Solubility of Krypton and Oxygen in Water and Aqueous Uranyl Sulfate Solutions at Elevated Temperatures

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THE PURPOSE of the study reported was to determine the solubility of krypton in water and uranyl sulfate solutions under homogeneous reactor temperature and pressure conditions—i.e., 100° to 300° C., low krypton partial pressures, and high oxygen overpressures. In a homogeneous reactor a knowledge of the solubility of fission product is important, since it enables the prediction of their behavior. The noble gases are particularly important because of biological hazard and neutron economy.

The solubility of gases in water and aqueous salt solutions has been studied extensively. In 1945, Schlegel (*4*) evaluated the solubilities of selected gases in water from 0° to 100° C. and was inclined to have little confidence in the krypton values reported by Antropoff (*1*) and in the International Critical Tables, since the solubility data for helium, which were part of the same series of measurements, are apparently erroneous. In 1952 (*2*) and 1956 (*3*) a group at Battelle Memorial Institute reported the solubility of oxygen and several other gases for the temperature range of 100° to 300° C. and at pressures up to 3000 p.s.i. However, there are no data available on the solubility of krypton in the temperature range of interest. Although the prime objective was to investigate krypton solubility, data were collected where possible on the solubility of oxygen.

EXPERIMENTAL

Analytical. The solubility measurements required the determination of krypton in the vapor and solvent phases. The extremely low krypton concentration and the chemical inertness of krypton precluded use of the usual methods of gas analysis. Therefore, stable Kr was tagged with Kr^{85} and the tracer technique was used to determine the concentration of krypton in both the vapor and liquid phase samples.

Apparatus. The apparatus is shown in schematic form in Figure 1.

The system consists of a 550-ml. stainless steel No. 347 reaction vessel (American Instrument Co., Inc., Catalog No. 41-4630), fitted with a head equipped with a thermocouple well and two openings. One opening contains a 1/16-inch o.d. capillary tube which extends to the bottom of the vessel and is connected via valve *A* to the liquid-sampling system. The sampling system consists of a short 1/8-inch i.d. tube condenser, a 15-mil graduated centrifuge tube, a stainless steel gas counting chamber, and a manometer connected in series. The second opening is connected to a tee with valve *C* on one leg and the double valve, *B*-*D*, on the other. *D* is attached to the pressure gage (0 to 2000 p.s.i.) and *B* to the vapor sample system. The latter is made up of a condenser, gas sample bulb, and manometer. The temperature of the liquid in the pressure vessel is measured to ±0.1° C. using a Chromel-Alumel thermo-

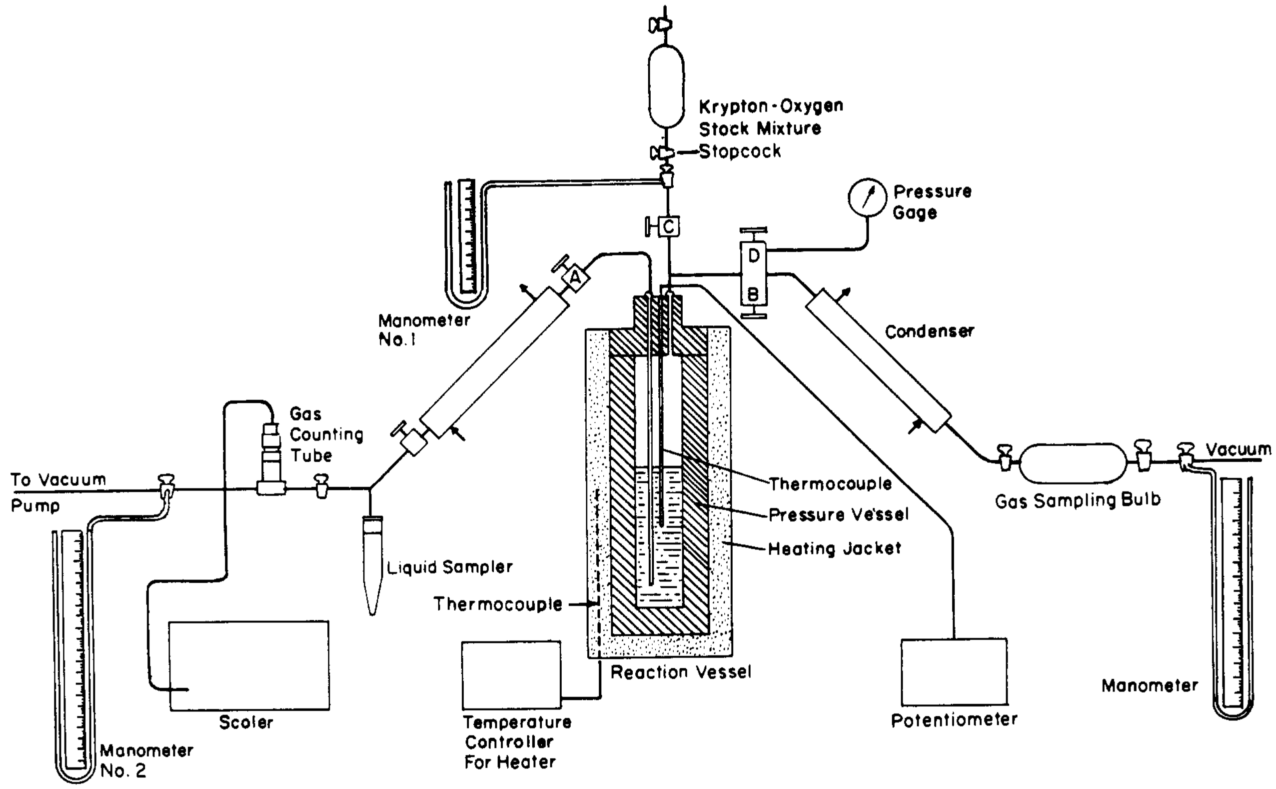

Figure 1. Apparatus for krypton solubility measurements

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couple and a Leeds and Northrup potentiometer, while the temperature of the vessel heater is controlled using a Wheelco controller (Model 404) (0° to 400° ±2° C.).

Procedure. At the start of the experiment, the pressure vessel containing 275 ml. of solvent is assembled as shown in Figure 1. The vessel is partially evacuated via valve *B* with valves *C* and *D* open and *A* and *E* closed. After evacuation, valve *B* is closed and the pressure reading on manometer 1 recorded. Stopcock *E* is opened and tagged krypton is admitted to the system. Stopcock is closed and the pressure reading recorded.

The approximate quantity of krypton added to the system can be calculated from the pressure increase, krypton concentration of the stock mixture, and the volume of the system. Valve *C* is closed and the gas bulb and manometer are removed. Then oxygen is added to the pressure vessel via valve *C* to give an overpressure. The bomb is heated and maintained at the specified temperature. Vapor and liquid samples are then removed simultaneously through valves *B* and *A*, respectively. The vapor sample is collected after passing through a cooling condenser in an evacuated sample bulb for subsequent krypton analysis where the moles of krypton per mole of gas are determined for the vapor sample.

In the case of the liquid sample, the liquid is collected in the graduated tube and the gases, which were previously dissolved in the liquid sample, are contained in the remainder of the liquid system—i.e., manometer 2, condenser, and counting chamber. The moles of gas above the liquid are calculated from the gas law and the moles of krypton per mole of gas are determined by an activity measurement of the gas. The mole fraction for krypton in the liquid at the test temperature is then calculated from the above data and the volume of the liquid sample.

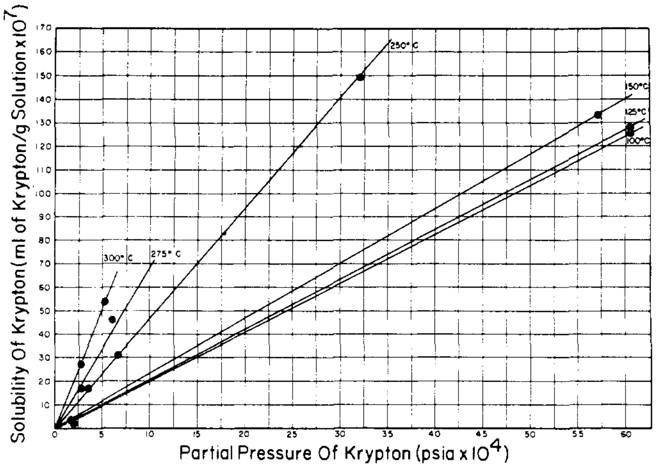

Figure 2. Isothermal solubility of krypton in water

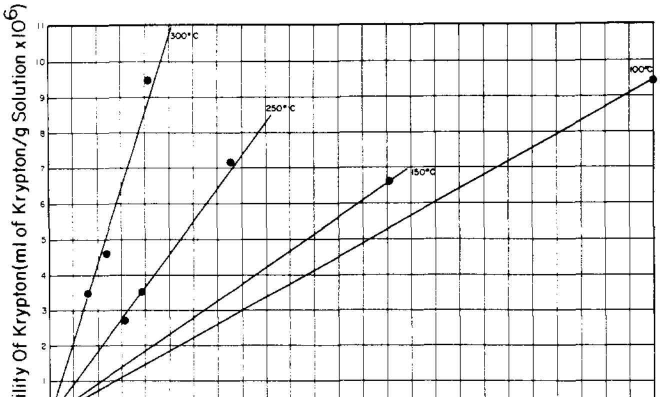

Figure 3. Isothermal solubility of krypton in uranyl sulfate A

RESULTS AND DISCUSSION

The solubilities of krypton and oxygen were measured in water and in two uranyl sulfate solutions (A and B). Table I summarizes the experimental conditions in terms of the chemical composition of the liquid phases, the temperature ranges, and the total and partial pressure intervals. In Table II are listed the test factors and results for the solubilities of krypton and oxygen in water, uranyl sulfate A, and uranyl sulfate B, respectively.

KRYPTON

The isothermal solubility (milliliters of krypton at STP per gram of solvent) *vs.* krypton partial pressure is plotted in Figures 2, 3, and 4 for water, uranyl sulfate A, and uranyl sulfate B, respectively. Since the isotherms are straight lines going through the origin, Henry's law constant is applicable to krypton in this partial pressure range. The temperature

Table I. Experimental Conditions

	H_2O	Uranyl Sulfate A	Uranyl Sulfate B
Chemical composition, mole/liter			
Uranyl sulfate	...	0.02	0.04
Copper sulfate	...	0.005	0.01
Sulfuric acid	...	0.005	0.01
Krypton measurement			
Temp. range, ° C.	100-300	100-300	100-300
Total pressure range, p.s.i.a.	270-1930	110-2015	350-1505
Partial pressure, p.s.i.a. × 10^{-4}			
Highest measured	60.6	53.2	73.0
Lowest measured	1.47	0.40	3.28
Oxygen measurements			
Temp. range, ° C.	125-200	100-300	100-300
Partial pressure, p.s.i.a.			
Highest measured	341	753	1505
Lowest measured	210	56	350

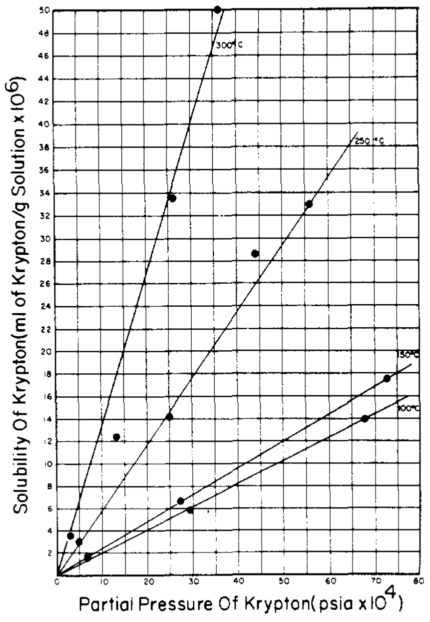

Figure 4. Isothermal solubility of krypton in uranyl sulfate B

Table II. Solubility of Krypton and Oxygen

Run	Sample	Length of Test, Hours	Temp., ° C.	Total Pressure, P.S.I.A.	Kr Partial Pressure, P.S.I.A.	O_2 Partial Pressure, P.S.I.A.	Mole Fraction O_2 in Liquid	K, P.S.I.A. per Mole Fraction Krypton	K, P.S.I.A. per Mole Fraction Oxygen
Solvent, H_2O									
Kr-8	1	2	250	1340	3.48×10^{-4}	763	...	2.54×10^5	...
	2	2	275	1560	2.77×10^{-4}	697	...	2.01×10^5	...
	3	2	300	1860	2.67×10^{-4}	613	...	1.21×10^5	...
Kr-9	1	2	250	1410	6.60×10^{-4}	833	...	2.64×10^5	...
	2	2	275	1615	6.03×10^{-4}	752	...	1.63×10^5	...
	3	2	300	1930	5.27×10^{-4}	683	...	1.22×10^5	...
Kr-10	1	2	100	270	1.99×10^{-4}	255	...	6.63×10^5	...
	2	16	125	280	1.53×10^{-4}	246	2.46×10^{-4}	5.88×10^5	10.0×10^5
	3	3.5	150	295	1.68×10^{-4}	226	2.55×10^{-4}	5.42×10^5	8.86×10^5
	4	22	200	435	1.47×10^{-4}	210	3.65×10^{-4}	3.87×10^5	5.75×10^5
Kr-11	1	17	100	400	60.6×10^{-4}	385	3.77×10^{-4}	6.00×10^5	10.2×10^5
	2	3	125	400	60.4×10^{-4}	366	...	5.86×10^5	...
	3	2	150	410	55.4×10^{-4}	341	3.69×10^{-4}	5.18×10^5	9.24×10^5
	4	18	180	400	40.4×10^{-4}	255	...	4.83×10^5	...
Kr-12	1	64	250	1000	32.0×10^{-4}	423	...	2.67×10^5	...
Solvent Uranyl Sulfate A									
Kr-2	1	2	250	1495	3.90×10^{-3}	918	...	2.38×10^5	...
	2	2	275	1715	4.29×10^{-3}	853	...	1.90×10^5	...
	3	2	300	2015	3.77×10^{-3}	769	...	1.49×10^5	...
Kr-3	1	1.5	251	1095	5.32×10^{-3}	518	...	2.08×10^5	...
	2	1.5	270	1235	4.41×10^{-3}	436	...	1.75×10^5	...
	3	1.5	305	1625	2.50×10^{-3}	299	...	1.01×10^5	...
Kr-5	1	2	250	1165	1.5×10^{-3}	588	...	2.7×10^5	...
	2	18	250	1120	1.5×10^{-3}	534	13.5×10^{-4}	2.6×10^5	3.95×10^5
	3	2	275	1340	1.1×10^{-3}	477	...	1.9×10^5	...
	4	2	300	1665	0.91×10^{-3}	438	...	1.1×10^5	...
	5	18	300	1577	0.70×10^{-3}	343	16.3×10^{-4}	1.0×10^5	2.10×10^5
Kr-6	1	2	250	1310	0.62×10^{-3}	733	17.2×10^{-4}	2.8×10^5	4.25×10^5
	2	2	275	1485	0.42×10^{-3}	622	20.5×10^{-4}	1.8×10^5	3.03×10^5
	3	19	300	1736	0.30×10^{-3}	508	22.9×10^{-4}	1.2×10^5	2.22×10^5
Kr-7	1	2	250	1330	0.72×10^{-3}	753	14.6×10^{-4}	2.6×10^5	5.15×10^5
	2	2	275	1565	0.60×10^{-3}	702	20.1×10^{-4}	2.0×10^5	3.49×10^5
	3	2	300	1870	0.45×10^{-3}	623	23.5×10^{-4}	1.3×10^5	2.65×10^5
13	1	2	100	115	0.093×10^{-3}	100	0.980×10^{-4}	6.37×10^5	10.2×10^5
	2	24	125	110	0.059×10^{-3}	76.3	0.763×10^{-4}	5.78×10^5	10.0×10^5
	3	6	150	125	0.04×10^{-3}	56	0.65×10^{-4}	5.1×10^5	8.6×10^5
Kr-14	1	18	100	365	5.03×10^{-3}	350	3.47×10^{-4}	6.66×10^5	10.1×10^5
	2	4	125	350	3.39×10^{-3}	316	3.40×10^{-4}	5.93×10^5	9.30×10^5
	3	17	150	315	2.82×10^{-3}	246	2.89×10^{-4}	5.20×10^5	8.50×10^5
Solvent Uranyl Sulfate B									
Kr-15	1	18	100	350	7.25×10^{-4}	335.3	3.209×10^{-4}	6.20×10^5	10.45×10^5
	2	6	150	410	6.93×10^{-4}	341	3.88×10^{-4}	5.73×10^5	8.80×10^5
	3	16	250	860	5.02×10^{-4}	283	8.04×10^{-4}	2.03×10^5	3.52×10^5
	4	4	300	1480	3.28×10^{-4}	233	9.59×10^{-4}	1.17×10^5	2.43×10^5
Kr-16	1	17	100	355	29.8×10^{-4}	340.3	3.400×10^{-4}	6.31×10^5	10.01×10^5
	2	6	150	400	27.6×10^{-4}	331	3.92×10^{-4}	5.19×10^5	8.45×10^5
	3	16	250	860	25.1×10^{-4}	283	8.27×10^{-4}	2.20×10^5	3.42×10^5
	4	5	300	1485	13.3×10^{-4}	238	10.9×10^{-4}	1.34×10^5	2.19×10^5
Kr-17	1	17	100	380	68.0×10^{-4}	365.3	3.529×10^{-4}	5.96×10^5	10.35×10^5
	2	4	150	445	73.0×10^{-4}	376	4.30×10^{-4}	5.18×10^5	8.74×10^5
	3	18	250	905	55.7×10^{-4}	328	10.2×10^{-4}	2.11×10^5	3.23×10^5
	4	5	300	1505	36.0×10^{-4}	258	14.7×10^{-4}	0.889×10^5	1.75×10^5
	5	16	250	825	43.7×10^{-4}	248	7.92×10^{-4}	1.90×10^5	3.13×10^5
	6	3	300	1440	26.0×10^{-4}	193	10.0×10^{-4}	0.970×10^5	1.93×10^5

dependence of Henry's law constant is discussed below for each system.

Water. Henry's law constant is plotted as a function of temperature in Figure 5. The solid line is the least squares line representing Henry's law constant as a function of temperature and is given by:

$$K = (9.126 \pm 0.0263\,T) \times 10^5 \text{ p.s.i.a. per mole fraction}$$

where K is Henry's law constant (p.s.i.a. per mole fraction), and T is the temperature (° C.).

A comparison of the variation of the means about the regression line to the point-to-point variation within temperature (variance-type test) indicated a strong linear relationship, thereby justifying the use of a linear fit of the data. The standard deviation of the variation about the line is 0.218×10^5 and can be considered the point-to-point variation. Since the least squares line is only an estimate of the true line of the relationship, the 95% confidence limits were calculated assuming no bias. These limits are interpreted as enclosing the true Henry's law constant unless, by chance, the experimental data have fallen into a pattern which has only a 0.05 probability of occurrence. The 95% confidence limits are shown in Figure 5 as dashed lines and are given by:

$$95\%\ \text{confidence limits} = K \pm 0.471 \times 10^5 \left[0.0667 + \frac{(T-202)^2}{75{,}334}\right]^{1/2}$$

Henry's law constant for the two temperature extremes (100° and 300° C.) are $(6.50 \pm 0.21) \times 10^5$ and $(1.24 \pm 0.21) \times 10^5$ p.s.i.a. per mole fraction.

Uranyl Sulfate A. A variance analysis of the data reported in Table II indicated a strong linear relationship between Henry's law constant and temperature. The best estimate (method of least squares) of this relationship is shown in Figure 6 as the solid line and is given by:

$$K = (9.188 - 0.267\,T) \times 10^5 \text{ p.s.i.a. per mole fraction}$$

The standard deviation of the variation (point-to-point variation) about the line is 0.170×10^5. The 95% confidence limits, shown by the dashed lines, are equal to:

$$95\%\ \text{confidence limits} = K \pm 0.357 \times 10^5 \left[0.05 + \frac{(T-230)^2}{130{,}000}\right]^{1/2}$$

Henry's constant for 100° and 300° C., the temperature extremes, are $(6.52 \pm 0.16) \times 10^5$ and $(1.18 \pm 0.11) \times 10^5$ p.s.i.a. per mole fraction.

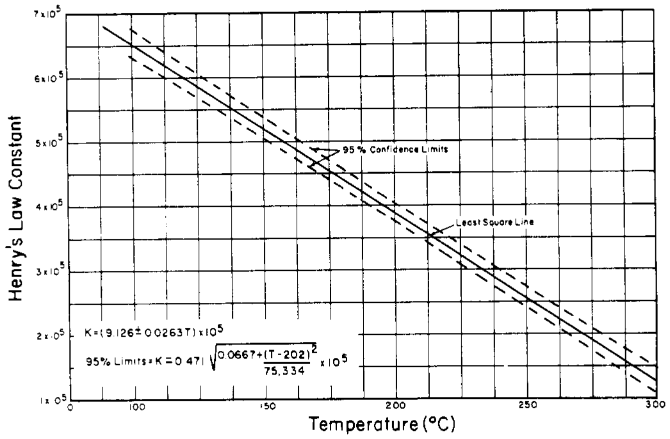

Figure 5. Solubility of krypton in water

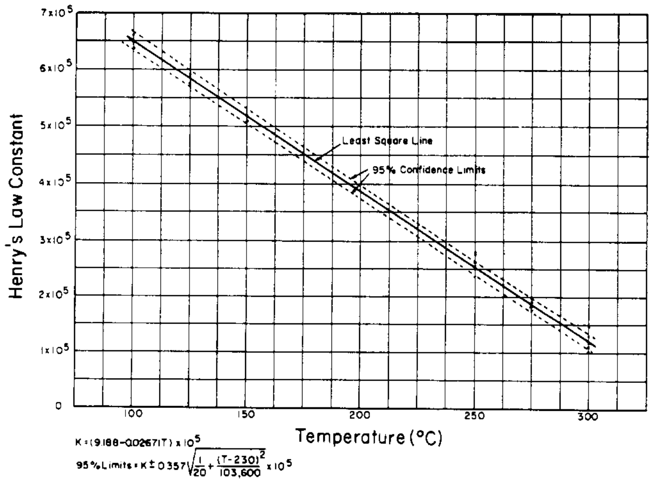

Figure 6. Solubility of krypton in uranyl sulfate A

Table III. Mean Values of *K*

Temp., ° C.	*K*, P.S.I.A. per Mole Fraction
Krypton in Uranyl Sulfate B	
100	$(6.18 \pm 0.26) \times 10^5$
150	$(5.36 \pm 0.26) \times 10^5$
250	$(2.06 \pm 0.23) \times 10^5$
300	$(1.09 \pm 0.23) \times 10^5$
Oxygen in Water Uranyl Sulfate A, and Uranyl Sulfate B	
100	$(10.2 \pm 0.3) \times 10^5$
125	$(9.75 \pm 0.28) \times 10^5$
150	$(8.66 \pm 0.23) \times 10^5$
200	$(5.75 \pm 0.56) \times 10^5$
250	$(3.45 \pm 0.25) \times 10^5$
300	$(2.10 \pm 0.23) \times 10^5$

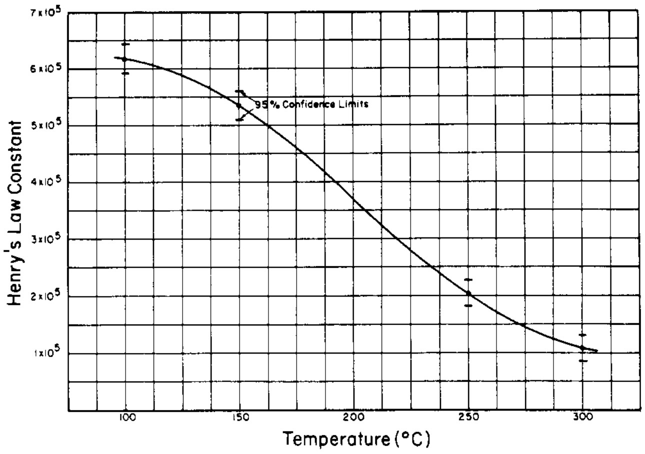

Figure 7. Henry's law constant for krypton vs. temperature
Uranyl sulfate B

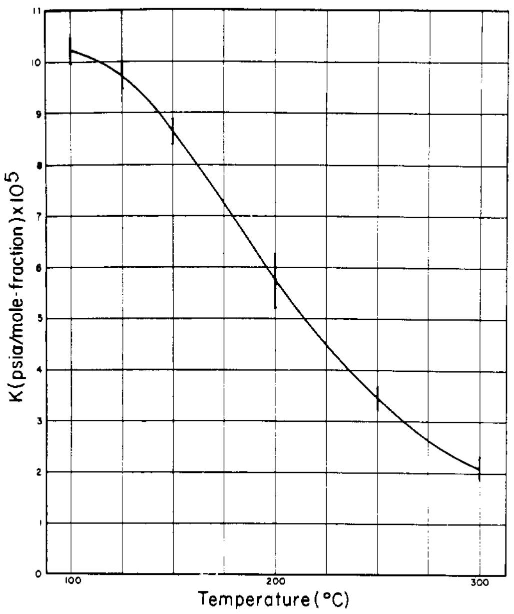

Figure 8. Mean value of K for oxygen in water, uranyl sulfate A, and uranyl sulfate B

The solubility of krypton in water and uranyl sulfate A appears to be the same under comparable conditions and there is no indication that the solubility-temperature equations are different. Therefore, the two sets of data can be pooled to formulate the new equation:

$$K = (9.162 - 0.0265\,T) \times 10^5 \text{ p.s.i.a. per mole fraction}$$

Uranyl Sulfate B. A variance analysis of the results (Table II) indicated that the data give no justification for assuming linearity. Since measurements were made at four temperatures, the means of these temperatures and the 95% confidence limits of the true means were calculated and are given in Table III. The point-to-point variability for these data is 0.203 × 10^5. The mean Henry's law constants are plotted as a function of temperature in Figure 7 with a line drawn through the mean values. The constant for the temperature extremes (100° and 300° C.) are 6.14 ± 0.26) × 10^5 and (1.09 ± 0.23) × 10^5 p.s.i.a. per mole fraction.

OXYGEN

The oxygen solubility data for the measurements in which 3.5 or more hours were allowed for reaching equilibrium are given for the three solvents in the form of Henry's law constant in Table II. The constants for less than 3.5 hours are not considered, since it is believed that this is a minimum period for reaching oxygen equilibrium. The oxygen partial pressures varied from 56 to 918 p.s.i.a. The homogeneity of the oxygen data for the three solvents was examined using a variance ratio test. The two measures of variability were the variation of the means for solution within temperature and run to run variation within temperature and solution. The analysis indicated that the solubility was not affected by the solvent. Therefore, the means constant and 95% confidence limits were calculated, neglecting the solvent parameter, for various temperatures (Table II and Figure 8). The standard deviation of point-to-point variation is 0.267 × 10^5. It is readily seen that the constant is not a linear function of temperature and that the 95% confidence limits include the solubility values reported by Battelle for oxygen in water. This confirmed, within the limits of the data, the values reported by Battelle.

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Solubility of Iodine in Dimethylsulfoxide

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SOLUBILITY of iodine in dimethylsulfoxide (DMSO) has been measured at temperatures from 27° to 38° C. The results are reported in Table I.

EXPERIMENTAL

Dimethylsulfoxide (Stepan Chemical Co., Chicago, Ill.) was distilled once before use. Resublimed iodine from Fisher and Mallinckrodt was used without further purification. Anhydrous sodium thiosulfate (Fisher certified reagent), potassium iodide (Baker analyzed reagent), and Thyodene indicator (Fisher) were also used without further treatment.

Two-milliliter samples of dimethylsulfoxide were placed in large test tubes, saturated with excess iodine, and the test tubes sealed by a flame. The tubes were then placed in a Precision temperature bath (±0.02°) equipped with a mechanical shaker for time intervals varying from 2 days to 4 weeks.

Table I. Solubility of Iodine in Dimethylsulfoxide

T, ° K.	x_2, Mole Fraction of Iodine
300.2	0.550
301.3	0.556
303.2	0.563
305.2	0.569
307.2	0.573
309.2	0.578
311.2	0.579

A 1-ml. aliquot of the equilibrated solution was added to a previously weighed amount of potassium iodide solution. The iodine-dimethylsulfoxide–potassium iodide solution was weighed, and the weight of the aliquot was determined by difference. In order to determine the amount of iodine, the iodine-dimethylsulfoxide solution in potassium iodide was titrated with standard thiosulfate solution using Thyodene as an indicator. The average precision of the results was approximately 1%.

Each value, except those at 27°, 32°, and 36°, represents an average of seven determinations. Nine determinations were made at 36° and 10 at the other two temperatures.

DISCUSSION

The solubilities presented in Table I were fitted to the equation

$$\ln x_2 = -433.2/T + 0.8511$$

by the method of least squares using an IBM 650 digital computer. The differential heat of solution of iodine from these data is 861 ± 3 cal. per mole.

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