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SOLUBILITIES OF Kr AND Xe IN FRESH AND SEA WATER

by

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ABSTRACT

A series of experimental determinations of the solubility of krypton and xenon were carried out in fresh water and seawater at $\sim 1^{\circ}$, $\sim 26^{\circ}$, and $\sim 47^{\circ}\text{C}$. The basic experimental technique was that of a recycling thin film in an atmosphere of the gas studied. The results are presented in the form of Henry's constants as a function of temperature.

SUMMARY

The Problem

To determine the solubility of krypton and xenon in fresh water and seawater from 0°C to 50°C.

Findings

The results, given in the form of Henry's constant, indicated a smoothly increasing function with temperature for both krypton and xenon. Henry's constant in seawater for both gases was approximately 25 % greater than the corresponding fresh water value.

INTRODUCTION

The determination of the solubilities of the gases krypton and xenon in fresh water and seawater was conducted as part of the broad national program evaluating the fate of fission products in aqueous environments.

A number of investigators¹⁻⁴ have determined the solubilities of the rare gases in pure water, and one investigator² has determined rare gas solubilities for a limited temperature range in seawater.

Several techniques were considered for obtaining and measuring equilibrium conditions for the solubilities of krypton and xenon in distilled water or synthetic seawater as functions of temperature and pressure. The method finally used was that of allowing the water to trickle-flow over a packed column of saddles in the presence of the gas under study. The water was continuously recycled under closely controlled temperature and pressure conditions until equilibrium was established.

The results of this experimental work are given in the form of Henry's constants for krypton and xenon as functions of temperature for the range of 0° to 50°C in fresh water and seawater (i.e., distilled water and synthetic seawater.)

EXPERIMENTAL PROCEDURE

The experimental system was composed of two distinct units. The first of these was the equilibrium system in which the gas and water were kept in intimate contact at constant temperature and pressure for sufficient time to allow the gas to come to equilibrium in the two phases. The second unit was the analysis system which was used to accurately determine the amount of gas dissolved in a given volume of water and the purity of the gas extracted from the water.

Solubility Equilibrium

The initial design of the equilibrium system used the principle of bubbling the gas through a column of water to establish equilibrium. Although this method has been used by other investigators^{5,6,7} with apparent success, the results obtained by the authors indicated the presence of several inherent problems in the technique which limited the accuracy of the results. One major difficulty for this system was in defining the pressure. When the gas was being circulated by a peristaltic pump there was a regular variation in pressure of 1 to 2 cm Hg. A series of test samples using distilled water and argon run in this system were analyzed for gas content. The results of these runs did not correlate well with even a rough estimate of run pressure. The values obtained for Henry's constant for argon at room temperature and approximately 1 atmosphere of gas pressure varied by almost a factor of 2.

A second and lesser problem, which led to apparent supersaturation, was bubble entrapment within the sample chamber. Since the actual pressure of the bubble was that of the mercury column in the manometer plus the water column in the sampler, which varied from 5 cm to 20 cm depending upon the bubble position, local enrichment could take place. Even if these bubbles were dislodged, it was necessary to wait a considerable time for the sample to come to equilibrium. This effect was also temporarily present for all the bubbles rising through the water column under normal running conditions. For these reasons the equipment was modified so that the water was circulated and allowed to flow freely over a packed column in the presence of the gas being studied. A detailed drawing of the final design of the equilibrium system is shown in Fig. 1.

The basic components of this system were: the sampler, which was designed to be removed from the system without affecting the equilibrium of the contained sample; the equilibrium column, which was packed with 4 mm Berl saddles to give a large surface area over which the water flows; the gas burette; the peristaltic circulating pump, which cycled the water in the packed column; the mercury manometer which was used to measure gas pressure; and the constant temperature bath.

The equilibrium system operated as follows: the entire system was evacuated to less than 50 μ Hg, a volume of degassed water was introduced from the water flask and the appropriate gas was bled into the gas burette. Next the system was isolated, and the gas was admitted into the equilibrium column. The circulating pump was then started to cycle the water through the column. At the end of the run the sampler was isolated from the rest of the system by means of stopcocks and was transferred to the analysis system.

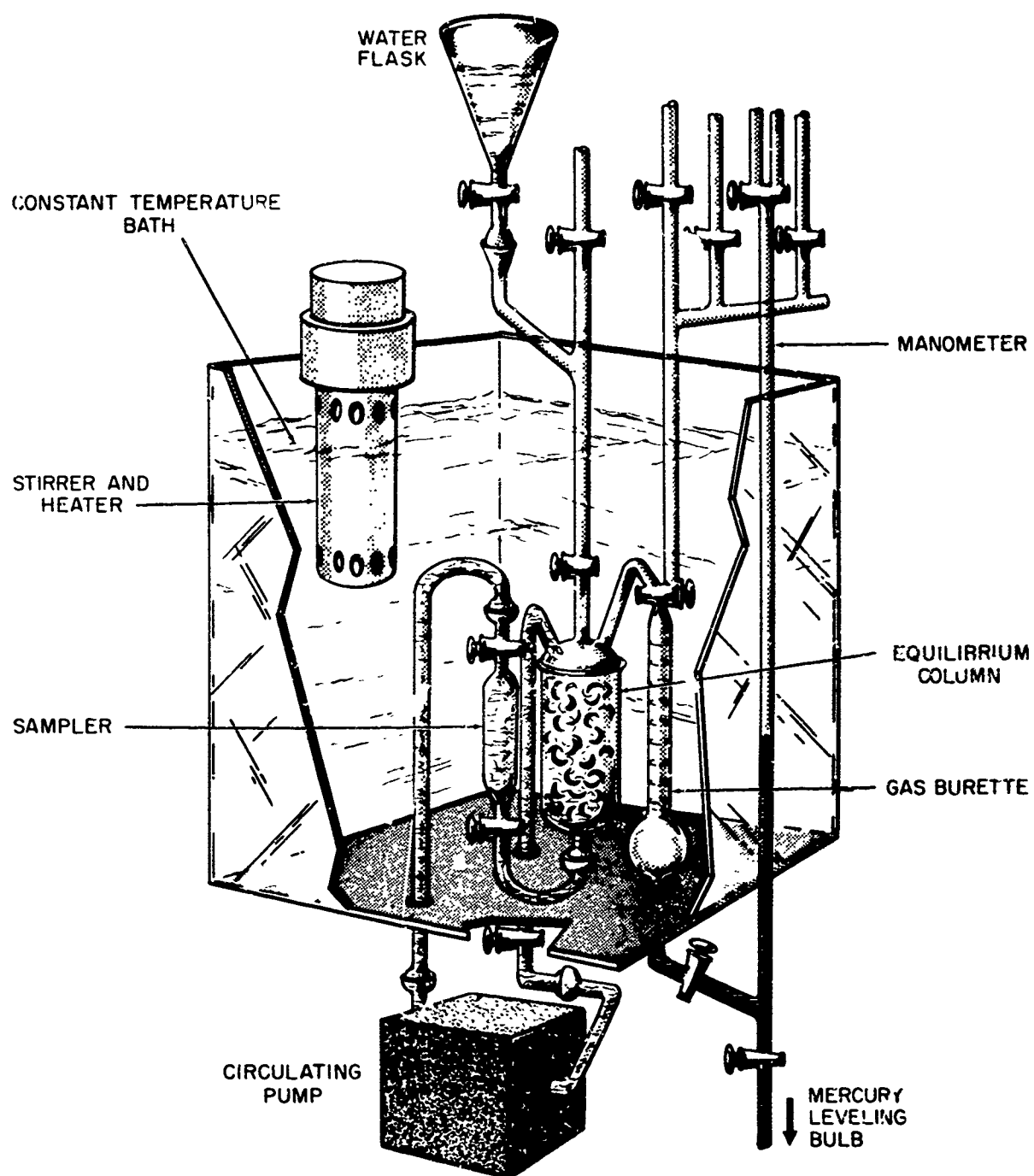


Fig. 1 Solubility Equilibrium Apparatus

A typical run for krypton or xenon used ~ 55 ml of degassed water and ~ 130 ml of gas at approximately 1 atmosphere pressure. The water circulation rate was ~ 110 ml/min with a flow that allowed rapid and complete mixing without bubble entrapment or frothing.

The rate of absorption of the gases was quite fast for the first 30 min or so; however, as the system neared equilibrium the rate of absorption decreased rapidly until equilibrium was approached asymptotically. The system for any single run was maintained under constant temperature and pressure conditions from 4 to 6 hr depending on the temperature. The cold runs (~ 0°C) and those near room temperature (~ 25°C) gave very good reproducible results after 4 hrs, while the temperature runs above room temperature (~ 50°C) required at least 5 hr for equilibrium to be established.

Temperature control and uniformity were assured by means of a differential copper-constantan thermocouple. It was found that the constant temperature bath exhibited temperature differences no greater than 0.1°, 0.005°, and 0.03°C for temperatures of 0°, 25°, and 42°C respectively. These differences were for extreme positions in the bath and are larger by a factor of 5 than the differences in the immediate vicinity of the sampler and equilibrium column.

The same differential thermocouple was used under normal run conditions to determine whether any temperature differences existed between the sampler and the constant temperature bath. A deviation which varied linearly with temperature was found. This deviation of sampler temperature from bath temperature went from +1.0° at 0°C to -0.5° at 50°C. These deviations were found to be constant through repeated measurements.

Since the bath temperature was the only temperature taken directly in a normal experimental run, all sample temperatures were corrected using the data mentioned above.

Solubility Analysis

The analysis system was designed to separate the gas from the water sample quantitatively and measure both its quantity and purity. The basic components of this apparatus were the vacuum system for degassing the water and the gas chromatograph.

The analysis system was used as follows: The sampler was attached to a trap and the entire system was evacuated to below 1 μ Hg. The

water was then allowed to expand into the trap. A cold trap, held at -96°C by a slush mixture of methanol, was opened to the first trap. This allowed the water to distill into the cold trap, liberating almost all of the dissolved gases. The water was kept frozen at -96°C while the gas was transferred to a gas burette by an automatic Toepler pump. The cold trap was then shut off from the gas burette and warmed up to room temperature to allow the ice to melt and any remaining dissolved gas to come out of solution. The water was then refrozen to -96°C , and the residual gas was pumped into the gas burette, where its pressure was measured with a mercury manometer at a fixed volume and temperature. This process was repeated until the pressure-volume product was reproducible. Under normal operating conditions this technique was quite fast and very efficient, taking only 2 to 4 freeze-pump-thaw cycles to obtain reproducibility. After the quantity of gas was accurately measured under controlled conditions, it was bled off and run through a thermal conductivity gas chromatograph for a purity check. The limit of detectability of air contamination in the normal gas sample was of the order of 1 part in 10^4 . Any sample in which this level was exceeded by more than a factor of 2 or 3 was not used for the determination of Henry's constant.

Quality Control of Materials

The gases used in the experimental work were supplied by the Air Reduction Corporation (AIRCO), with an analysis certificate indicating a 0.015 % xenon impurity in the krypton and a combined 0.0042 % of krypton and nitrogen in the xenon.

The water used for the fresh water runs was triply distilled before being subjected to a degassing procedure in preparation for the solubility runs. The technique used to degas the water was that of adding enough of the distilled water for one run (~ 70 ml) to a 500-ml filtration flask, connecting the flask to the vacuum system, rapidly stirring the water by means of a magnetic stirrer, and exposing the filtration flask and contents to an evacuated cold trap for 15-sec intervals. This last step was repeated several times. Samples of the degassed water were checked periodically in the analysis system for complete degassing. In all cases the gas content was undetectable.

The seawater used was prepared in the laboratory using the formula of Lyman and Fleming.⁸ A slight modification of their formula was used (Table 1).

For degassing the seawater without changing its salinity, a cold trap was placed between the filtration flask and the vacuum system. The seawater was degassed by exposing it to the vacuum system as in the fresh water system; however, the water vapor was frozen out in the cold

TABLE 1

Comparison of Composition of Natural Seawater with that of Synthetic Seawater

Salt	Lyman and Fleming g/kg soln	Present Work
NaCl	23.476	23.476
MgCl ₂	4.981	4.981*
Na ₂ SO ₄	3.917	3.917
CaCl ₂	1.102	1.102
KCl	0.664	0.664
NaHCO ₃	0.192	- **
KBr	0.096	0.096
H ₃ BO ₃	0.026	0.026
SrCl ₂	0.024	0.024
NaF	0.003	0.003
NaCl (Additional)	-	0.438*
	34.481	34.727

Using the formula given by Lyman and Fleming

$$\text{Chlorinity } \text{‰} = \frac{\text{total dissolved solids } \text{‰} - 0.073}{1.8110}$$

The chlorinity was determined as:

Chlorinity	19.00‰	19.14‰
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* When the seawater solution was made up, the MgCl₂ would not dissolve completely. A new solution was made forming the MgCl₂ by dissolving magnesium metal in concentrated hydrochloric acid. The excess hydrochloric acid was neutralized with a measured quantity of 6N sodium hydroxide. This left the additional sodium chloride as a by-product.

**The NaHCO₃ was not used because of the anticipated degassing of the water. It was felt that CO₂ gas would be drawn off from the NaHCO₃ in the degassing process, thus reducing the chlorinity by an indeterminate amount. The additional NaCl from the neutralizing process as mentioned above was more than enough to allow for the decrease in total solids due to leaving out the NaHCO₃.

trap while the undesirable gases were allowed to be pulled away by the vacuum pump. The collected water vapor was then distilled back into the flask containing the seawater. This method proved to be quite effective in degassing the seawater while maintaining the known salinity.

RESULTS AND DISCUSSION

The results of the experimental work are presented in Figs. 2 and 3 in the form of Henry's constants for krypton or xenon as functions of temperature for both fresh water and seawater. For comparison with other work, the results of Konig² are presented also in Figs. 2 and 3. The data points presented in the figures are the values for Henry's constant calculated from the actual experimental results. The points presented represent only about 40 % of the total number of experimental runs. The remaining 60 % were discarded because of actual or suspected experimental uncertainties somewhere in the procedure. The values for Henry's constants calculated from the experimental data were determined from the equations

$$K = \frac{P_g}{X_g} \quad (1)$$

$$X_g = \frac{N_g}{N_g + N_w + N_s} \quad (2)$$

where K = Henry's constant of gas
 P_g = equilibrium partial pressure of gas
 X_g = mole fraction of gas
 N_g = number of moles of gas
 N_w = number of moles of water
 N_s = number of moles of salt

The value for N_g was determined using the equation

$$N_g = \frac{P_a V_a}{RT_a} \quad (3)$$

where P_a = gas pressure in analysis system
 V_a = volume of gas in analysis system
 T_a = temperature of gas burette of analysis system
 R = gas constant

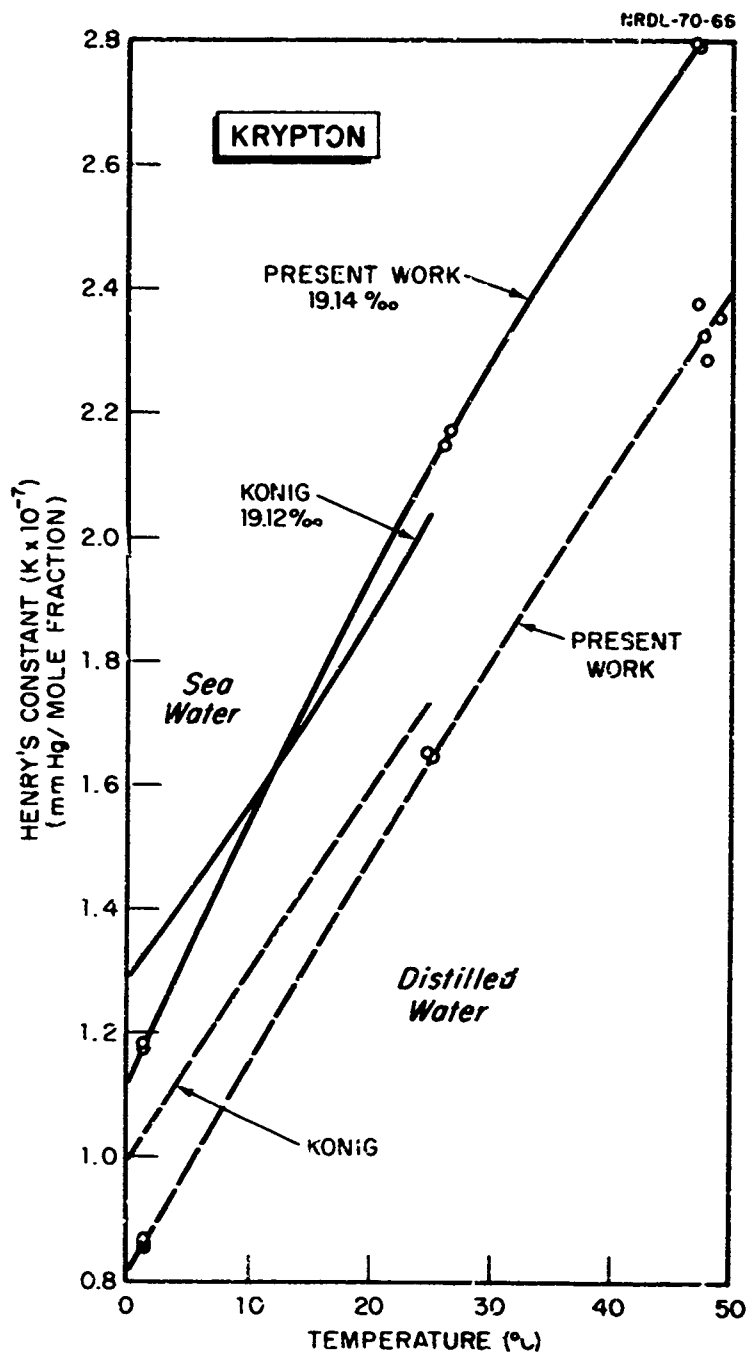


Fig. 2 Henry's Constant for Krypton as a Function of Temperature

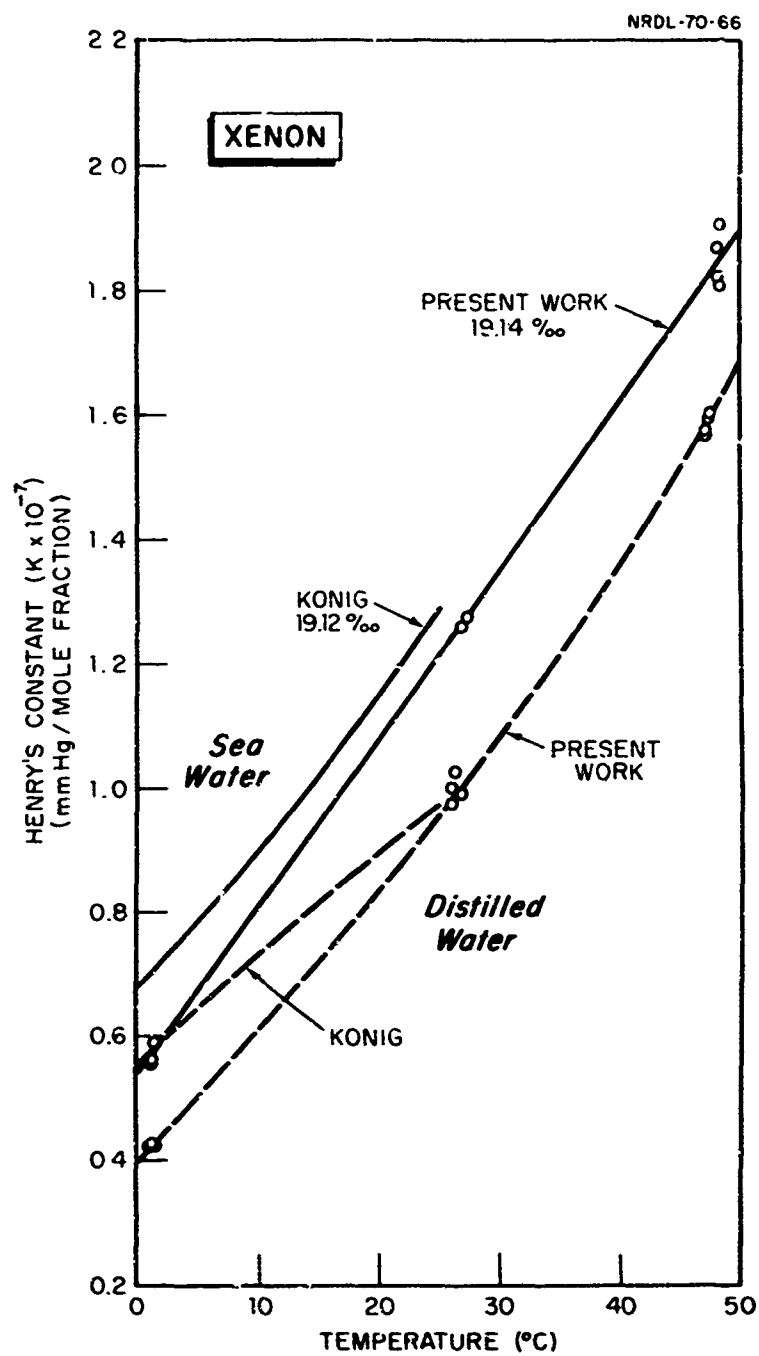


Fig. 3 Henry's Constant for Xenon as a Function of Temperature

Initially the virial equation of state was considered, but a preliminary check indicated that Eq. (3) was sufficiently accurate for this work if the RT_a term for the particular gas was accurately known. The RT_a values used in this work were from the table of M.I.T. coefficients as given by Cook.⁹

The uncertainty of all pressure measurements of P_g and P_a was considered to be no greater than $\pm 0.1\%$. All pressure readings were taken by mercury manometers and were corrected for temperature and gravity effects on the mercury columns. For pressure readings taken in the equilibrium apparatus the vapor pressure of fresh water or seawater was taken into account.

The mercury thermometers used to measure the bath temperature were calibrated against a thermometer which had been checked with an NBS certified standard. All temperatures were measured with an accuracy of $\pm 0.05^\circ\text{C}$.

The volumes of the gas burette and sample cells were calibrated by using the weight of the contained mercury. The sampler volumes, approximately 5 ml, were known to ± 0.002 ml. The 1 ml gas burette had an overall accuracy of ± 0.001 ml for each of the 0.1 ml markings. The usual gas sample extracted from the 5 ml water sample varied from 0.6 to 1.9 ml at a pressure of ~ 300 mm Hg. The temperature of the gas burette was controlled by means of a water jacket and was known to within $\pm 0.05^\circ\text{C}$.

If all of these errors are taken into account for a typical run, the overall error in the value of Henry's constant should be no greater than $\pm 0.5\%$.

The actual spread in experimental results is indicated in Table 2 where mean values of Henry's constant are given for the different experimental conditions. The percentage error is that determined by the maximum spread between the experimental points.

The final results of this work indicate a higher solubility of xenon and krypton in water than most previous works do. It is believed that the major reason for this difference is due to insufficient time in allowing the gas-water system to come to equilibrium in previous works. As was mentioned earlier, it was necessary to cycle a relatively small volume of water over a large area for a minimum of several hours before a steady state was reached.

TABLE 2

Henry's Constants and Corresponding Error Spread

Temperature (°C)	Henry's Constant (mm Hg/mole fract.)	Percentage Error	Number of Experi- mental Determinations
<u>Krypton in Distilled Water</u>			
1.3	0.866×10^7	$\pm 0.3 \%$	3
25.0	1.653×10^7	$\pm 0.4 \%$	2
47.8	2.340×10^7	$\pm 2.1 \%$	4
<u>Krypton in Seawater (19.14 ‰)</u>			
1.4	1.181×10^7	$\pm 0.3 \%$	2
26.4	2.163×10^7	$\pm 0.1 \%$	2
47.2	2.792×10^7	$\pm 0.3 \%$	2
<u>Xenon in Distilled Water</u>			
1.3	0.425×10^7	$\pm 0.5 \%$	3
26.2	0.987×10^7	$\pm 2.0 \%$	4
47.2	1.586×10^7	$\pm 0.6 \%$	4
<u>Xenon in Seawater (19.14 ‰)</u>			
1.3	0.568×10^7	$\pm 2.1 \%$	3
27.0	1.267×10^7	$\pm 0.0 \%$	2
48.1	1.848×10^7	$\pm 2.5 \%$	4

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