The Dissociation of $LaFe(CN)_6 \cdot 5H_2O$ to $LaFe(CN)_6 \cdot 4H_2O$

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The dissociation pressure for the loss of 1 mol of water from the compound $LaFe(CN)_6 \cdot 5H_2O$ was measured at 20, 25, 26, 28, and 30 °C. The heat of dissociation for this reaction was calculated to be 9.2 ± 0.3 kcal mol^{-1}. The $LaFe(CN)_6 \cdot 4H_2O$ so formed was found to be stable over a brief pressure range. At the dissociation pressure of $LaFe(CN)_6 \cdot 4H_2O$ the existence of lower hydrates disappeared into a two-phase equilibrium between water vapor and water vapor adsorbed on $LaFe(CN)_6$.

Introduction

The chemistry of lanthanum ferricyanide has received some attention over the past years. Much of the interest has been devoted to the electrochemistry of aqueous solutions of the salt (*2–8*). Originally the compound was reported to have 4.5 mol of water associated with one formula unit of the salt (*8*). The stoichiometry was reported by Davies and James (*3*) and confirmed by Milligan et al. (*1*) to be $LaFe(CN)_6 \cdot 5H_2O$. Davies and James (*3*) also reported that 1 mol of water could be removed from the compound if left over concentrated sulfuric acid and under vacuum for 1 month.

Structure work was reported by Milligan et al. (*1*). These investigators reported three molecules of water were coordinated to the La^{3+} ion and two were located in "holes" within the crystal lattice.

The purpose of this investigation was to obtain single crystals of $LaFe(CN)_6 \cdot 4H_2O$ for x-ray study in the laboratory of Professor Milligan. We also wanted to measure the dissociation pressure of the hydrate for the loss of 1 mol of water and to calculate the heat of dissociation for that reaction. In addition, we wanted to ascertain how many moles of water could be removed in a stepwise manner.

Experimental Section

Single crystals of $LaFe(CN)_6 \cdot 5H_2O$ were obtained from the laboratories of Professor W. O. Milligan. No further analysis or purification of the sample was undertaken.

Isotherms were obtained for the dissociation and recombination of the salt from mass and pressure changes. Mass changes were recorded by a Cahn RG electrobalance. Pressure measurements were recorded by an MKS pressure meter in conjunction with a Model 77-H-3 pressure head. The pressure and mass changes were followed continuously with a strip chart recorder.

The sample of $LaFe(CN)_6 \cdot 5H_2O$ was initially degassed for 24 h at liquid nitrogen temperature. In order that undesirable dissociation of the ferricyanide compound would not commence below room temperature, water vapor from previously degassed $BaCl_2 \cdot 2H_2O$ was admitted into the balance sample chamber as the temperature was increased from liquid nitrogen temperature to room temperature. When room temperature was attained, the balance chamber containing the sample was surrounded by a water bath whose temperature was controlled to ±0.01 °C by a Precision Electronic Relay and Microset thermoregulator.

Dissociation and recombination measurements were made at 20, 25, 26, 28, and 30 °C. These were accomplished by decreasing the pressure of water vapor in the system until the mass of the $LaFe(CN)_6 \cdot 5H_2O$ just began to decrease. At that time, further decrease of pressure was stopped and the system was allowed to come to equilibrium. When equilibrium was established, the mass of the sample and the pressure of the system were recorded. The pressure was then decreased slightly and the system was allowed to return again to equilibrium. This was done until the entire first mole of water was removed.

Table I. Dehydration Pressure for the Loss of One Mole of Water from $LaFe(CN)_6 \cdot 5H_2O$

Temp of isotherm, °C	Dehydration pressure, Torr
20	2.968 ± 0.040
25	3.758 ± 0.045
26	3.998 ± 0.028
28	4.479 ± 0.036
30	4.993 ± 0.042

Recombination measurements were made in a similar manner, but rather than decreasing the pressure of the water vapor, it was increased slightly. Equilibrium was established, pressure and mass measurements were made, and the process was repeated until all of the $LaFe(CN)_6 \cdot 4H_2O$ was converted to $LaFe(CN)_6 \cdot 5H_2O$. In most cases the overshooting of the equilibrium pressure could be reconciled by considering minor desorption from or adsorption onto the walls of the balance system. The only times this could not be used as a ballast was on the occasion of overshooting the dissociation pressure to a large degree.

Results and Discussion

A complete isotherm for the dissociation of $LaFe(CN)_6 \cdot 5H_2O$ to $LaFe(CN)_6 \cdot 4H_2O$ at 20 °C is shown in Figure 1. Similar isotherms were obtained at 25, 26, 28, and 30 °C. A summary of the dissociation pressures is given in Table I.

A number of attempts were made to dissociate the $LaFe(CN)_6 \cdot 5H_2O$ to definite hydrates of lower composition than $LaFe(CN)_6 \cdot 4H_2O$. Isotherms were obtained up to temperatures of 60 °C. At each temperature more than 1 mol of water could be removed. However, only the first two moles could be removed in discrete steps. Because of the low pressure at which the second mole of water was removed and the lack of sensitivity of our pressure measuring device at these low pressures, we felt it unwise to report the dissociation pressure except to say that at each temperature it was less than 0.02 Torr. Even though 97.62% of the water was removed, no hydrates of composition lower than $LaFe(CN)_6 \cdot 4H_2O$ were observed. Rather, what we observed was a typical adsorption–desorption isotherm, a two-phase equilibrium between water adsorbed on the solid $LaFe(CN)_6$ and water vapor.

In the course of increasing the temperature of the sample of $LaFe(CN)_6 \cdot 5H_2O$ in order that isotherms at other temperatures might be measured, excess water vapor was always admitted into the weighing chamber. Each time this was done, regardless of the temperature, the mass of the ferricyanide always attained the mass of the original nondissociated sample. Because that mass was obtained, the dissociation pressure for the loss of 1 mol of water was measured at least one time at each temperature. The pressure so measured was approximately that

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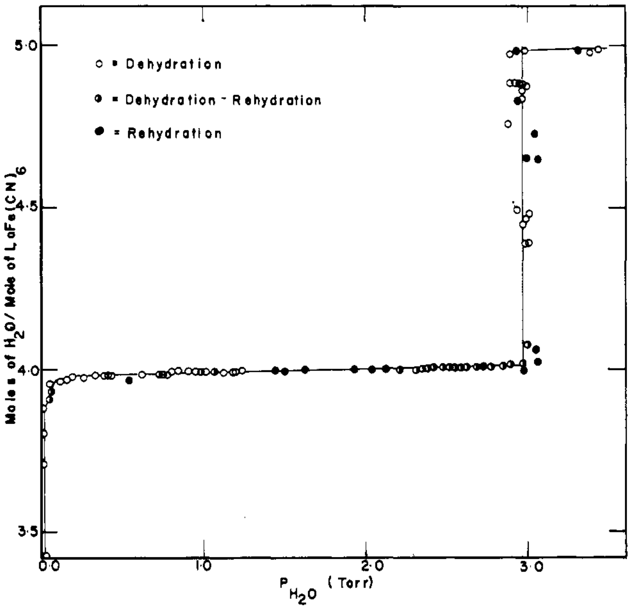

Figure 1. Isotherm for the dissociation of $LaFe(CN)_6{\cdot}5H_2O$ obtained at 20 °C.

expected from the interpolation of a plot of the Clapeyron equation.

The heat of dissociation for the removal of 1 mol of water was obtained from a plot of the data according to the Clapeyron equation shown in Figure 2. The value obtained was 9.2 kcal mol^{-1} with a probable error of ±0.3 kcal mol^{-1}. It should be mentioned that the correlation coefficient for the data in Figure 2 was −0.998 and that the range of error was due to the number of sample points chosen (five). Nevertheless, the magnitude of the heat of dissociation would indicate a fairly strong bonding of the water molecules in the "holes" of the crystal lattice. Also, the fact that the value reported was less than the heat of vaporization of water would tend to confirm the belief reported by Milligan et al. (*1*) that hydrogen bonds between these two water molecules were indeed very long or nonexistent. In addition, the fourth mole of water appears to play an important role in the formation of the hydrate since its loss is accompanied by a disappearance of lower hydrates and the appearance of a two-phase equilibrium between water adsorbed on $LaFe(CN)_6$ and water vapor above the sample. Unfortunately, because of our set up we were unable to measure precisely the heat of reaction when the composition of the system attained the proper pressure for the formation of $LaFe(CN)_6{\cdot}4H_2O$.

Upon completion of the dissociation experiment, the $LaFe(CN)_6$ was rehydrated to $LaFe(CN)_6{\cdot}5H_2O$ and removed from the weighing chamber. The compound had changed from a red-purple color to red-orange during the course of the experiments. In addition, many of the single crystals had fractured into smaller crystals. Some of these crystals were placed back in the vacuum system and were dissociated to $LaFe(CN)_6{\cdot}4H_2O$ for x-ray study in another laboratory.

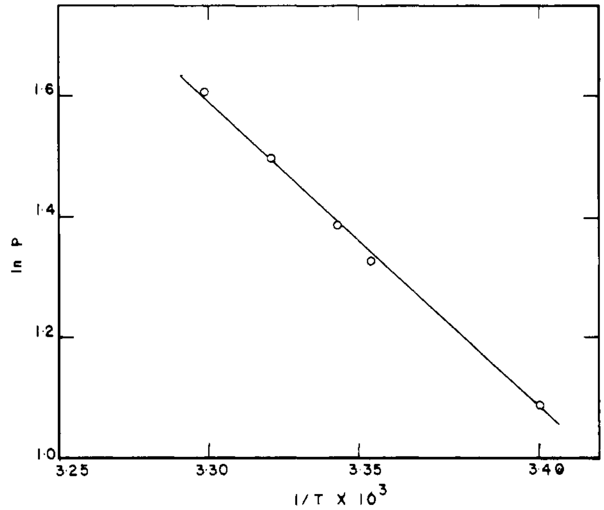

Figure 2. Plot of ln *P* vs. 1/*T* for the determination of the heat of dissociation.

Conclusions

The $LaFe(CN)_6{\cdot}5H_2O$ can be reversibly dissociated to $LaFe(CN)_6{\cdot}4H_2O$. Dissociation through the first 2 mol of water proceeds in a stepwise manner, although because of our experimental set up, only the loss of the first mole could be measured with accuracy. No hydrates of lower composition than $LaFe(CN)_6{\cdot}4H_2O$ were observed to exist. The dissociation pressure for the loss of 1 mol of water was measured and the heat of dissociation for that reaction was calculated.

Acknowledgment

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