Dissociation Pressure and Other Thermodynamic Properties of Xenon-Water Clathrate

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The dissociation pressure of the xenon-water clathrate was measured in the 0–12°C range. The decomposition temperature of the clathrate was -3.6°C at 1 atm, and the dissociation pressure was 1.52 atm at 0°C. $\Delta H_r{}^\circ$ was -15.5 kcal/mol, and the values obtained for $\Delta G_r{}^\circ$ and $\Delta S_r{}^\circ$ at 5°C were $+0.50$ kcal/mol and -54.0 eu, respectively.

As part of a study of the interaction between leguminous hemoglobin and nitrogen and xenon (2), we measured the solubility of the two gases in water at 5°, 15°, and 25°C and reevaluated the dissociation pressure of the $Xe{\cdot}H_2O$ clathrate in the 0–12°C temperature range. In addition, other thermodynamic properties of the clathrate such as the decomposition temperature, standard free energy, entropy, and enthalpy of reaction for Reaction 1:

$$6H_2O(l) + Xe(g) \longrightarrow Xe{\cdot}6H_2O(s) \qquad (1)$$

were determined. A summary of the results along with a comparison with some values previously reported is presented.

Experimental Methods

Sample. The xenon used was supplied by J. T. Baker Chemical Co. It was reagent grade and reported to contain the following impurities: Kr 10 ppm, N_2 50 ppm, O_2 5 ppm, H_2 5 ppm, hydrocarbons 15 ppm, and moisture 5 ppm. Mass spectra analysis of the sample indicated the presence of no detectable impurities other than those reported by the supplier.

Manometric apparatus. The experimental apparatus consisted of a gauge, stainless-steel reaction vessel provided with a magnetic stirrer, water pump, and a constant-temperature bath. The reaction vessel used had a capacity of 20 ml and was manufactured from 303 stainless steel by Ottesen Machine Co., Las Cruces, N.M. The gauge employed covered the range from 0 to 5 atm and was built by Heise Bourdon Tube Co., Inc., Newton, Conn. It had a maximum hysteresis of 3.5 mm, was sensitive to the nearest 0.5 mm Hg, and was temperature compensated over the range from -30° to $+50$°C. Since Bourdon gauges respond to the difference in pressure between the system and its surroundings, the absolute pressure of the gas in the system was obtained by adding the barometric pressure to the gauge reading.

The manifold contained three Hoke valves and was constructed out of 0.25 in 303 stainless-steel tubing of 0.030 in. inside diameter. The connections in the manifold were made with Parker-Hannifin Ferulok fittings obtained from Metropolitan Supply Co., Phoenix, Ariz. The seal between the manifold and the reaction vessel was provided by a rubber O-ring. All of the manometric system, with the exception of the gauge, were placed in a constant-temperature bath that could be regulated to within ±0.1°C. The experiments were performed in a climatic chamber where the temperature was maintained within ±0.5°C of the bath temperature.

Solubility determinations. Aliquots of 17 ml of deionized water were introduced in the reaction vessel, degassed, and then allowed to equilibrate with xenon at the desired temperature. The solution was stirred during the experiments by means of a magnetic bar driven by an immersed stirrer. The average equilibration time required for xenon and water was about 5 hr. The amount of gas dissolved was determined by applying the ideal gas equation in the form

$$\Delta n = \frac{(\Delta P)(V)}{RT}$$

where Δn = number of moles of gas absorbed, V = volume of gas above solution in ml, R = gas constant 6.24 $\times 10^4$ mm ml/deg mol, T = temperature in K, and ΔP = change in pressure in mm. A least-squares treatment of the experimental data with confidence limits of 50% for the error was performed and yielded Henry's law constants for the desired temperatures.

Measurement of dissociation pressure of clathrate. The dissociation pressure of the xenon-water clathrate was determined in two ways. The first method involved the measurement of the dissociation pressure, P_{diss}, only at 5°C and was a direct result of the solubility determination at this temperature. The equilibrium pressure for the absorption of xenon attained a constant value and corresponded to the dissociation pressure of the clathrate at 5°C.

The second method involved the measurement of the dissociation pressure in the 0–12°C range. Exactly 17 ml of deionized water were placed along with the magnetic stirrer in the stainless-steel reaction vessel, and the system was allowed to equilibrate at 12°C. The water sample and the remainder of the system were then degassed with a vacuum pump, and enough xenon was added to exceed the solubility reported for that temperature. Whether or not the clathrate was formed was easily ascertained by comparing the solubility of xenon in the experiment with that calculated from Henry's law for 12°C.

After the system equilibrated (the pressure of xenon above the solution became constant), a record was made of the gauge and barometric pressure. The temperature of the constant bath and the climatic chamber were then decreased at intervals of two or more degrees, and a new equilibrium pressure, which corresponded to the new dissociation pressure, was determined at a given temperature. Once a set of measurements was taken down to 0°C, the system was allowed to warm up and reattain equilibrium at different temperatures. The dissociation pressures obtained with various aliquots of xenon and water were essentially the same, regardless of whether the system was heated or cooled in the experimental temperature range. The equilibration at a given temperature usually required about 5 hr.

Results and Discussion

The Henry's law constants determined experimentally for the solubility of xenon in water are summarized in

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Table I and are compared to values obtained by Wood and Caputi (*10*), Ewing and Maestas (*3*), and Morrison and Johnstone, (*5*). The value of 131 for 5°C was calculated from the data of Morrison and Johnstone (*5*) by extrapolation, since their measurements were made from 12.7° to 71.7°C. In general, the agreement between the constants in Table I is good, and the differences are within the limits of experimental error. The present set of measurements also agrees with earlier evidence in the literature that the solubility of xenon in water does not deviate significantly from Henry's law from 0 to 5 atm at temperatures of 5-25°C, except when clathrate formation occurs.

Table I. Henry's Law Constants for Solubility of Xenon in Water

Source	Henry's law constants, atm/mol		
	5°C	15°C	25°C
Present study	109 ± 10	171 ± 8	217 ± 6
Wood and Caputi (*10*)	114	171	225
Ewing and Maestas (*3*)	...	...	227
Morrison and Johnstone (*5*)	131	179	223

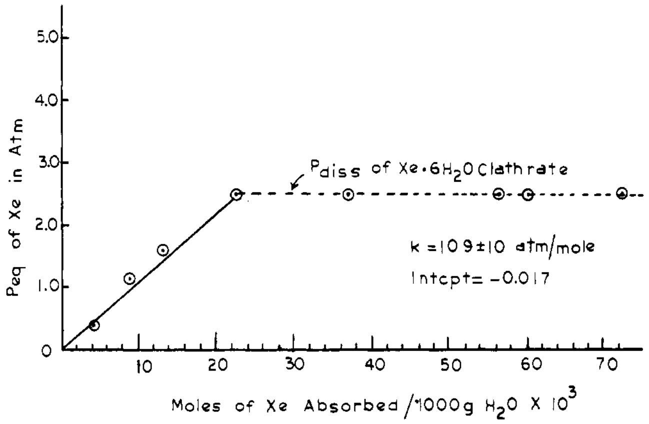

Figure 1. Solubility of xenon in H_2O at 5°C

Table II. Dissociation Pressure of Xenon-Water Clathrate

Temp, °C	P_{diss}, mm Hg	P_{diss}, atm
0.0	1155 ± 3	1.52 ± 0.00
2.0	1343 ± 4	1.77 ± 0.00
4.0	1654 ± 11	2.18 ± 0.01
5.0	1890 ± 6	2.49 ± 0.01
6.0	2127 ± 2	2.80 ± 0.00
8.0	2570 ± 11	3.39 ± 0.01
10.0	3140 ± 9	4.13 ± 0.01
12.0	3730 ± 4	4.91 ± 0.00

For the solubility of xenon in water at 5°C, we observed a marked deviation from Henry's law. From Figure 1, the deviation begins at about 2.48 atm. The straight line changes slope and levels off at 2.49 atm. This leveling off indicates the formation of the Xe-H_2O clathrate, and the equilibrium pressure of 2.49 atm corresponds to the dissociation pressure of the clathrate at 5°C.

A summary of the results obtained for the dissociation pressure of the clathrate is given in Table II. These experimental values vary considerably from those determined by De Forcrand (*1*) in 1925 by means of the Cailletet apparatus. The difference in results can probably be attributed to the purity of the xenon used by De Forcrand or to differences in temperature control. The small sample obtained by him from Lepape after many years of waiting could have contained some impurity such as nitrogen or argon. The ability of gases such as H_2, N_2, O_2, and CO_2 to stabilize certain clathrates has been discussed in the literature (*7*).

The standard heat of reaction of xenon with water to form the clathrate, $\Delta H_r°$, for Reaction 1 was determined by use of the Clausius-Clapeyron equation. A least-squares plot of log P_{diss} vs. $(1/T)$ gave a straight line with a slope having a value of $-3.391 \pm 0.053 \times 10^3$ and an intercept of $3.710 \pm 0.005 \times 10^{-3}$. These correspond to a $\Delta H_r°$ of -15.5 ± 0.2 kcal/mol and a decomposition temperature of 269.5 ± 0.4K or −3.6° ± 0.4°C.

Assuming that the activities of the solid clathrate and liquid water are approximately unity and that the activity of xenon gas is about the same as its pressure, the equilibrium constant, K_p, for Reaction 1 at a certain temperature is given by $K_p = 1/P_{Xe}$, where P_{Xe} denotes the equilibrium pressure of xenon or the dissociation pressure of the clathrate at that temperature. We have determined the reaction free energy, $\Delta G°_{5°C}$, and the reaction entropy, $\Delta S°_{5°C}$, for clathrate formation at 5°C using xenon gas at 1 atm and liquid water as standard states. These results along with other thermodynamic properties of the clathrate are summarized in Table III. In general, the values of the present study agree well with those of Von Stackelberg and his associates (*8*, *9*). The differences in the dissociation pressure and decomposition temperature are within the limits of experimental error. The results of De Forcrand are significantly different for reasons already described.

The experimental entropy of reaction for Reaction 1 agrees well with the estimated value of −53 eu. The entropy of formation of the clathrate from monatomic xenon gas was estimated to be −53 eu by considering the entropy of solidification of six moles of water, −31 eu, and the entropy necessary to trap the gas in the cage formed by ice (*4*). The second term is approximately equal to Trouton's contant, i.e., −21 eu. In actuality, the entropy of solidification of xenon is about −3.4 eu, and that of condensation is −18.3, giving a total of −21.7 eu (*6*).

Heats of reaction for clathrate formation according to Reaction 1 by use of different standard states for the reactants have been determined, and the entropy of

Table III. Summary of Thermodynamic Properties of Xenon-Water Clathrate

Source	P_{diss}, 0°C (atm)	Decomposition temp, 1 atm (°C)	$\Delta H_r°$ from liq H_2O and Xe gas, 1 atm (kcal/mol)	$\Delta G_r°$ from liq H_2O and Xe gas, 1 atm, 5°C (kcal/mol)	$\Delta S_r°$ from liq H_2O and Xe gas, 1 atm, 5°C (eu)
Present study	1.52 ± 0.00	−3.6 ± 0.4	−15.5 ± 0.2	+0.50 ± 0.00	−54.0 ± 0.8
De Forcrand (*1*)	1.15	−1.13	−18.27	+0.43[a]	−67.2[a]
Von Stackelberg and Müller (*8*, *9*)	1.50	−3.4	−16.8 ± 0.5	...	...

[a] Calculated from the data of De Forcrand.

reaction has been estimated in several ways (*4*). The results seem to suggest that the clathrate is first formed in the liquid state, and it subsequently undergoes a phase transition and solidifies.

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Relative Viscosities of Some Aqueous Rare Earth Chloride Solutions at 25°C

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The relative viscosities of aqueous solutions of $PrCl_3$, $EuCl_3$, $GdCl_3$, $TmCl_3$, $YbCl_3$, and $LuCl_3$ were determined over the concentration range of approximately 0.05*m* to saturation at 25°C. The Jones-Dole B-coefficients were determined for all of these salts, and the variation of this parameter across the rare earth series is discussed in terms of ion-solvent interactions. The concentration dependence of the relative viscosity is briefly discussed in terms of various quasi theoretical models and in terms of ion-solvent interactions and the modification of the solvent structure.

Aqueous rare earth salt solutions differ in their transport and thermodynamic properties mainly because of a slight change in the cation radius across the rare earth series. The rare earth chlorides, perchlorates, and nitrates form good series of salts to study the variation of these properties as a function of the cation size. This laboratory is involved in the study of these properties from dilute solution to saturation, and one of these studies is reported here.

Transport (*13–15, 17, 19–21*), thermodynamic (*16, 18*), and spectral (*9, 10*) properties indicate that in aqueous electrolyte solutions, the light and heavy rare earth cations have different inner sphere hydration numbers, whereas Nd to Tb are mixtures of these two hydrated forms. Little concentrated electrolyte solution transport data are available for higher valence salt solutions except for the viscosity of seven rare earth chlorides (*17*) and conductance data for 11 rare earth perchlorates (*20*) and 13 rare earth chlorides (*21*). This paper deals with the viscosity of six additional rare earth chlorides.

One of the earliest significant equations dealing with the viscosity of electrolyte solutions was the two-parameter Jones-Dole equation (*4, 6*). This equation accurately represents dilute solution relative viscosity behavior, and the *A* parameter of this equation was later shown to be theoretically calculable for many electrolyte systems including the aqueous rare earth chlorides (*5, 7*). Although a completely theoretical justification for the B-coefficient is lacking, it is generally found to be an additive parameter for the ions in the system, and its sign and magnitude are considered a measure of the effect of the electrolyte on the solvent structure (*2, 8*).

The next major viscosity equation was that of Vand (*25*) who originally derived his equation, assuming hard spheres in a viscous continuum. In fact, Vand first tested his theory with glass beads of variable sizes (*26*). His equation allowed the effect of the size and shape of these "obstructions to flow" to be related to the concentration dependence of the viscosity. Although not strictly applicable to electrolyte solutions in terms of its physical model, Robinson and Stokes (*12, 23*) have shown that a slight modification of the Vand equation gives a fair representation of the concentration dependence of electrolyte solution viscosities, provided one or both of the ions are strongly hydrated. They interpreted the validity of the modified Vand equation as indicating that the interference of the hydrated ions with the streamlines of the flowing solvent was the most important factor in viscosity behavior at moderate concentrations.

Spedding and Pikal (*17*) reasoned that although the modified Vand equation represented viscosity behavior moderately well, its major defect was the absence of an ion–ion interaction term. Consequently, they added a term taken from Pitts' viscosity theory (*11*). While the justification for this procedure was nonrigorous, the resulting Pitts-Vand equation represented rare earth chloride aqueous solution viscosity data up to saturation well within experimental error.

Although the above approach may seem reasonable for dilute and moderately concentrated electrolyte solutions, the application of this "theory" to highly concentrated electrolyte solutions where little, if any, free solvent remains is clearly unjustified. Angell and Bressel (*1*) have tackled this problem from the concentrated solution end, using equations based on those derived for transport properties in glass-forming liquids. Their derivation involved a number of empirical correlations and resulted in the basic functional form of the Vand portion of the Pitts-Vand equation. The main importance of their work, as it concerns us here, is that it justifies the use of Vand-type equations over the entire concentration range experimentally obtainable. In addition, the parameters of the Vand-type equations should be interpreted with caution since they may represent different physical effects at different concentrations.

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