascribed to the decrease in attenuation by the trichloroethylene as its density decreases. The observed small differences between the three sets of data are considered relatively insignificant.

Fig. 5. Density-corrected counting-rate ratio vs bath temperature.

Obtaining counting data for determining Y_{Xe}/X_{Xe} --temperature approached from below. The earlier procedure of attaining equilibrium was not considered to be feasible in the case of the Group II measurements because of the necessity of maintaining a portion of the gas phase at a higher temperature and due to the presence of the thermocouples. Instead, cylinder B was simply placed in the vertical position employed during counting; the bath level was maintained as already described. Two different modes of approach to the final temperature (or temperature of the determination) were used. The procedure corresponding to the case of the "temperature approached from below," which involved six determinations covering a temperature range of -40 to -20°C , will be described first.

With cylinder B in place, the bath temperature (and, with it, the liquid CO_2 temperature) was lowered to a value about 10°C lower than the final temperature; this lower temperature was maintained for 1 to 2.5 hr. The bath temperature was then raised to the final temperature, which was maintained for 1 to 5 hr. After a period (at the final temperature) which varied from about 0.5 to about 2.5 hr, the Xe-CO_2 system was indicated to be at or near equilibrium (based on the near-constancy of the gas-counting rate). The counting data actually used for the Y/X evaluations were obtained during the latter part of the holding period at the final temperature. In certain cases, the counting data were obtained in such a sequence (e.g., gas counting, liquid counting, and then gas counting again) and over a sufficiently short time that decay corrections were unnecessary. Background counting rates were obtained as usual.

Obtaining counting data for determining Y_{Xe}/X_{Xe} --temperature approached from above. Two determinations were made at -21°C under this condition. With cylinder B in place, the bath temperature was lowered to the temperature of the determination and maintained for about 6 hr. During this time, the gas counting rate increased, essentially monotonically, although the increase rate decreased as time elapsed. The gas counting rate was measured frequently, and the liquid counting rate was measured near the end of the holding period. Each of the two latter rates involved was based on at least two individual measurements.

In order to provide counting rates for the evaluation of Y/X , the following techniques were used for each of the two determinations. A plot was made of the background- and decay-corrected gas counting rate as a function of reciprocal time; since all but the first few points fell on a straight line, the latter was extrapolated to a reciprocal time of zero, which corresponds to an equilibrium time of infinity. One of these plots is shown in Fig. 6. This extrapolation provided the gas counting rate that was used. The calculated liquid counting rate for an equilibrium time of infinity was obtained by compensating the measured liquid counting rate for the increase in the gas counting rate as obtained by extrapolation. Thus, the liquid counting rate used in each of these particular Y/X calculations was lower than the measured counting rate. The compensating adjustment involved: (1) using the plot to obtain the gas counting rate at the midpoint of the time period during which the liquid counting rate was measured; and (2) performing a counts balance to obtain the desired liquid counting rate. The calculated volumes of gaseous and liquid CO_2 were used in the second step.

Calculation of Group II distribution ratios, or $Y_{\text{Xe}}/X_{\text{Xe}}$. The lower layer of the gas phase, representing a thickness of about 1-7/8 in., was below the bath level. Thus, the gaseous CO_2 immediately adjacent to the liquid CO_2 should have been at virtually the same temperature as the liquid. However, the gas that was counted was about 10°C higher than the liquid. This higher temperature was measured using the two Chromel-Alumel thermocouples with junctions located as already described. The vertical temperature gradients were probably close to being linear in this region of cylinder B. Also, with regard to the horizontal gradient, the average axial temperature and the average temperature at or near the wall did not differ by more than 0.2°C during the later part of a Y/X determination, at which time the more important counting data were obtained. The average of these two average temperatures was used as the temperature of the gas counted.

Since the temperature of the gas that was counted was higher than the temperature of the liquid, a density correction factor was used to convert the gas counting rate to a value more nearly corresponding to gas in equilibrium with and at the same temperature as the liquid. No actual P-V-T data were found for superheated CO_2 under the particular conditions

Fig. 6. Gas counting rate-reciprocal time plot for determination of γ_{Xe}/X_{Xe} at -20.5°C .

of temperature and pressure involved in these measurements. Therefore, a generalized compressibility chart was used that was based on tables of Lydersen, Greenhorn, and Hougen¹² for a critical compressibility of 0.27. Based on one set of critical values,¹³ the critical compressibility of CO₂ is 0.2745. The density correction factor, designated F_d , is based on the gas law $PV = ZnRT$ and has the following form:

$$F_d = \frac{\rho_g}{\rho_g'} = \frac{Z'T'}{ZT} \quad (5)$$

where ρ , Z , and T are density, compressibility factor, and absolute temperature, respectively; unprimed quantities refer to gas at the temperature of the liquid; and primed quantities refer to gas in the zone that was counted.

A density-corrected counting-rate ratio, $R_{t/b}$, is also involved in relating Y/X and the counting rates. The equation which includes this ratio and the preceding factor, and which was used for the Group II Y/X calculations, follows:

$$Y_{Xe}/X_{Xe} = \frac{F_d C_g' / \rho_g (1 - U_{Dg} / F_d)}{R_{t/b} C_l / \rho_l (1 - U_{Dl})} \quad (6)$$

where

C_g' = observed or deduced counting rate for gas at a temperature about 10°C higher than the liquid, background- and decay-corrected where necessary, and

C_l = observed or deduced counting rate for liquid, background- and decay-corrected where necessary.

3. RESULTS AND DISCUSSION

3.1 Group I Y_{Xe}/X_{Xe} Values and Related Results

3.1.1 Y_{Xe}/X_{Xe} values

The Group I Y/X values or distribution ratios are presented in Table 1. They are also shown graphically in Fig. 7 as a semilog plot of the distribution ratio vs the temperature. This particular type of plot was made because the analogous Kr-CO₂ results, when similarly plotted, approximated a straight line for temperatures below 22°C.

Table 1. Distribution ratios for the Xe-CO₂ system—Group 1 results

Temperature (°C)	Analyzer ^a	Photon energy ^b (keV)	Distribution ratio (Y _{Xe} /X _{Xe})
-54.8	M	81	7.53
-54.4	M	81	7.38
-52.6	M	81	7.24
-50.4	M	81	6.96
-46.2	M	81	5.90
-46.1	M	81	6.00
-36.3	S	>10	4.80
-36.3	S	81	4.80
-26.9	M	81	3.74
-20.6	M	81	3.28
-18.0	S	>10	3.16
-18.0	S	81	3.06
- 9.3	S	>10	2.76
- 9.2	S	81	2.78
- 0.2	S	>10	2.32
- 0.2	S	81	2.33
10.3	S	81	1.94
10.4	S	>10	1.95
10.4	M	81	1.87
19.4	M	81	1.59
20.8	S	81	1.50
20.9	S	>10	1.59
21.0	M	81	1.57
21.1	M	81	1.57
22.0	M	81	1.44
22.9	M	81	1.49
24.9	M	81	1.42
27.0	M	81	1.31
29.1	M	81	1.22
30.0	M	81	1.18
30.5	M	81	1.10

^aM denotes multichannel analyzer; S, single channel analyzer.

^bTracer was Xe-133.

Fig. 7. Xenon distribution between gaseous and liquid CO₂.

However, the Xe-CO₂ results (Fig. 7) approximate linearity over a less extended region, and the results tend to correspond to an S-shaped curve. The upward curvature at low temperatures is in qualitative agreement with that exhibited by the theoretical separation factor-temperature data for the Xe-CO₂ system as calculated by Davis for the case of nonideal solution--nonideal vapor.¹⁴ The downward curvature at the higher temperatures (also observed for the Kr-CO₂ data) is in agreement with the expectation that the distribution ratio must approach unity as the system temperature approaches the critical temperature of CO₂. The average background- and decay-corrected counting rates and the alignment correction factors on which these measured Y/X values for the Xe-CO₂ system are based are tabulated in Appendix A.

When compared on an equal-temperature basis, the experimental Xe-CO₂ distribution ratios are lower than the analogous Kr-CO₂ values, which is in accord with the relative volatilities. The quotient Xe-CO₂ distribution ratio/Kr-CO₂ distribution ratio is about 0.25 at -50°C and increases with temperature, finally approaching a value of unity near the critical temperature.

The theoretical calculations of Davis¹⁴ also included the cases of nonideal solution--ideal vapor and ideal solution--ideal vapor (in addition to nonideal solution--nonideal vapor) for the temperature range of -55 to +5°C. In general, the agreement between the experimental distribution ratio--temperature curve and any of the theoretical Xe-CO₂ separation factor--temperature curves is poor, especially at temperatures below 0°C. In this region, the experimental values are moderately to considerably higher (more so at the lower temperatures) than the theoretical values for any of the three cases. At lower temperatures, the experimental Kr-CO₂ distribution ratios are also higher than the variously calculated theoretical Kr-CO₂ separation factors.⁶ The discrepancies between experimental and theoretical values prompted, in part, the extension of this investigation to include the Group 11 measurements, the results of which are presented in Sect. 3.2.

3.1.2 Henry's law constants

Henry's law may be written as:

$$p_2 = k_H X_2, \quad (7)$$

where

p_2 = partial pressure of the low-concentration component in the gas phase,

k_H = Henry's law constant for a given temperature, and

X_2 = mole fraction of the low-concentration component dissolved in the liquid phase.

By mathematical manipulation similar to that given previously,⁶ Eq. (7) can be put into the following form for the Xe-CO₂ system:

$$k_H = (Y_{Xe}/X_{Xe})p_{CO_2}, \quad (8)$$

where p_{CO_2} is the vapor pressure of CO₂ at the temperature corresponding to the Y/X value. Implicit in Eq. (8) are the assumptions that the compressibility factors for xenon and CO₂ in the vapor are equal, that the concentration of xenon in the vapor is negligible relative to that for CO₂, and that the CO₂ partial pressure is given by the vapor pressure of the pure substance. Values of k_H for the Xe-CO₂ system, calculated by using Eq. (8) together with Y/X values from the smoothed curve of Fig. 7, are presented in Table 2. The CO₂ vapor pressures were based on the tabulation of Vukalovich and Altunin.¹¹

As expected, the Henry's law constants for the Xe-CO₂ system are considerably lower than the analogous values for the Kr-CO₂ system. The latter values ranged from 174 atm at -50°C to 189 atm (not necessarily a maximum) at -20°C, and then down to 117 atm at 28°C. Thus, both groups of values pass through a maximum, with that for xenon occurring at a higher temperature (between 10 and 25°C as compared to between -30 and -10°C for krypton). According to Eq. (8), replacing xenon by krypton when appropriate, and the behavior of Y/X at higher temperatures, the Henry's law constant k_H for both systems should approach a value of 72.87 atm, the critical pressure of CO₂, as the critical temperature, 31.05°C, is approached. The observed behavior is consistent with the preceding in both cases.

Table 2. Calculated Henry's law constants (k_H 's) for the Xe-CO₂ system

Temperature (°C)	Distribution ratio (Y_{Xe}/X_{Xe})	k_H (atm)
- 50	6.53	44.0
- 40	5.08	50.4
- 30	4.03	56.8
- 20	3.31	64.3
- 10	2.76	72.1
0	2.34	80.4
10	1.94	86.1
20	1.58	89.3
25	1.39	88.3
30	1.15	81.8
(31.05) ^a	(1.00)	(72.87)

^aCritical temperature of CO₂.

3.1.3 Bunsen and Ostwald coefficients

The Bunsen absorption coefficient, α , is defined as the volume of gas referred to STP (0°C, 1 atm) dissolved by unit volume of the solvent at the pertaining temperature and under a partial pressure of the gas of 1 atm.¹⁵ The coefficient, α , may be calculated using the following equation:

$$\alpha = 22,414 \cdot \rho_{\text{CO}_2} / 44.01 \cdot k_H \quad (9)$$

where the units of ρ_{CO_2} , and k_H are atm^{-1} , g/cm^3 , and atm, respectively.

The Ostwald coefficient of solubility β is defined as the volume of gas, measured under the temperature and pressure (partial) at which it dissolves, per unit volume of the liquid.¹⁵ This coefficient may be calculated from the Bunsen coefficient using the following equation:

$$\beta = \alpha T / 273.15, \quad (10)$$

where T is the absolute temperature (K). The derivation of Eq. (10) assumes ideal gas-law behavior. Consequently, β , as calculated for the Xe and Xe-CO₂ systems using this equation, should not be regarded as corresponding too precisely to the coefficient as defined.

Values of these coefficients, based on the k_H values of Table 2 and calculated using Eqs. (9) and (10), are presented in Table 3. These coefficients are higher than the analogous Kr-CO₂ coefficients and exhibit a considerably greater dependency on temperature.

3.1.4 Heat of solution

A van't Hoff-type of equation can be used to relate the differential heat of solution ΔH_{sol} to the Bunsen coefficient;¹⁶ a variation of such an equation follows:

$$\ln \alpha = (-\Delta H_{\text{sol}}/RT) + c, \quad (11)$$

where ΔH_{sol} is assumed to be independent of temperature, and c is a constant. If ΔH_{sol} is indeed constant, a plot of $\ln \alpha$ vs T^{-1} should be a straight line with slope $-\Delta H_{\text{sol}}/R$. A plot of $\ln \alpha$ vs T^{-1} for the Xe-CO₂ system using the α values of Table 3 is shown in Fig. 8. The points for temperatures $\leq 20^\circ\text{C}$ ($10^3 T^{-1} \geq 3.411$) approximate a straight line. The calculated slope was based on only the $+20$ and -50°C points, leading to a calculated $-\Delta H_{\text{sol}}$ of 2047 cal/mole. A related quantity, but one which is not actually comparable,¹⁷ is the latent heat of vaporization of Xe at the normal boiling point (approximately -108°C). For this quantity, the value 3100 cal/mole has been reported.¹⁸

Table 1. Calculated and experimental coefficients, α , and solubility coefficients, β , for CO_2 in water.

Temperature (°C)	α (atm ⁻¹)	β (atm ⁻¹)
-50	13.51	10.20
-40	11.20	8.61
-30	9.62	8.10
-20	8.10	7.50
-10	6.94	6.90
0	5.88	6.30
10	5.11	5.70
20	4.50	5.10
25	4.12	4.70
30	3.69	4.10
(37.00)	(3.27)	(3.60)

ORNL DWG 76-1415

Fig. 8. Plot of $\ln a$ vs reciprocal absolute temperature for Xe-CO₂ system.

The analogous plot for the Kr-CO₂ system,⁶ including the calculated point corresponding to the critical temperature of CO₂, is shown in Fig. 9. The apparently divergent behavior for the two systems in the vicinity of the critical point may be an artifact resulting from the underlying assumptions and/or boundary conditions implicit in Eq. (11). However, in both graphs the actual data extrapolate to the independent point at the critical temperature, this point being determined solely by the properties of CO₂, thus indicating internal self-consistency in the data and in the calculation of α .

3.2 Group II Y_{Xe}/X_{X_2} Values

In determining these values, the portion of the gas phase that was gamma counted was maintained at a higher temperature than that of the liquid and the gas immediately adjacent to it. This was done in an effort to eliminate or at least substantially reduce any film or mist effects that may have been encountered in the isothermal determinations of Y/X . The results are presented in Table 4, which also includes distribution ratios taken from the smoothed curve of Fig. 7 for comparison. The two sets of results are in good agreement, thus indicating that the Xe-CO₂ distribution ratio data of Table 1 (or Fig. 7) and the previously reported Kr-CO₂ distribution ratio data⁶ were not significantly affected by film and/or mist effects.

4. ACKNOWLEDGEMENTS

The authors wish to express their appreciation to D. C. Watkin, Engineering Division, for designing some of the pressure vessels used in this work, and for following their construction and pressure review.

Fig. 9. Plot of $\ln \alpha$ vs reciprocal absolute temperature for Kr- CO_2 system.

Table 4. Distribution ratios for the Xe-CO₂ system--comparison of Group II and Group I results

Liquid temperature ^a (°C)	Vapor temperature ^b (°C)	Approach to target temperature	Distribution ratio (Y_{Xe}/X_{Xe})	
			Group II results	Group I results ^c
-20.6	-12.5	From below	3.30	3.35
-20.7	-12.9		3.35	3.36
-20.5	-12.6		3.27	3.34
-21.0	- 8.9		3.19	3.38
-30.5	-21.1		4.02	4.08
-39.7	-28.1	From above	5.08	5.05
-20.6	-12.9		3.39	3.35
-20.5	-11.3		3.33	3.34

^aThe temperature of principal interest with respect to the corresponding Group II result.

^bFor the zone used in gamma counting.

^cFor the corresponding temperature in the left column. (The second and third columns are not applicable to these values.)

5. REFERENCES

1. K. J. Notz, An Overview of HTGR Fuel Recycle, ORNL/TM-4747 (January 1976).
2. D. E. Ferguson, P. A. Haas, and R. E. Leuze, "Quantitative Recovery of Krypton from Gas Mixtures Mainly Comprising Carbon Dioxide," U. S. Patent 3,742,720 (July 3, 1973).
3. M. E. Whatley, R. W. Glass, P. A. Haas, A. B. Meservey, and K. J. Notz, "Decontamination of HTGR Reprocessing Off-Gases," pp. 86-99 in Proceedings of the Twelfth AEC Air Cleaning Conference, Oak Ridge, 28-31 August 1972, CONF-720823, Vol. 1.
4. R. W. Glass, H. D. Cochran, Jr., D. M. Levins, J. W. Snider, D. C. Watkin, W. M. Woods, and M. E. Whatley, System Features and Component Descriptions for the Unit Operations Off-Gas Decontamination Facility, ORNL/TM-4596 (February 1975).
5. R. W. Glass, H. W. R. Beaujean, H. D. Cochran, Jr., P. A. Haas, D. M. Levins, and W. M. Woods, "Development of the Krypton Absorption in Liquid Carbon Dioxide (KALC) Process for HTGR Off-Gas Reprocessing," pp. 232-45 in Proceedings of the Thirteenth AEC Air Cleaning Conference, San Francisco, 12-15 August 1974, CONF-740807, Vol. 1.
6. K. J. Notz and A. B. Meservey, The Solubility of Krypton in Liquid CO₂, ORNL-5121 (June 1976).
7. M. P. Vukalovich and V. V. Altunin, Thermophysical Properties of Carbon Dioxide, translation ed. by D. S. Gaunt, pp. 76, 92, Collet's, London and Wellingborough, 1968.
8. R. D. Evans, The Atomic Nucleus, pp. 713-15, McGraw-Hill, New York, 1955.
9. Perry's Chemical Engineer's Handbook, 4th ed., p. 13-2, McGraw-Hill, New York, 1963.
10. C. J. King, Separation Processes, p. 25, McGraw-Hill, New York, 1971.
11. M. P. Vukalovich and V. V. Altunin, Thermophysical Properties of Carbon Dioxide, translation ed. by L. S. Gaunt, pp. 243-44, Collet's, London and Wellingborough, 1968.

12. Perry's Chemical Engineer's Handbook, 4th ed., pp. 3-218, 4-50, McGraw-Hill, New York, 1963.
13. M. P. Vukalovich and V. V. Altunin, Thermophysical Properties of Carbon Dioxide, translation ed. by D. S. Gaunt, p. 92, Collet's, London and Wellingborough, 1968.
14. W. Davis, Jr., Calculated Liquid-Vapor Equilibria in the Systems--CO₂-Xe and CO₂-Kr at -55 to +5°C, ORNL/TM-3622 (December 1971).
15. Samuel Glasstone, Textbook of Physical Chemistry, 2nd ed., p. 694, D. Van Nostrand, New York, 1946.
16. Ibid., p. 695.
17. Samuel Glasstone, Thermodynamics for Chemists, pp. 326-27, D. Van Nostrand, New York, 1947.
18. Argon, Helium, and the Rare Gases, ed. by Gerhard A. Cook, p. 347, Interscience, New York, 1961.

6. APPENDIX A

COUNTING RATES AND ALIGNMENT CORRECTION FACTORS FOR GROUP I
 Y_{Xe}/X_{Xe} VALUES

These are given in Table A-1 in the same order as that used for Table 1, Sect. 3.1.1. The counting rates, which are average values in most cases, are corrected for background and decay but not for alignment or attenuation, and each pair is for the counting-time period of 1 min, 4 min, or longer. As discussed in Sect. 2.1.2, the alignment correction factor L for the majority of the results was assumed to change linearly with time, from 1.0110 to 1.0605 for the > 10 keV counting mode, and from 1.0196 to 1.0605 for the 81 keV counting mode. The preceding does not apply to the results for -54.4 , -20.6 , and $\geq 27.0^\circ\text{C}$. For these particular results, a time-independent L was used that varied somewhat with temperature. However, any small variation corresponding to the narrow temperature range of 27.0 to 30.5°C was ignored.

Table A-1. Counting rates and L's corresponding to Group I results

Temperature (°C)	Energy (keV)	Relative background- and decay- corrected counting rates		L ^a
		Gas	Liquid	
-54.8	81	29,017	281,282	1.0380
-54.4	81	12,040	114,354	1.0111
-52.6	81	23,728	220,388	1.0466
-50.4	81	112,891	978,647	1.0382
-46.2	81	63,401	543,971	1.0369
-46.1	81	113,887	955,649	1.0382
-36.3	>10	760,317	5,528,970	1.0114
-36.3	81	92,994	657,973	1.0198
-26.9	81	89,992	586,101	1.0366
-20.6	81	17,939	103,127	1.0088
-18.0	>10	118,322	664,794	1.0162
-18.0	81	34,044	193,349	1.0237
- 9.3	>10	306,158	1,454,812	1.0219
- 9.2	81	163,797	753,624	1.0285
- 0.2	>10	117,112	472,299	1.0168
- 0.2	81	54,934	216,242	1.0241
10.3	81	242,623	758,465	1.0276
10.4	>10	793,985	2,512,892	1.0205
10.4	81	77,169	250,607	1.0305
19.6	81	220,867	564,646	1.0511
20.8	81	145,794	360,961	1.0269
20.9	>10	1,287,459	3,037,156	1.0200
21.0	81	90,063	217,563	1.0527
21.1	81	103,012	247,509	1.0525
22.0	81	114,057	279,436	1.0398
22.9	81	105,672	240,296	1.0525
24.9	81	219,910	460,670	1.0513
27.0	81	59,417	108,879	1.0047
29.1	81	109,361	174,782	1.0047
30.0	81	67,859	99,199	1.0047
30.5	81	105,638	143,207	1.0047

^aAlignment correction factor.