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The Solubility of Krypton in Liquid CO₂

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Reprocessing Development

THE SOLUBILITY OF KRYPTON IN LIQUID CO₂

K. J. Notz
A. B. Meservey*

* Retired

JUNE 1976

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ABSTRACT

The solubility of krypton in liquid CO₂ was measured experimentally over essentially the entire liquid range of CO₂, from -53 to 29°C. A tracer technique using ⁸⁵Kr was employed, and equilibrated gas-liquid samples were analyzed in situ with a collimated counter. Dilute concentrations of krypton were used, and the data are expressed as a distribution ratio, Y_{Kr}/X_{Kr} , the log of which is nearly linear with respect to temperature from the lowest temperature to about 20°C, above which the values fall off rapidly toward a value of unity at the critical temperature. The numerical values obtained for the distribution ratio increase from 1.44 at 29°C to 29.4 at -53°C.

1. INTRODUCTION

The reprocessing of spent HTGR fuel releases large quantities of CO₂ containing small amounts of ⁸⁵Kr, which may have to be removed before the CO₂ is discharged to atmosphere.¹ The preferred method to accomplish this removal of ⁸⁵Kr is the KALC process.^{2,3} The acronym is derived from the first step in this process, Krypton Absorption in Liquid CO₂; subsequent steps are fractionation and stripping. The KALC process is currently in the final stages of engineering-scale development.⁴⁻⁹ During the early stages of paper studies related to this process,¹⁰ information was needed on the distribution of Kr between gaseous and liquid CO₂, which prompted the experimental study described in this report.

Initially, krypton solubility was calculated, at first assuming ideality of both phases, and later correcting for non-ideality in the liquid phase and then also for non-ideality in the gaseous phase (see Sect. 4.2). The results varied rather widely, depending on the assumptions, and it was

deemed necessary to obtain experimental data. The first attempts were based on a sampling-and-analysis procedure, which caused considerable difficulties, and was therefore abandoned in favor of the in situ counting procedure which is the experimental basis of the work described in this report. After our work was started, we became aware of similar work being done at KFA Jülich and of some Kr distribution data which they had obtained by a sampling method.^{11,12}

From a more general point of view, data of this nature are of interest from theoretical considerations, because they provide checkpoints against which solution theories can be tested. In this context, the present study is of considerable interest since it deals with a rare gas solute and a highly non-ideal solvent and because it covers almost the entire liquid range of the solvent, from the triple point to the critical temperature. In this regard, subsequent work¹³ on the solubility of xenon in liquid CO₂ provides pertinent and complementary data.

2. EXPERIMENTAL

2.1 General Method

The krypton distribution between gaseous and liquid CO₂ was measured at various temperatures over the entire liquid range of CO₂ by comparing the gamma activities from ⁸⁵Kr in equal volumes of the two phases. The krypton tracer (~ 100 mCi) was added to a 1-in.-diameter stainless steel cylinder approximately half full of liquid CO₂, and equilibrated between the two phases. Activities were measured in situ, through the cylinder wall, by means of collimated gamma beams and a scintillation counter. Two gamma energy ranges were used - the range above 0.4 MeV, consisting chiefly of the 0.51 MeV peak; and the range above 40 keV, which included the lower energy bremsstrahlung as well.

2.2 Equipment

A schematic diagram of the apparatus is shown in Fig. 1. The assembly was operated in a fume hood because of the toxicity of the trichloroethylene (TCE) used in the cold bath and because of the possibility of leakage of ⁸⁵Kr.

- A - Counterweight
- B - Lead-shielded scintillation counter
- C - Cylinder in counting position
- C' - Cylinder in equilibrating position
- D - Controlled temperature bath
- E - Motor-driven oscillator

- F - Circulating pump
- G - Dry ice/solvent cold reservoir
- H - Temperature controller
- I - Sensing element
- J - 250 watt heater

Fig. 1. Schematic drawing of equipment for measuring krypton solubility.

A photograph of the assembly and associated instrumentation is shown in Fig. 2.

2.2.1 Controlled-Temperature Cold Bath (D)

This was constructed of 16 gage welded aluminum sheet, in the form of an open tank 10 in. wide, 15 in. long, and 18 in. high, insulated with 2 in. of pressed cork except for the left end. For accurate lateral placement of the counter and shield (pig) assembly, this end was insulated with glued layers of two 1/2-in. layers of cork and one 1/4-in. layer of plywood; also, this end of the box was made of 1/4-in. aluminum sheet for rigidity. The top of the bath was covered by removable 1-in. Styrofoam slabs, which were wrapped in aluminum foil to protect them from solvent vapors.

2.2.2 Dry Ice Reservoir (G)

A dry ice/TCE bath maintained at dry ice temperature (-78°C) provided the primary refrigerant for the cold bath (D). This was a cylindrical stainless steel vessel 11 in. diameter x 16 in. high with 2 in. of insulation.

2.2.3 Pump and Cooling Coil (F)

A stainless steel Eastern centrifugal pump, model D-11, was fitted with 3/8-in. copper tubing to circulate TCE from the cold bath through 10 coils in the dry ice reservoir. Flow through the reservoir was metered, and a bypass loop was provided. The pump also provided circulation in the cold bath. Metered flows of TCE for maintaining the desired temperatures were achieved by means of a rotameter and needle valve, whose feed was filtered to prevent clogging. A Fulflow filter with a Honeycomb filter tube 175 mm x 67 mm OD, 25 mm ID was used. Initial rapid cooldown was achieved by bypassing the rotameter and filter.

2.2.4 Precision Mercury/Thallium Thermoregulator (I)

This was a JUMO model MS DBP, with a range of -59 to 40°C . This regulator could be set manually within 1 or 2° of a desired temperature,

Fig. 2. Photograph of equipment for measuring krypton solubility.

and, once set, would hold the set-point temperature within ± 0.03 .

2.2.5 Temperature Controller (H)

Lapine electronic relay, 20 amp., which was actuated by the thermostat.

2.2.6 Immersion Heater (J)

Stainless steel knife blade type, 250 W, 115 V, deriving power via the temperature controller.

2.2.7 Precision Temperature Measurement

A four-junction, copper-constantan thermopile was used versus a water-ice reference junction. The thermopile had been previously calibrated to $\pm 0.01^\circ\text{C}$ and a Honeywell model 2732 potentiometer was used for precision readout. The constancy of temperature control was monitored continuously via the same thermopile reading through a Mosely potentiometer model 7100B strip-chart recorder.

2.2.8 Scintillation Crystal and Shielding

A Harshaw NaI (Tl-doped) scintillation crystal 1-7/8 in. in diameter x 1 in. long was used. The crystal, photomultiplier tube, and voltage divider were encased in a lead shield (pig) with 2-in. walls. The face of the pig adjacent to the crystal was pierced by a horizontal collimator slot 1/4 in. high and 2 in. wide. The pig, which weighed about 100 lb, was counterweighted for ease of height positioning. The shield and collimator geometry are shown in Fig. 3.

2.2.9 Gamma Counter and Spectrometer Assembly

This system consisted of:

Victoreen linear amplifier model DD-2, 851A.

ORNL logarithmic counter rate meter model Q-1454B-1R16.

ORNL decade scaler model Q-1743C-1, with timer.

Brown recorder.

Victoreen high-voltage power supply.

Fig. 3. Geometry of cylinder, crystal, and collimator.

2.2.10 Cylinder Rocking Device (E)

A modified flask shaker, belt-driven through a speed reducer, and adjusted to raise and lower an arm at 24 cycles per minute, with a 12-cm amplitude, rocked the sample cylinder. One end of the CO₂ cylinder was suspended from the arm by a wire for mixing as shown.

2.2.11 Sample Cylinder (C,C')

The sample cylinders were made of 1-in.-O.D. 16 gage stainless steel tubing (0.07-in. wall thickness), either 11 in. or 12 in. long, with welded end caps and a Hoke or Whitey cone seat valve (Fig. 4). The bottom ends were fitted with a 1-in.-long centering tip, for exact vertical positioning for counting, that also served as a suspension pivot rod during cylinder rocking. The top end of the cylinder was secured during counting by a Teflon rod threaded into the valve and then clamped. The cylinders were hydrostatically tested to 3000 lb/in.². The internal volume of each cylinder (~ 100 ml) was determined to ± 0.05 ml by evacuating, filling with water, and weighing.

2.2.12 Vacuum Manifold

This was used for transfer of CO₂ and Kr (to load the cylinders) by a combination of evacuation and chilling with liquid nitrogen. The CO₂ content of a cylinder was determined by weighing.

2.3 Materials

Commercial dry ice and trichloroethylene were used in the cold baths. The CO₂ used for the solubility measurements was Matheson research grade, and the cold krypton was UHP grade, from Cryogenic Rare Gas Labs, Inc. The ⁸⁵Kr tracer was supplied by the Isotopes Division of ORNL, and was normally about 5% ⁸⁵Kr, 95% stable Kr isotopes, with > 99% radiochemical purity, and contained only trace quantities of atmospheric and rare gases. The oxygen used for solubility measurements in the ternary system was Matheson extra dry high-purity grade.

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Fig. 4. Sample cylinder.

2.4 Preparatory Procedures

This work involved both general procedures (e.g., deadtime and background determinations) and specific procedures (e.g., correction for attenuation by the CO₂ solvent).

2.4.1 Resolving Time (Deadtime) Measurements

The DD2 amplifier resolving time was determined to be 2.0 ± 0.2 μ sec. Two ¹³⁷Cs sources of 0.1 mc each were used for this calibration, employing the standard method of counting the sources separately and then together.¹⁴ The deadtime correction in a typical experimental measurement was about 0.25% of the value of the ratio, which is nearly negligible.

2.4.2 Gamma-Ray Spectrum

The 10.7-year ⁸⁵Kr isotope is chiefly a beta emitter, 99.6% of the disintegrations resulting in the emission of beta particles having a maximum energy of 0.68 MeV. The daughter is stable ⁸⁵Rb. About 0.4% of the disintegrations, however, result in the emission of a 0.51-MeV gamma ray through the decay of a metastable ⁸⁵Rb with a half-life of 0.9 μ sec.¹⁵ Our observed gamma spectrum therefore consisted of considerable bremsstrahlung from the beta particles, along with the 0.51-MeV gamma peak. Our observed spectrum is nearly identical to the one published in 1957 for a 3-in. x 3-in. NaI detector crystal.¹⁶ A small shoulder at 279 keV is probably due to Compton scattering within the detector crystal.¹⁷ Increasing the pressure of CO₂ in a cylinder containing ⁸⁵Kr increases the internal attenuation of the beta particles and decreases the bremsstrahlung emission through a decrease in the quantity and energy of beta particles reaching the metal container walls. Figure 5 shows the overall spectrum and also the bremsstrahlung decrease when ~ 100 mCi of ⁸⁵Kr has about 1000 psi CO₂ added to it. Note that the counting rate at about 75 keV is decreased by 50%. This effect can cause counting errors if not corrected for by means of appropriate attenuation curves (described in Section 2.4.7).

Fig. 5. Relative decrease in bremsstrahlung due to increase in CO₂ content.

Based on the gamma spectrum, ^{85}Kr activity was counted over two energy ranges: $> 40 \text{ keV}$ and $> 0.4 \text{ MeV}$. The former is the entire spectrum except for the extreme low end, and therefore gives the best statistics because of the large count. It is also a much higher count rate than background, but it does require a significant correction for CO_2 density because of the attenuation effect around 100 keV . Above 0.4 MeV , the gamma peak is the major contributor to the count rate, and it is relatively free of attenuation by CO_2 , but the statistics are less favorable and background becomes more significant. It was felt desirable to work with both energy ranges in order to have an internal check on the self-consistency of the method and the results.

2.4.3 Uniformity of Gamma Count Along Cylinder

Since the gamma activity of an equilibrated cylinder was to be measured at different levels for comparison of liquid and gas phases, it was important first to establish that the activity was uniform along the vertical axis of the cylinder when it contained only gaseous krypton. This was verified for each cylinder used, with ^{85}Kr tracer and before carbon dioxide was added. This gave indirect proof that the cylinder walls were of uniform thickness and that the cylinders were mounted parallel to the left face of the cold bath.

2.4.4 Stability of Gamma Counter

Drifting of the gain level of the amplifier during an analysis would result in an error in the ratio of gas-to-liquid activities. Suitable replicate counts, alternating between liquid and gas phases, guarded against this type of error. When the amplifier was set to count only those pulses above 0.4 MeV , it was particularly important to watch for shifts in acceptance level, since the count rate would be strongly affected by movement of the cutoff point out of the valley at 0.4 MeV (see Fig. 5). Generally, drift was minimal during the course of a determination, which took about three hours, and was handled by replicating counts, as described above.

2.4.5 Counter Background

The background count of the shielded scintillation crystal was measured frequently. During the first part of this work the background was about 5% of the ^{85}Kr counting rate for the energies over 0.4 MeV and about 1.3% of the rate for the energies over 40 keV. Later on, the background count was reduced about 75% by increasing the shielding around some uranium and thorium compounds stored in the same room. The precision of the background count was such that it contributed less than $\pm 0.1\%$ error to the final results.

No correction was made for the contribution to background of the ^{85}Kr itself; i.e., non-collimated radiation from the bulk of the sample, which penetrated the lead shield. The contribution of non-collimated radiation could not easily be determined directly, but was determined indirectly by turning the shield sideways toward the cylinder. Under these conditions, the contribution was about equal to the normal background. The effect tends to be self-cancelling since it applies more-or-less equally to both phases and it is estimated that the maximum error to the separation factor which could result from this source is 0.6% at -53°C , and proportionately less at higher temperatures. Self-cancellation would be complete at the critical temperature of CO_2 , where the distribution ratio becomes unity.

2.4.6 Gamma Attenuation Curve

The gamma counting method for the determination of krypton in gaseous and liquid CO_2 would have been seriously biased had we not corrected for the gamma attenuation by CO_2 which was mentioned in Sect. 2.4.2. Initially, this correction was determined directly, for CO_2 densities from zero to 0.49 g/cc, by incrementally adding CO_2 to a cylinder containing 100 mCi ^{85}Kr and reading the counting rate at energies > 40 keV and > 0.4 MeV. At the higher densities it was necessary to warm the cylinder above the critical temperature to ensure having all the CO_2 in the gaseous state, which was necessary in order to have a homogeneous sample. The percentage attenuation was plotted as a function of CO_2 density (Fig. 6). As shown

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Fig. 6. Gamma attenuation curves for ^{85}Kr as a function of density of CO_2 .

in the figure, for > 40 keV the attenuation rises quite steeply and then levels off at a density of about 0.4 g/cc to a value of $26.0 \pm 0.5\%$. For the > 40 MeV energy range, a much smaller effect occurs which levels off at $4 \pm 1.5\%$ at a density of about 0.1 g/cc. The precision of the > 0.4 MeV attenuation curve above a density of 0.2 g/cc became relatively poor, due to instrumental drift in the energy cutoff point over the period of several days required to determine the curve.

The density attenuation curve was used to correct the observed count to what it would be in the absence of CO_2 by dividing the observed value by the fraction not attenuated:

$$\text{Corrected Count (CC)} = \frac{\text{Observed Count}}{[1 - (\% \text{ attenuation}/100)]} \quad (1)$$

A more detailed description of the procedure for obtaining the empirical calibration curves follows. The evacuated cylinder was chilled in liquid nitrogen and $100 \text{ mCi } ^{85}\text{Kr}$ transferred into it by means of the vacuum manifold. The uniformity of gamma counts along the length of the cylinder was verified by mounting the cylinder in its vertical position in the TCE bath and measuring the counting rate every centimeter. As a base figure to determine the gamma attenuation, it was first necessary to obtain precision counting rates of the krypton before CO_2 was added. This was done at two positions, at $1/4$ and $3/4$ the height of the cylinder, corresponding roughly to the anticipated centers of the liquid and gas phases, in order to have a set of duplicate determinations and to insure that there was no significant difference between the two positions.

The cylinder was then loaded with CO_2 in 12 incremental steps, corresponding to the 12 density points on Fig. 6. Known volumes and pressures of CO_2 were added via the vacuum manifold and chilling with liquid nitrogen. The amounts added were also measured directly by the weight gains of the cylinder. After each addition, the cylinder was warmed, and the krypton and CO_2 gases were mixed by inverting the cylinder many times and by heating the lower end to generate gas convection currents. Gamma counts in the two energy ranges were then taken at room temperature

($25 \pm 1^\circ\text{C}$) up to a density of 0.2035. No liquid phase was present, since the condensation temperature of CO_2 at this density is 21.7°C . Mixtures above this density were counted only after they had been warmed to $33\text{--}36^\circ\text{C}$ (i.e., above the critical temperature of 31°C) in the TCE bath, with thorough mixing. Thus only a gas phase was present in the cylinder. We made no direct gamma attenuation measurements above a density of 0.49 g/cc, because of the very high pressures involved above the critical temperature at higher densities.

After this work was completed, indirect attenuation values were determined at higher densities by filling the cylinder almost full of liquid CO_2 and correcting for the fraction of krypton in the gas phase by means of the distribution ratios measured experimentally during the course of this work. The results (Fig. 7) verified the previous attenuation values and also justified, within experimental error, the extrapolations made previously to a CO_2 density greater than 0.49 g/cc. The data in Fig. 7 include a correction for the increased density of TCE at the low temperature (-35°C) required for the highest density. This correction is about 3%, and results from the increased attenuation by the increase in TCE density at lower temperatures. This correction is required for self-consistency of the attenuation correction curve itself, which is related to the base count obtained at ambient temperatures. However, in measurements of distribution ratios a correction for the TCE density is not necessary since the factor cancels out in the ratio.

2.4.7 Density of CO_2

The densities of CO_2 liquid and vapor as a function of temperature are required for two reasons: to use the density attenuation curve, and to calculate the distribution ratio (see Sect. 2.5.3). Published data on CO_2 densities¹⁸ were used, and for temperatures known with an accuracy of $\pm 0.1^\circ\text{C}$ the precision on the CO_2 gas density is $\pm 0.5\%$; on the liquid density it is $\pm 0.1\%$. A graph of the density data is given in Fig. 8, based on ref. 18. The data in ref. 18 were taken from the "G. C. Hodson Tables," which were prepared from the compilation of

Fig. 7. Gamma attenuation curves to a density of 1 g/cc.

Fig. 3. CO₂ density as a function of temperature.

Plank and Kuprianoff,¹⁹ who drew on the original work of Lowry and Erickson,²⁰ Amagat, Behn, and Jenkin. Quinn and Jones²¹ tabulate the data of the last three authors. Din²² also includes a compilation of CO₂ densities, and several Russian papers²³⁻²⁵ are known, which are substantially in agreement with ref. 18. It should be noted that the data given in the Handbook of Chemistry and Physics²⁶ are in error.

In calculating distribution ratios from ⁸⁵Kr count data, it is the ratios of CO₂ liquid/gas densities which are of interest. The calculated ratios are plotted in Fig. 9.

The effect of decay heat from ⁸⁵Kr tracer on the temperature of the CO₂ within the sample cylinder was calculated and found to be negligible. The thermal power²⁷ of 100 mCi of ⁸⁵Kr is 1.6×10^{-4} watts, or 0.4×10^{-4} cal/sec. The equation for ΔT (in °C) from centerline to periphery in an infinite cylinder is:

$$\Delta T = QR^2/4k,$$

where

Q = heat generation rate (in cal sec⁻¹ cm⁻³),

R = radius (in cm),

k = thermal conductivity (cal sec⁻¹ cm⁻¹/°C).

For the cylinders used, the volume is 100 ml and R is 1.2 cm. The value of k for gaseous CO₂ (at 1 atm) is 3.4×10^{-5} ; for liquid CO₂, it is about ten times larger (estimated from CS₂). The calculated ΔT s are 0.004 and 0.0004°C, respectively.

2.4.8 Gamma Profiles of Loaded Cylinder

For the CO₂-loaded cylinder described in Sect. 2.4.7, the single-phase maximum density was 0.49 g/cc. Below 31°C, the CO₂ separated into liquid and gas phases, the relative volumes depending on the temperature. For example, at 21°C the liquid volume was about 52% and at -52.8°C it was 41% of the cylinder volume, as computed from the densities at these two temperatures. Figure 10 shows the count activity profiles as a

Fig. 9. CO₂ L/G density ratios.

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Fig. 10. Counting profiles along length of sample cylinder.

function of vertical position for this charge of carbon dioxide with 100 mCi ^{85}Kr at these two extremes of temperature. In each case, the location of the gas/liquid interface is clearly indicated. Most of the krypton is contained in the liquid phase, although the krypton activity per gram of CO_2 is higher in the gas phase.

By means of these counting profiles, optimum counting points for high-precision counting of the two phases were selected. For liquid phase counting, 6 to 8 cm was used, depending on the temperature, and for gas phase counting 21 cm was used at all temperatures. The liquid level changed relatively little with temperature because at lower temperatures, where more CO_2 was liquid, the density was greater.

2.5 Procedure for Gas/Liquid Ratio Determination

2.5.1 Cylinder Cooldown and Equilibration

The procedure for cooling and equilibrating the CO_2 -Kr cylinder was straightforward. The dry ice reservoir was stocked with lumps of dry ice, which were replenished as necessary. The CO_2 cylinder was mounted in the horizontal position and the rocking device was actuated. The desired temperature was set on the thermoregulator and the temperature controller was turned on. The pump was started and the bypass valves set to allow the maximum flow through the cooling coil for rapid cooldown. The thermocouple cold junction was prepared from ice and distilled water, and the potentiometer and recorder were zeroed. As soon as the controller first called for heat from the immersion heater, the flow of TCE through the reservoir was cut back and routed through the filter and rotameter at such a rate that the heater cycled on and off approximately every 20 to 30 seconds. The control valve to the cold bath was normally fully open at this stage, to provide high turbulence and thorough mixing of the TCE in the cold bath. When this steady cycling was reached, the precise temperature was monitored by bucking out the thermopile voltage with the potentiometer and recording the fluctuations with the recorder set at maximum sensitivity, with zero at midscale. After the temperature had

remained constant within $\pm 0.1^\circ\text{C}$ for at least 30 minutes, the cylinder rocking device was stopped and the cylinder transferred to the vertical holding brackets while keeping it constantly fully immersed in the circulating TCE.

2.5.2 Gamma Counting

With the trichloroethylene circulating at the stabilized control temperature, the collimator was set at the appropriate gas or liquid counting position, the desired energy range was set on the electronic gate circuit, and the timer and counter simultaneously started. The count was stopped after a suitable Poisson precision had been reached (at least 2×10^5 counts, for a statistical standard deviation $\leq 0.25\%$), which was usually 10 to 20 minutes. The gate was then reset to the other energy range and the count repeated. The collimator was then moved to the other counting position and the two energy ranges counted as before.

2.5.3 Calculations

The relative volatility²⁸ is a useful way to express gas solubilities:

$$RV = \frac{Y_{Kr} / Y_{CO_2}}{X_{Kr} / X_{CO_2}}, \quad (2)$$

where

Y_i = mole fraction in the gas phase,

X_i = mole fraction in the liquid phase.

At low concentrations of krypton, Y_{CO_2} and X_{CO_2} are nearly unity, and Eq. (2) simplifies to:

$$RV = Y_{Kr} / X_{Kr}, \quad (3)$$

which may also be called a distribution ratio.

The Kr concentration data are obtained as counts per unit volume, where the volume (V) is that which is swept out by the collimator. Neither this

volume nor the actual mole ratios of Kr need be determined in order to obtain quantitative values for the ratio of Eq. (3). By definition, Eq. (3) may be restated:

$$RV = \frac{m_{Kr_g} / (m_{Kr_g} + m_{CO_2_g})}{m_{Kr_l} / (m_{Kr_l} + m_{CO_2_l})} \quad (4)$$

where m_i = moles per swept-out volume V . At dilute concentration of Kr:

$$RV = \left(\frac{m_{Kr_g}}{m_{Kr_l}} \right) \left(\frac{m_{CO_2_l}}{m_{CO_2_g}} \right) \quad (5)$$

The first term is equal to the ratio of the counts after correction by Eq. (1) and the second term, at low Kr concentrations, is equal to the ratio of the CO_2 densities in liquid and gas phases. Therefore, to calculate the distribution ratio at a specific temperature:

$$RV_T = \left(\frac{CC_g}{CC_l} \right) \left(\frac{\rho_{CO_2_l}}{\rho_{CO_2_g}} \right) \quad (6)$$

where the corrected counts and the densities are at temperature T .

The calculation is illustrated below by the data obtained at $-13.55^\circ C$. Precisions are quoted as 95% confidence limits. The CO_2 gas and liquid densities, obtained from the ASRE data,¹⁸ are 0.0625 ± 0.0003 and 1.000 ± 0.001 g/ml. The gamma counts were first taken in the liquid position at the two energies, then in the gas position, and were then repeated in both positions. There being no significant difference between determinations as shown by limits of error calculated from the Poisson distribution, the data were pooled, with 32 and 30 minutes of counting time for the > 0.4 MeV energy in the liquid and gas positions, and 22 and 26 minutes for the > 40 keV energy range. Table 1a shows the data after normalization to counts/minute, with the calculated confidence

Table 1a. Gamma counting rates at -13.55°C

	> 0.4 MeV		> 40 keV	
	Liquid	Gas	Liquid	Gas
Observed	30,995 $\pm$ 62	15,510 $\pm$ 45	141,372 $\pm$ 160	78,137 $\pm$ 110
Background	137 $\pm$ 10	137 $\pm$ 10	245 $\pm$ 15	245 $\pm$ 15
Net counts/min	30,818 $\pm$ 63	15,373 $\pm$ 46	141,127 $\pm$ 161	77,892 $\pm$ 111
Gamma Attenuation, %	4.0 $\pm$ 1.0	3.5 $\pm$ 0.5	26.0 $\pm$ 0.5	18.1 $\pm$ 0.2
γ fraction not attenuated	0.96 $\pm$ 0.01	0.965 $\pm$ 0.005	0.740 $\pm$ 0.005	0.819 $\pm$ 0.002
Corrected counts/min	32,102	15,931	190,712	95,106

Table 1b. Distribution ratios at -13.55°C

	> 0.4 MeV	> 40 keV
Input values	$\left(\frac{15,931}{32,102}\right)\left(\frac{1.000}{0.0625}\right)$	$\left(\frac{95,106}{190,712}\right)\left(\frac{1.000}{0.0625}\right)$
Distribution ratios	7.94 $\pm$ 0.10	7.98 $\pm$ 0.07

Note: at -13.55°C: CO₂ gas density = 0.0625 $\pm$ 0.0003

CO₂ liquid density = 1.000 $\pm$ 0.001

limits, and the corrections made for background. The gamma attenuation values were read from Fig. 6. Using Eq. (6), the distribution ratios were calculated; the results are shown in Table 1b. The 95% confidence limits shown for the SF at both energy ranges include only the known precision on the attenuation factor, the CO_2 densities, and the counting rates; and the relative contribution from these three sources declines in the order listed. In this instance the two values are within the calculated limits of each other, but this was not always the case.

2.6 Gas/Liquid Equilibrium

The attainment of equilibrium was demonstrated two ways: by repeated measurements over a period of time at a fixed temperature, and by approaching a given temperature both from above and from below.

Krypton distribution between gaseous and liquid CO_2 came to equilibrium at -33°C in a 40-minute cooldown from room temperature followed by 45 minutes at the stabilized temperature. This was shown by first counting after the 45 minutes at stabilized temperature, and then counting three more times at 30-minute intervals, each of which included additional mixing in the horizontal position. As shown in Table 2a, there was no significant difference among ratios in either energy range, although in this case there was a small difference between the two energy ranges.

A second equilibrium test at -26.9°C showed that the same krypton distribution ratio was attained whether the target temperature was approached from below or from above. After the routine measurement of a ratio at -43°C , the temperature was raised to -26.9°C and the CO_2 cylinder remixed for 45 minutes. This new ratio was then obtained, and the bath and cylinder were allowed to warm up. Three days later, the bath was cooled down again to -26.9°C with the cylinder being mixed, and the ratio redetermined. Results are shown in Table 2b.

Table 2a. Replicate distribution ratios at $-33.01^\circ \pm 0.07^\circ\text{C}$
(sample cylinder remixed 30 min between determinations)

Determinations	> 0.4 MeV	> 40 keV
1	14.544 ± 0.22	14.380 ± 0.16
2	14.494 ± 0.22	14.419 ± 0.16
3	14.486 ± 0.22	14.428 ± 0.16
4	14.528 ± 0.22	14.384 ± 0.16
Avg.	14.513 ± 0.044	14.403 ± 0.038

Table 2b. Distribution ratios at -26.9°C ,
approached from below and above

	> 0.4 MeV	> 40 keV
From -43°C	11.83 ± 0.18	11.88 ± 0.13
From $+22^\circ\text{C}$	11.81 ± 0.18	11.85 ± 0.13

2.7 Verification of Method

2.7.1 Cross-Check with Other Counting Apparatus

Excellent agreement was obtained using other counting equipment in another laboratory location. The same CO₂ cylinder, collimator, and crystal were used, but it was not practicable to use the trichloroethylene cold bath; instead, an ice bath was used for one determination, and several measurements were made at ambient air temperature. These values are included in the tabulation given in the Results Section.

2.7.2 Solubility of Kr in Water

Direct confirmation of our method was obtained by measuring the solubility of Kr in water at ambient temperature. A number of workers have reported data on the aqueous solubility of Kr,²⁹⁻³³ in good agreement with each other (Table 3). (At ambient temperatures, the solubility of Kr in H₂O is rather sensitive to temperature, passing through a minimum value at about 90°C, then increasing at higher temperatures;^{30,31} see Fig. 11.) Our results are also shown in Table 3, and are also in agreement. A description of our procedures and results follows.

Figure 12 is a gamma counting profile of a standard 1-in. x 12-in. cylinder containing 26 cc of nonradioactive krypton spiked with about 50 mCi ⁸⁵Kr, at a pressure of 96 psia, over 85 ml of distilled water. The two phases had been mixed for 1 hour in the TCE bath at 23.8°C, then erected and counted for 2 minutes in each position. The counting rate is plotted on a semi-logarithmic scale, because of the large difference in counting rate between the two phases, caused by the low solubility of Kr in water. The high counting rate of the gas phase affects the observed rate in the liquid phase much more for water than for CO₂. Also, this effect is greater in the > 40 keV energy range than in the > 0.4 MeV range, and the former data were not used to calculate the solubility because there is no liquid-phase plateau. There was some question if the gas phase count for > 0.4 MeV was really on a plateau, so some water was removed and the count repeated (Fig. 13). The results were quite similar.

Table 3. The solubility of Kr in water

Source	Temp. (°C)	B* (cc/ml)
Ref. 28 (by interpolation)	23	0.059
Ref. 29 (from equation)	23	0.056
Ref. 31 (reported value)	25	0.057
Ref. 32 (from graph)	23	0.057
This work (> 0.4 MeV)	23.8	0.061
This work (> 0.4 MeV)	22.8	0.062
This work (> 0.4 MeV)	23.0	0.060

*Bunsen coefficient: cc of Kr (STP) dissolver per ml of water
at $P_{Kr} = 1$ atm.

Fig. 11. The solubility of krypton in water.

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Fig. 12. Counting profile for krypton-water system (85 cc water).

Fig. 13. Counting profile for krypton-water system (55 cc water).

The data given on the two figures are adequate to calculate the Bunsen coefficients. No attenuation corrections were made, but this should not introduce significant errors since only the > 0.4 MeV data were used. No attenuation factors were obtained for H_2O and Kr, but by analogy with the CO_2 factor (Fig. 6), corrections of 4% for the liquid phase and 2 to 3% for the gas phase would be anticipated, and these are largely self-cancelling anyway.

2.8 Wall Wetting

After completion of the experimental part of this work, a question was raised concerning the effects of a possible liquid layer of CO_2 on the cylinder wall in the gas phase region.³⁴ This had been considered earlier and thought to be highly unlikely because of the very low viscosity of liquid CO_2 ³⁵ and because of its very low surface tension.³⁶ However, if such a film did exist, the result would be a larger value for the distribution ratio, which is the direction in which our results lie relative to the Jülich data.¹¹ The presence of such a film was clearly disproved in related and similar work on the Xe- CO_2 system.¹³ Xenon, rather than krypton, was used to demonstrate the nonexistence of a significant liquid film because it provides a more sensitive test than does Kr, because Xe is more soluble than Kr. Since the film, if it existed, would depend on CO_2 properties, the Xe results can be extended to include Kr.

3. RESULTS

3.1 Experimentally Determined Distribution Ratios

Using the procedures described in the previous section, the results tabulated in Table 4 were obtained (some of the raw data are given in Table 8). The data are presented graphically in Fig. 14. The table and figure show all the data points which were obtained; no data were discarded. All data fall very close to a smooth curve, except for three points obtained early in this work with a 2-in. cylinder and several points obtained with added oxygen.

Table 4. Distribution ratios (Y/X) for Kr in CO₂

Temp. (°C)	Y/X		Comments
	>0.4 MeV [*]	> 40 keV [*]	
20.9	2.73		20 mCi, 2-in. cylinder ^c
- 21.2	10.35		20 mCi, 2-in. cylinder ^c
- 33.2	15.72		20 mCi, 2-in. cylinder ^c
- 50.8	26.92	27.10	100 mCi, 1-in. cylinder
- 42.6	20.09	19.86	100 mCi, 1-in. cylinder
20.3	2.70	2.68	100 mCi, 1-in. cylinder
21.6	2.56	2.53	100 mCi, 1-in. cylinder
- 33.0	14.51 ^a	14.40 ^b	100 mCi, 1-in. cylinder
- 4.6	6.57	5.91	120 mCi, 2-in. cylinder ^c
- 43.0	20.15	20.16	100 mCi, 1-in. cylinder ^{**}
- 26.9	11.83	11.88	Equilibrium reached from below
- 26.9	11.81	11.85	Equilibrium reached from above
- 48.6	24.84	24.82	
21.0	2.67	2.62	
5.30	4.40	4.39	
- 13.55	7.94	7.98	
- 52.8	29.34	29.53	
25.1	2.19	2.21	d
29.1	1.43	1.44	With other counting equipment ^d
28.2	1.76	1.80	With other counting equipment ^d
0.0	5.19	5.12	With other counting equipment
- 19.03	9.29	9.38	
- 19.03	9.32	9.51	With 100 psi krypton
- 19.03	9.47	9.54	With 100 psi oxygen
- 19.03	9.86	9.65	With 450 psi oxygen ^e
- 19.03	9.90	9.92	With 450 psi oxygen, for recalculated attenuation ^e

* Gamma energy range counted.

** Second loading of Kr-85 in 1-in. cylinder. This was used for the remaining determinations.

^a Average of four determinations: 14.54, 14.49, 14.49, 14.53.

^b Average of four determinations: 14.38, 14.42, 14.43, 14.38.

^c Not used in computing the least-squares line because a non-standard cylinder was used.

^d Not used because the temperature is in the non-linear region.

^e Not used because of the high oxygen content.

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Fig. 14. Krypton distribution between gaseous and liquid CO₂.

The data, as plotted in Fig. 14, are nearly linear, except for the data at 25°C and higher. The higher temperature values extrapolate to a value of unity at the critical temperature, in agreement with the fact that at T_c there is, in fact, no separation. The other data were fitted to a straight-line equation of the form $\log y = a + bx$:

$$\log_{10}(\text{DR}) = 0.7090 - 0.01395 t, \quad (7)$$

where t is the temperature in °C. The constants in Eq. (7) were obtained by the method of least squares, using those data points indicated in Table 4. A total of 40 data points were used in the least-squares calculations. The correlation coefficient for the fit is 0.9992, and the 95% confidence intervals for the constants are 0.7090 ± 0.0040 and -0.01395 ± 0.00013 . These limits, which are equivalent to about $\pm 1.5\%$, are representative of the calculated or estimated known errors, as described previously, and are due to uncertainties in the count rate, the temperature, and the density of CO_2 .

Closer examination of Fig. 14 shows a slight, but systematic, positive curvature below -40°C. Glass,⁷ who is more concerned with lower temperatures in his work, and in which he needs a more general equation, fitted the data below 10°C to the three-constant Valentine equation:

$$\log \left(\frac{Y P^*}{X} \right) = a + b \log T + \frac{c}{T},$$

where P^* = the saturation vapor pressure of CO_2 at T .

3.2 Effect of Added Oxygen (and Krypton)

Ideally, the partial pressure of Kr above liquid CO_2 should be nearly independent of other gases, except to the degree that they dissolve in the liquid CO_2 and thereby make X_{Kr} smaller and, therefore, the partial pressure also. Within the limits of this work, no significant effects due to oxygen addition were observed. Table 4 includes data at one temperature in which oxygen was added to the cylinder. Oxygen was used since it is the other major component in the KALC process, and is therefore of the most interest from a practical aspect. The distribution ratios shown for the ternary

system are pseudo-ratios, since they do not admit the effect of oxygen on the mole fraction of krypton, which is a rather large effect for the gas-phase composition. As calculated, these ratios are concentration terms, rather than mole ratio terms. However, for the present purpose, this is the preferred mode of expression, since it allows direct comparison with the control data.

After a standard determination of the separation factor at -19°C , additional stable Kr was added. The amount added is about 10^3 times as much as was originally present, and it had no effect on the distribution ratio. This is in agreement with ideal behavior and indicates that, technically, the krypton concentration is still "dilute."

Oxygen was then added in two increments, to a total pressure of 450 psi. The maximum pressure was limited by the capability of the sample cylinder. As shown in Table 4, the addition of oxygen caused a small increase in the values for the distribution ratio, but the change is not necessarily significant and may simply be an artifact. A gamma attenuation curve was not prepared for oxygen, and the values for the distribution ratio for recalculated attenuation were obtained by assuming that attenuation due to the added oxygen is the same as attenuation due to CO_2 at an equal gas density. The direction of the change in the distribution ratio is opposite to that expected and, if real, must be due to the non-ideality of the CO_2 - O_2 system.³⁷⁻⁴⁰ The change is, in fact, in the proper direction for the reported non-ideality of this system, where the activity coefficient of CO_2 is ~ 1.02 under these conditions.³⁹

3.3 Calculation of Henry's Law Constants

Henry's Law states that the quantity of gas in solution is proportional to its pressure. This relationship is expressed in either of two ways:

$$P_i = H X_i ,$$

$$X_i = k P_i ,$$

where $H = 1/k$. Since $P_i = Y_i P_t$,

$$H = \frac{Y_i}{X_i} P_t \quad (8)$$

and for small values of X_i , $P_t = P_{CO_2}$, where P_{CO_2} is the saturation vapor pressure of CO_2 . Calculated values of H are listed in Table 5, along with the corresponding values of k . The vapor pressure data for CO_2 are in the literature.^{41,42}

3.4 Calculation of Bunsen and Ostwald Coefficients

The Bunsen absorption coefficient (α) is defined as the quantity of gas, expressed as the volume (V_o) under standard conditions, which will dissolve in a unit volume of solvent (V) under a gas partial pressure of 1 atm:

$$\alpha = V_o / V P_{Kr} \quad (9)$$

Since $P_{Kr} = H X_{Kr}$ and

$$V_o = (\text{moles of } CO_2) (22,400) X_{Kr} ,$$

$$V = (\text{moles of } CO_2) (44) / \rho_{CO_2} ,$$

Eq. (9) may be recast as:

$$\alpha = \frac{22,400 \rho_{CO_2}}{44 H} \quad (10)$$

The Ostwald coefficient of solubility (β) is defined as the volume of gas, measured at the temperature and pressure under which solution occurs, per unit volume of solvent. This coefficient may be calculated from the Bunsen coefficient:⁴³

$$\beta = \alpha T_a / 273 , \quad (11)$$

where T_a is the absolute temperature.

Table 5. Henry's Law constants for Kr in CO₂

T (°C)	Y/X	P _{CO₂} (atm) ^a	H (atm)	k (atm ⁻¹)
- 50	25.8	6.74	173.9	5.75 x 10 ⁻³
- 40	18.3	9.91	181.4	5.51
- 30	13.4	14.1	188.9	5.29
- 20	9.70	19.5	189.2	5.29
- 10	7.05	26.2	184.7	5.41
0	5.12	34.6	177.2	5.64
10	3.72	44.5	165.5	6.04
20	2.69	56.7	152.5	6.56
24	2.29	62.2	142.4	7.02
28	1.72	68.1	117.1	8.54

^aData of Michels et al.^{41,42}

Using Eqs. (10) and (11), the values tabulated in Table 6 were calculated. The Bunsen coefficient generally increases with decreasing temperature, while the Ostwald coefficient remains constant. This behavior is shown by the values in Table 6, except at 28°C, which is quite close to the critical temperature of CO₂.

3.5 Calculation of the Heat of Solution

The heat of solution (ΔH_s) of Kr in CO₂ may be related to the Bunsen coefficient by the van't Hoff type equation:⁴⁴

$$\ln \alpha = -\Delta H_s / RT_s + \text{constant} \quad (12)$$

Thus, a plot of $\ln \alpha$ vs $1/T_s$ gives a curve whose slope is $-\Delta H_s/R$. Values of $\ln \alpha$ and $1/T_s$ are tabulated in Table 7, and the plot is shown as Fig. 15. A smoothed curve is drawn through the data since the fine structure is probably not real. The point at 28°C is obviously erratic, presumably because of nearness to the critical temperature of CO₂.

The heat of solution, as determined graphically from Fig. 15, is about -900 cal/mole at -50°C and about -200 cal/mole at 10°C. The curve levels out above 20°C, indicating a ΔH_s of zero as the critical temperature is approached.

4. DISCUSSION

4.1 Comparison with Other Data

The Jülich data,¹¹ referred to previously, are shown in Fig. 16. They differ from our results in two respects: (1) over the region of interest to KALC, their values are lower by a factor of about 2, and (2) as the critical temperature is approached, their values level off at about 2 (the singular point at 30° is questionable because of nearness to T_c).

Private discussions with both Laser and Beaujean failed to disclose an explanation for the differences shown in Fig. 16. However, from our own, earlier difficulties with a sampling procedure, we conclude that

Table 6. Bunsen (α) and Ostwald (β) coefficients for Kr in liquid CO_2

T ($^{\circ}\text{C}$)	ρ_{CO_2} (g/ml)	α (atm^{-1})	β (atm^{-1})
- 50	1.151	3.370	2.75
- 40	1.114	3.126	2.67
- 30	1.074	2.894	2.57
- 20	1.030	2.771	2.57
- 10	0.980	2.701	2.60
0	0.924	2.655	2.66
10	0.859	2.642	2.74
20	0.768	2.564	2.75
24	0.718	2.567	2.79
28	0.646	2.808	3.10

Table 7. Data to plot Equation (12)

T ($^{\circ}\text{C}$)	$1000/T_a$	$\ln \alpha$
- 50	4.481	1.215
- 40	4.289	1.140
- 30	4.113	1.063
- 20	3.950	1.019
- 10	3.800	0.994
0	3.661	0.976
10	3.532	0.972
20	3.411	0.942
24	3.365	0.943
28	3.321	1.032

$$T_a = t \text{ (}^{\circ}\text{C)} + 273.15.$$

Fig. 15. Graph to determine heat of solution.

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Fig. 16. Comparison of ORNL results with Jülich data.

they incurred a systematic error from this source. At the one point where our data are in agreement, it is clear that their results are showing an improbable behavior.

4.2 Comparison with Calculated Solubilities

For the ideal case, the value of the distribution ratio is simply the ratio of the vapor pressures. From Raoult's Law, $P_{Kr} = X_{Kr} P_{Kr}^*$, where P_{Kr}^* is the vapor pressure of the pure component, and from Dalton's law, $P_{Kr} = Y_{Kr} P_t$, where P_t is the total pressure, whereby $Y_{Kr}/X_{Kr} = P_{Kr}^*/P_t$. At dilute concentrations of krypton, $P_t \approx P_{CO_2}^*$, so that

$$\frac{Y_{Kr}}{X_{Kr}}_{ideal} = \frac{P_{Kr}^*}{P_{CO_2}^*} \quad (13)$$

Vapor pressure data are, of course, available for CO_2 ,^{40,41} but for Kr, which is here above its critical temperature of $-64^\circ C$, P^* must be estimated. This can be done by several methods, which differ slightly in their results. Thus, a range of calculated values is obtained from Eq. (13) for the ideal case, as indicated by the shaded region in Fig. 17.

Improvements can be made in the calculations by applying regular solution theory, as developed by Hildebrand, Prausnitz, and Scott,⁴⁵⁻⁴⁷ and by allowing for the known, real behavior of gaseous CO_2 , which has a significant Z factor (see Fig. 18). These improved calculations have been made by Davis,⁴⁸ and are also shown in Fig. 17.

Two observations are worth noting: (1) none of the calculated curves represent the experimental results very well, and (2) none of the calculated curves approach a value of unity at the critical temperature. This latter point suggests that the models for the calculations are either being used out of their range or they are incomplete in not allowing for behavior near the critical region.

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Fig. 17. Comparison of ORNL results with calculated values.

Fig. 18. Non-ideality of CO_2 saturated vapor.

4.3 The Solubility Parameter

A related calculated quantity of interest is the so-called Cohesive Energy Density (CED), the square root of which is sometimes referred to as the "solubility parameter".⁴⁶ This calculation is used to compare relative solubility, and reflects the philosophy that "like dissolves like." Thus, if solvent and solute have nearly identical solubility parameters, that solute should show a relatively high solubility in that solvent. This correlation has been tested by Steinberg and Manowitz for Kr and Xe,⁴⁹ and is the basis for the Freon process⁵⁰ currently under development at ORGDP.⁵¹ From the definition of CED,

$$\text{CED} = \frac{\Delta H_v}{\text{molar volume}}$$

the solubility parameter of Kr is calculated to be $7.9 (\text{cal/cc})^{0.5}$ at its boiling point,⁴⁹ in close agreement with the parameters for the hydrocarbons (7 to 9) and Freon-12 (7.6) that have been used as solvents for the rare gases. [For comparison, the solubility parameter of water is $23(\text{cal/cc})^{0.5}$ and for silicone oils it is about $5(\text{cal/cc})^{0.5}$.] For CO_2 , the solubility parameter is in a favorable range, with values of 9.5, 8.3, and $7.1 (\text{cal/cc})^{0.5}$ at temperatures of -40 , -20 , and 0°C , respectively.

4.4 Comparison with Other Solutes

One basis for relating the solubility of various solutes in a given solvent is in terms of the Henry's Law constant vs the molar energy of vaporization, ΔE_b^v , cal/g-mole.⁴⁶ This relationship has been plotted by Mullins for those few gases where the solubility in CO_2 is known,⁵² as shown in Fig. 19. The general validity of this relationship is demonstrated for CO_2 . Internal fine structure, e.g., for the similar series $\text{N}_2/\text{CO}/\text{O}_2$, may exist. The Jülich data¹¹ are seen to fall furthest off the estimated line. The xenon data are from the ORNL work.¹³

Fig. 19. Henry's Law constants for CO_2 systems at -20°C .

4.5 Comparison with Absorption Data

By operating an absorption column in a "pinched" condition, the value of the separation factor can be deduced from the L/V ratio. This has recently been done in conjunction with KALC engineering development work.⁸ The experimental and calculated values are compared in Fig. 20, and fall close to the 45° line, indicating good agreement.

4.6 Material Balance

A standard procedure to check the internal self-consistency of any experiment is to do a material balance and determine if a satisfactory "closure," or accounting of material, is obtained. For these experiments, a material balance of total counts was conducted with data obtained from the second loading of the 1-in. cylinder. These data are shown in Table 4 starting with the -43.0°C data; data are listed in Table 4 in chronological order. Data obtained "with other counting equipment" cannot be used in this exercise since the counting geometry and statistics are different from the other data.

A count total was obtained for each applicable data point described above. The procedure used was to multiply the counts/min for each phase by the calculated volume of that phase, then sum the two products. (The gas and liquid volumes were calculated from the known cylinder volume and CO₂ content, and from the literature values for the densities.) The counts/min are for the volume swept out by the collimator. Although this volume is not known, it is constant for all measurements and is defined to be the unit volume. This procedure was applied to the counts taken at both energy ranges. A correction was then made for radioactive decay over the time interval involved. The numerical results are given in Table 8. Inspection of the results shows overall constancy, with ranges of $\pm 9\%$ on the > 0.4 MeV energy and $\pm 5\%$ on the > 40 keV energy.

Fig. 20. A comparison of predicted and measured values of $(Y/X)_{Kr}$ for the equilibrium experiments.

Table B. Count material balance^a

Temp. (°C)	Elapsed time (days)	Decay Factor ^b	Obs. counts ^{30.4 keV}		Obs. counts ^{540 keV}		CO ₂ density (g/ml)		Calculated Vol. (ml) ^c		γ Attenuation (%)		Sum of Total Counts ^d	
			Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	^{30.4 keV} Gas Phase ^e	^{540 keV} Gas Phase ^e	> 0.4 MeV	> 40 keV
Control ^f	0	1.000											241 ± 10 ⁴	1475 ± 10 ⁴
-43.0	27	0.995	37271	16024	152623	79119	1.126	0.0237	42.00	57.26	7.7	9.6	259	1374
-26.6	29	0.995	35991	16571	148868	78918	1.061	0.0410	43.71	55.53	7.3	14.4	260	1397
-26.9	32	0.994	32249	14819	146246	78500	1.061	0.0410	43.71	55.53	7.3	14.4	232	1393
-48.6	32	0.994	32901	13903	151606	78184	1.145	0.0192	41.52	57.72	7.6	8.3	226	1351
-21.0	35	0.994	27000	18000	127500	89000	0.760	0.198	51.60	47.64	4.0	24.4	240	1659
-5.3	48	0.992	29180	16722	134920	80741	0.890	0.115	48.05	51.19	4.0	21.9	238	1417
-13.55	49	0.991	30818	15373	141127	77892	1.000	0.0625	45.28	51.96	3.5	18.1	233	1389
-52.8	49	0.991	31799	13129	150205	77244	1.163	0.0182	41.02	58.22	3.0	7.5	217	1331
-19.03	112	0.980	31704	15156	143178	77595	1.026	0.0525	44.82	56.82	3.5	16.5	236	1399
-19.03	113	0.980	31470	15079	143652	76728	1.026	0.0525	44.82	56.82	3.5	16.5	236	1408
-19.03	117	0.978	30122	14665	142532	76518	1.026	0.0525	44.82	56.82	3.5	16.5	228	1402

^aAll counts given as counts/min.^b $I_t = I_0 e^{-\lambda t}$, where $I_0 = 1$, I_t is the value shown, and $\lambda = 0.000177 \text{ days}^{-1}$.^cThe volume of this cylinder is 99.24 ml.^dAttenuation was 4.02 for all liquid densities.^eAttenuation was 26.02 for all liquid densities.^fEach total is the sum of (counts × volume) for both phases, corrected for radioactive decay.^gPrior to addition of CO₂; only Kr present. Nominal temperature, 25°C.

Since the observed variations were larger than was expected, a systematic basis was sought. The results were plotted two ways: chronologically and as a function of temperature (Figs. 21 and 22). The data were analyzed statistically, and the pertinent values are shown on the graphs. Two of the tested relationships show a significant correlation: the temperature effect on the > 40 keV gamma count (correlation factor of 89%), and the chronology effect on the > 0.4 MeV gamma count (correlation factor of 35%).

The temperature effect was noted earlier, and is due to the increased density of the TCE cold bath at lower temperatures (Sect. 2.4.6). Previously, a measured correction of 3% was required at -35°C , which extrapolates to 4% over the entire temperature range, vs the 7% actually observed. A temperature effect does not occur with the > 0.4 MeV count since the higher energies are not seriously attenuated by the TCE.

The chronology effect on the > 0.4 MeV count shows considerable scatter, but is real (the "t" test shows that the slope is not zero, at the 95% C.L.). This effect is of uncertain origin. Based on the > 40 keV counts, no ^{85}Kr was lost during the series of measurements. It is postulated that instrumental drift was responsible since a slight shift in the position of the 0.4-MeV gate would have a relatively large effect on the observed count.

4.7 Attenuation Effects

The 0.51-MeV gamma peak should be relatively free of attenuation by CO_2 because of the low atomic numbers of carbon and oxygen. This is verified by the small (4% maximum) effect determined for the > 0.4 MeV range.

The beta decay, which accounts for 99.6% of the ^{85}Kr decay, is largely attenuated by ion pair production, with a small fraction being attenuated by bremsstrahlung. Based on the beta energies and the CO_2 densities involved, it is estimated that nearly all the beta radiation could be attenuated by ion pair production.⁵³

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Fig. 21. Count material balance as a function of chronology.

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Fig. 22. Count material balance as a function of temperature.

Bremsstrahlung attenuation is important only for higher energy (E) betas, and with absorbers of high atomic number (Z). The ratio of attenuation by bremsstrahlung/ionization is about $54 \text{ EZ}/800$, and for CO_2 and the steel cylinder these values are about 0.5 and 1.5%, respectively, for a total of 2%. This agrees exactly with the observation that, although there is 250X as much beta radiation as gamma (from 99.6/0.4), the recorded spectrum shows only about 5X as much bremsstrahlung as it does gamma peak, or 50X less (i.e., 2%) bremsstrahlung than ion-pair production.

Backscatter (or dose buildup) occurs whenever there is a significant quantity of absorber,⁵⁵ and for our range of CO_2 densities the saturation distance is estimated to range from 2 to 35 mm. Thus, a significant increase in count is expected at increasing CO_2 density from this source.

A combination of these effects accounts for our density attenuation curves (Figs. 6 and 7), which flatten out and then remain essentially constant. It is obvious that compensating effects are at work, and bremsstrahlung attenuation and backscatter are two such effects. The 4% attenuation for $> 0.4 \text{ MeV}$ counts is probably from attenuation of the bremsstrahlung component since the gamma peak at 0.51 MeV should be relatively unaffected by the changing CO_2 density and, if it were, the effect should be linear with density.

4.8 Error Sources

A number of error sources have been mentioned and discussed, as they occurred throughout the text. For convenience, they are all listed here:

- Counting statistics (Sect. 2.5.2)
- Counter dead time (Sect. 2.4.1)
- Instrument drift (Sect. 2.4.4)
- Gate position (Sect. 2.4.4)
- Background (Sect. 2.4.5)
- Temperature (Sects. 2.2.4 and 2.2.7)
- CO_2 density (Sect. 2.4.7)
- Internal attenuation (Sect. 2.4.5)
- Collimation (Sect. 2.4.8)
- Position of counter (Sect. 2.4.3)

In general, most errors are largely self-cancelling because the quantity which was directly measured is a ratio. Those error sources which, by their nature, could not be self-cancelling (e.g., internal attenuation) were indirectly shown to be quite small by means of (1) excellent agreement between the two energy ranges used for counting, (2) a satisfactory material balance, and (3) good agreement with published data for the water-Kr system.

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