

Solubility of Xenon in Liquid Sodium

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The solubility of xenon in liquid sodium was measured as a function of pressure (2–8 atm) and temperature (350–600°C). Henry's law was obeyed with the value of the Henry's law constant, $K_H = N_{Xe}/P$, ranging from $1.38 \times 10^{-10} \text{ atm}^{-1}$ at 350°C to $1.59 \times 10^{-8} \text{ atm}^{-1}$ at 600°C, where N_{Xe} and P are the atom fraction and the partial pressure of xenon, respectively. The temperature dependence of solubility may be represented by $\log_{10} \lambda = (0.663 \pm 0.01) - (4500 \pm 73) T^{-1}$, where λ is the Ostwald coefficient (the volume of xenon dissolved per unit volume of sodium at the temperature of the experiment). The heat of solution of xenon in sodium was $20.6 \pm 0.7 \text{ kcal/mol}$, where the standard state of xenon is defined as that of 1 mol of an ideal gas, confined to a volume equal to the molar volume of sodium.

The solubility of noble gases in liquid sodium is of considerable interest because of the use of sodium as a coolant in nuclear fission reactors. Helium and argon are frequently used as sodium blanketing gases, and krypton and xenon are fission product gases which may be released to sodium from the fuel-pins. The solubilities of helium and argon in liquid sodium have been reported (9, 10), and that of krypton has been determined (7). Measurement of the solubility of xenon was undertaken to provide data necessary for the evaluation of the consequences of fuel-pin cladding failure.

Experimental

Reference 10 describes the details of the method used for the determination of the trace solubilities of gases in liquid metals and shows a schematic diagram of the solubility apparatus. In the present application, the procedure was as follows. Approximately 2500 cm³ of liquid sodium contained in a large vessel (saturator) was saturated with natural xenon at a preselected temperature and pressure by circulating the gas through the liquid via a coiled, perforated tube placed near the bottom of the saturator. A measured amount (~1500 cm³) of the saturated sodium was then transferred to another vessel (stripper) via a heated, valved 1/4-in. sodium-transfer line which interconnected the bottom plates of the vessels. The volume of sodium transferred was calculated from the known geometry of the stripper and the liquid levels of sodium before and after transfer. The levels were measured with a Mine Safety Appliances Corp. liquid level probe operating on the capacitance principle.

In the stripper the dissolved gas was separated from sodium by sparging with helium, which was introduced through an immersed 10-cm stainless-steel dispersion disc (Micrometallic Corp., 5- μm mean pore size). The resulting xenon-helium mixture was then slowly exhausted through a 6-mm \times 8-cm column of activated silica gel cooled to -196°C, on which the xenon was adsorbed while most of the helium passed through unadsorbed. The gel was then heated at 300°C and the desorbed gas, now enriched in xenon, was analyzed for xenon with a Beckman GC-5 gas chromatograph used in conjunction with an electron capture detector.

In this procedure the following precautions were taken to assure the accuracy of the solubility measurements. Good contact of xenon with sodium in the saturator was provided by prolonged (1–2 hr) bubbling of the gas through the liquid. The saturated sodium remained undisturbed for a sufficiently long period of time (overnight) to allow the coalescence and escape of gas bubbles. Only the bottom portion of the liquid was transferred to the stripper, and the transfer rate was kept low to avoid the entrainment of the interfacial liquid, which might have been enriched in xenon. Efficient stripping of the dissolved xenon from the liquid was effected by cooling it to ~150°C (a temperature at which the solubility of xenon was negligible) and then sparging it with 400 cm³/min helium for 2 hr. Tests of this procedure with xenon-helium mixtures of known compositions showed that within experimental uncertainties, a quantitative recovery of xenon was achieved and that recourse to a radiometric method with β -active Xe¹³³ was unnecessary.

Xenon (99.995%) was purchased from the Baker Chemical Co. The only detected impurities were N₂ (15 ppm), Kr (10 ppm), and Ar (8 ppm). Approximately 25 l. (STP) of the gas was stored in a 2.5-l. reservoir connected to the saturator and containing a small trap filled with activated charcoal. Xenon could be pumped in and out of the reservoir by either cooling (to -196°C) or warming the trap. For conservation the undissolved xenon in the saturator was returned to the reservoir after each solubility experiment. Ultrahigh purity (99.999%) helium was purchased from the Matheson Co. Reactor-grade sodium used in this work was purified in situ by periodic transfers from the saturator to a special vessel where it was cooled to 150°C and passed through a porous metal filter to remove insolubles.

Results and Discussion

Solubility determinations were made at various pressures and temperatures. The uncertainties owing to the stripping, recovery, and analysis of minute quantities of xenon (<0.1 std cm³) made statistical analysis of the data imperative. The isothermal pressure dependence of solubility was determined from 17 experiments at temperatures near 500°C and xenon partial pressures ranging from 2 to 8 atm. The purpose of these experiments was to establish the validity of Henry's law for the Xe-Na system. The results are shown in Figure 1 where the atom fraction solubility of xenon, N_{Xe} (corrected to exactly 500°C), is plotted against the xenon pressure, P . The data were fitted to a linear equation. On the basis of the statistical F-test (2), the value of the intercept was not significant; hence, within the experimental error, the data can be represented by Henry's law, $N_{Xe} = K_H P$, with the Henry's law constant $K_H = 3.0 \times 10^{-9} \text{ atm}^{-1}$. Solubility relationships of the form $N_{Xe} = K P^n$, which include Henry's law and Sieverts' law as special cases, were also tested. A linear least-squares analysis of $\log N_{Xe}$ vs. $\log P$ yielded a slope of $n = 0.9 \pm 0.3$, which the F-test showed to be not significantly different from unity, supporting the adequacy of a Henry's law representation.

The temperature dependence of the solubility was determined from 47 experiments performed at various temperatures within ~3° of 350°, 400°, 450°, 500°, 550°, and 600°C. The results are shown in Figure 2. The measured

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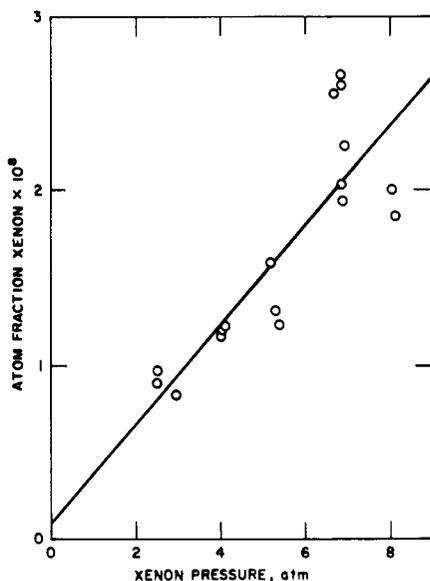


Figure 1. Pressure dependence of solubility of xenon in sodium at 500°C

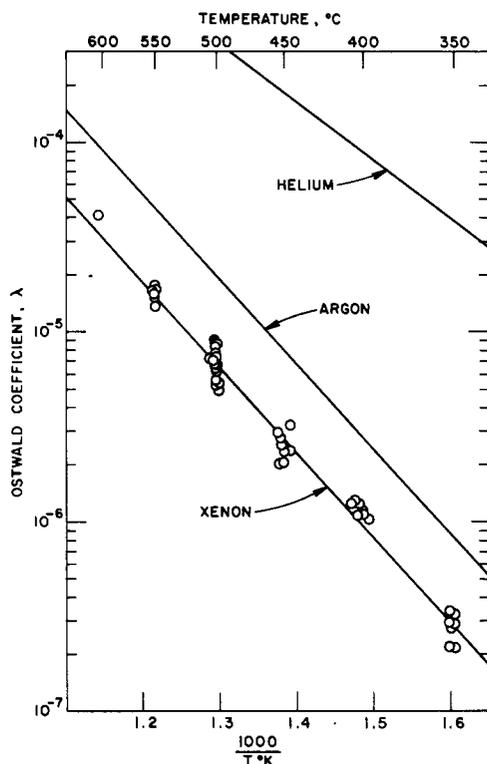


Figure 2. Temperature dependence of solubility of helium, argon, and xenon in liquid sodium

Table I. Solubility of Xenon in Liquid Sodium

Temp, °C	Henry's law constant, atom fraction/atm	Ostwald coeff, cm ³ gas/cm ³ liquid	Relative SD, %	No. of determinations
600	1.59×10^{-8}	4.00×10^{-5}	...	1
550	6.61×10^{-9}	1.59×10^{-5}	9	6
500	3.00×10^{-9}	6.89×10^{-6}	17	17
450	1.13×10^{-9}	2.46×10^{-6}	18	9
400	5.36×10^{-10}	1.10×10^{-6}	6	7
350	1.38×10^{-10}	2.66×10^{-7}	17	7

atom fractions were corrected to the above 50°-interval temperatures by the use of the temperature-dependence equation obtained from the least-squares analysis of the complete data. The individual determinations of the Henry's law constants at each temperature were logarithmically averaged and are shown in Table I, together with the more familiar Ostwald coefficients, the ratio of the volume of gas absorbed to the volume of absorbing liquid, all measured at the same temperature (4). For gases which are ideal over the measured range, both units are independent of pressure. Their thermodynamic significance has been discussed elsewhere (10, 11). The Ostwald coefficient, λ , is related to the Henry's law constant, K_H , by the equation

$$\lambda = \frac{RTd_{Na}}{M_{Na}} \cdot K_H \quad (1)$$

where $R = 82.06 \text{ cm}^3\text{-atm/deg-mol}$ is the gas constant, d_{Na} is the density of liquid sodium, M_{Na} is the molecular weight of sodium, and T is the temperature. For the density of liquid sodium, use was made of the recommended equation (3, 8) $d_{Na} (\text{g/cm}^3) = 0.950 - (2.30 \times 10^{-4})t - (1.46 \times 10^{-8})t^2 + (5.64 \times 10^{-12})t^3$ where t is the Celsius temperature.

Figure 2 is a semilogarithmic plot of λ vs. $1/T$. For xenon the regression line may be represented by

$$(350\text{--}600^\circ\text{C}) \log_{10} \lambda = (0.663 \pm 0.100) - (4500 \pm 73)/T \quad (2)$$

The heat of solution, 20.6 ± 0.7 (95% confidence limits) kcal/mol, calculated from Equation 2, corresponds to $[\bar{H}_{Xe}(\text{soln}, T, P) - \bar{H}_{Xe}(g, T, P = RTd_{Na}/M_{Na})]$, where the standard state is defined to be that of 1 mol of ideal gas at temperature T in a volume equal to the molar volume of sodium. The previously determined solubilities for helium and argon (10) are also shown in Figure 2.

The information available on the solubility of noble gases in liquid alkali metals has been reviewed (6). The only other experimental study on the solubility of xenon in liquid sodium appears to be that of Mitra (5). His procedure involved radiometric measurement of the quantity of xenon liberated when an "almost instantaneously" frozen aliquot of sodium saturated with radioactive xenon gas was remelted in an evacuated vessel. Mitra's solubilities, however, are higher than those reported here by a factor of 10^5 and are inconsistent with any reasonable expectation based on the available data for other noble gases in sodium (6, 10). A theoretical model that satisfactorily accounts for the measured solubilities of noble gases in liquid sodium, including these data for xenon, has been developed (7) in this laboratory.

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