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EQUILIBRIUM WATER VAPOR PRESSURE AND TOTAL
MOISTURE CONTENT MEASUREMENTS ON TATB

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February 23, 1976

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Prepared for U.S. Energy Research & Development Administration under contract No. W-7405-Eng-48.

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EQUILIBRIUM WATER VAPOR PRESSURE AND TOTAL MOISTURE CONTENT MEASUREMENTS ON TATB

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Abstract

Equilibrium water vapor pressure and total moisture content were measured for samples of TATB-10% Kel-F, TATB-6% Estane, and TATB-9% Viton in a temperature range from 296 to 365 K. Heats of vaporization were obtained for temperatures from 296 to 333°K. Below 333 K the water in the samples behaved as dissolved water and the Clausius-Clapeyron equation was applicable, while above 333 K the water dissolved in the samples became very mobile and for practical purposes it was considered to be available in its entirety in the gas phase. The total moisture content of the samples was found to be <0.0021, 0.0102, and 0.0165 weight percent for TATB-Kel-F, TATB-Estane, and TATB-Viton, respectively.

Our data indicate that the transport of water in the samples was controlled by the permeation characteristics of the binders. Fair agreement was found between published relative permeation constants for the three binders and those derived from our experimental results.

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INTRODUCTION

A knowledge of the vapor pressure of dissolved water and total moisture content of the high explosive TATB (Tri-amino-trinitrobenzene) is needed to define the driving force for the water oxidation of reactive metals that may come in contact with this explosive. We will describe in this paper the technique employed to make the water measurements and report preliminary results obtained using TATB specimens fabricated with Kel-F, Estane, and Viton-A as binders.

EXPERIMENTAL

An apparatus has been built to measure the partial pressure of water over organic materials as a function of temperature. The method is based on the measurement of the diffusion of water vapor through a membrane that has a low permeability to water, such as mylar. On the upstream side of the membrane, we had pressures that were in the 0.13 to 13 kPa range, while in the downstream, or measurement side, the water concentration in the carrier gas (argon) varied from 10 to 100 ppm by volume. Water in the low partial pressure side of the membrane was detected using an electrolytic hygrometer. Figure 1 shows the details of the diffusion cell, and Figure 2 is a schematic representation of the complete system.

Calibration of the membrane was done at several temperatures by measuring the diffusion of water vapor through a 5×10^{-2} mm thick mylar membrane, using either pure water or saturated salt solutions having well known water vapor pressures. These calibration measurements allowed the calculation of the permeability constant for the membrane as a function of temperature. The unknown partial pressure of water over the sample was calculated from the membrane permeability

Figure 1. Diffusion cell.

Figure 2. Flow diagram of apparatus.

constant at a chosen temperature and the measured rate of permeation at steady state by the following formula:

$$p_2 = \frac{F \times C_2 \times Z \times 10^{-6}}{P \times A} \quad (1)$$

where, F is the carrier gas flow rate in m^3/s .

p_2 is the unknown partial pressure of water in kilopascals.

C_2 is the downstream concentration of water measured in ppm by volume.

Z is the membrane thickness in m.

P is the permeability constant for the membrane in $m^3/s - m^2 - (kPa/m)$.

A is the membrane area in m^2 .

TATB discs 203 mm in diameter, 12.7 mm thick, and weighing 0.79 kg were used. The TATB was purposely selected from a batch that was known to turn black on heating, so that the results obtained from the water measurements could be used in interpreting other related experiments (phase-1 core samples).¹ The test discs were pressed at Pantex according to their standard fabricating procedure, and have been handled in 40-60% RH air. The following formulations were studied:

1. 90% TATB + 10% Kel-F
2. 94% TATB + 6% Estane
3. 91% TATB + 9% Viton-A

The structures of the binders used in this study are shown in Figure 3. The moisture content of the samples to be tested varies as a function of the partial pressure of water in the atmosphere in which they are handled. Therefore, we are measuring the partial pressure of water over a sample both as a function of temperature and of total initial water content. Water vapor pressures were

1. See memorandum to C. F. Bender from C. Colmenares/D. Seaton, "Water Measurements in TATB and Silastic," (CAC:/4-11), November 13, 1974

Kel-F

Co-polymer of monochlorotrifluoro ethylene (75 mole percent) and vinylidene fluoride (25 mole percent)

Viton-A

Co-polymer of tetrafluoro ethylene (3 1/2 parts) and vinylidene fluoride (1 part)

Estane

Polyurethane polyester

Figure 3. Binder materials.

measured in a temperature cycle from 296 K to about 383 K and back to 296 K. Because the amount of material tested was large, very little water was removed by permeation through the mylar membrane during the test. The system was allowed to reach permeation steady state for each of the temperatures in a cycle. This usually was achieved in two or three hours. The total moisture content of a sample was measured by maintaining the temperature of the sample near 383 K until all of the water in the explosive was removed by permeation through the mylar membrane. The total moisture removed was calculated by integrating the area under a plot of hygrometer-readout (ppm) versus time. Calibrations were performed using pure water and salt solutions for the vapor pressure measurements, and drying of hydrated salts for total moisture determination.

RESULTS

Experimental results are presented in Figures 4 through 9. Two types of plots have been used. The first shows the measured water level, in ppm, in the downstream section of the permeation cell versus time. Sample temperatures are also indicated in this type of plot. The second type of graph shows the calculated vapor pressure of water over the explosive (see equation (1)) under steady state conditions of permeation and temperature versus $1/T$. This kind of plot should be linear provided water is truly in solution in a solid for the range of temperature studied. For the three different types of samples studied, steady state water permeation at constant temperature was achieved up to about 333 K (60°C); above this temperature, water was rapidly removed from the explosive samples through the mylar membrane producing a continuous decrease in the amount of water detected in the low concentration side of the permeation cell. This behavior is clearly shown in Figures 4, 6, and 8, and further clarified in Figures 5, 7, and 9 where the calculated water partial pressure over the solid is plotted versus $1/T$. A good linear relationship is obtained for the three samples for values of $1/T$ from 3.0 to 3.4. These results imply that the Clausius-Clapeyron equation is applicable over the range of observed linearity. Writing

TATB+KEL-F FABRICATED AND HANDLED IN 40-60% RH DEPLETION OF WATER

Figure 4

TATB + KEL-F FABRICATED AND HANDLED IN 40-60%RH

TATB+ESTANE FABRICATED AND HANDLED IN 40-60 % RH

Figure 6

TATB + ESTANE FABRICATED AND HANDLED IN 40-60% RH

Figure 7

TATB + VITON A FABRICATED AND HANDLED IN 40-60% RH

DEPLETION OF WATER

Figure 8

TATB+VITON A FABRICATED AND HANDLED IN 40-60% RH

Figure 9

this equation as,

$$\log \frac{p}{p_0} = \frac{\lambda}{2.303R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \quad (2)$$

where p and p_0 = vapor pressure at temperatures T and T_0 ($^{\circ}\text{K}$) respectively
 λ = molal heat of vaporization, kJ/mol (kcal/mol)
 R = gas-law constant

Values of λ for the TATB samples studied are tabulated in Table 1, and are considerably lower than the heat required to vaporize water at standard temperatures and pressure conditions, which is 44.04 kJ/mol (10.52 kcal/mol). This, in a way, indicates that water is very loosely bound in the formulations studied, with the TATB-Estane sample having the closest value to the heat of vaporization of liquid water.

In the case of TATB/Kel-F which was the only sample run through the complete temperature cycle, it is important to note that in the cool-down portion, lower vapor pressures were measured as shown in Figure 5. The heat of vaporization calculated for this portion of the plot is $49.0 \pm 11.8 \text{ kJ/mol}$ ($11.7 \pm 2.8 \text{ kcal/mol}$) at the 80% confidence level. This value is so close to the heat of vaporization of water, that it may be concluded that this portion of the data represents water adsorbed and not dissolved in the sample, since the heat of adsorption of water in solids can have a maximum value of 58.5 kJ/mol (14 kcal/mol) and usually is very close to the latent heat of vaporization, 44.04 kJ/mol .²

The results presented in Table 2 may be interpreted in terms of permeability, solubility and diffusion coefficient of water in the high explosive using an

2. D. O. Hayward and B. M. W. Trapnell, "Chemisorption," Butterworths, Washington, 2nd ed. (1964), p. 198.

Table I

CALCULATED HEATS OF VAPORIZATION

	ΔH
TATB + Kel-F	15.4 ± 3.9 kJ/mol (4.0 ± 0.9 kcal/mol) (90% C.L.; 3 D.F.)
TATB + Estane	27.8 ± 2.8 kJ/mol (6.7 ± 0.7 kcal/mol) (90% C.L.; 2 D.F.)
TATB + Viton	23.5 ± 5.1 kJ/mol (5.6 ± 1.2 kcal/mol) (90% C.L.; 2 D.F.)

Table II

SUMMARY OF TOTAL H₂O CONTENT RESULTS

	Dry Sample Weight, g.	Water Removed, mg.	H ₂ O Content Wt/O (Solubility)	Time to Remove H ₂ O, hr.
TATB-10% Kel-F	793.1	16.7	<0.0021	260
TATB-6% Estane	782.4	80.2	0.0102	190
TATB-9% Viton	763.0	126.0	0.0165	1190

approach that will yield relative answers. A further refinement will be made later by introducing the behavior of the mylar membrane in the data analysis to obtain absolute values. Because the areas and thicknesses of the high explosive samples are equal and the mylar membrane is the same for the three measurements, then we may assume that the rate of permeation of water out of the HE is linear and may be very roughly estimated by taking the ratio of the total water removed to the time it took to do so. Then an apparent permeability constant P_a may be expressed as,

$$P_a \propto R = \text{weight H}_2\text{O removed/time} \quad (3)$$

also

$$P_a = D_a \times S \quad (5)$$

where

D_a = diffusion constant, cm^{-2}

S = solubility, g/g.

An apparent diffusion coefficient D_a may be calculated since the solubility S has been measured experimentally. Table III summarizes the results of our calculations

Table III
APPARENT PERMEATION AND DIFFUSION CONSTANTS

	Permeation Rate $\propto P_a$	Solubility g/g	Apparent Diffusion Coefficient, D_a
1) TATB-10% Kel-F	0.064	0.002 1.0	30.5
2) TATB-6% Estane	0.422	0.010 4.9	41.4
3) TATB-9% Viton	0.106	0.107 7.9	6.4

The values listed in Table III are normalized using the sample with the Kel-F binder as a standard. The results are tabulated in Table IV.

Table IV
NORMALIZED PERMEATION AND DIFFUSION CONSTANTS
(Values given are relative to TATB-10% Kel-F sample)

	Normalized Permeability, P_a	Normalized Solubility, S	Normalized Diffusion Coefficient D_a
1) TATB-10% Kel-F	1.0	1.0	1.0
2) TATB-6% Estane	6.6	4.9	1.3
3) TATB-9% Viton	1.6	7.9	0.2

The normalized permeability values in Table IV show the right trend when compared to published values of Kel-F, polyester-based polyurethane Estane 58029 and Viton A,³ as follows,

Table V
RELATIVE PERMEATION AND PERMEABILITY CONSTANTS

	Permeability Constant, $\text{cm}^3(\text{STP})\text{cm}^2/\text{mm}/\text{sec}/\text{cm Hg} \times 10^{10}$	Permeability Relative to Kel-F
Kel-F	360	1.0
Estane	29,000	80
Viton-A	520	1.4

3. A. Libovitz, Modern Plastics, March (1966), p. 139.

The comparisons made here are very rough on account of the large variation in permeation characteristics encountered with polymeric materials from different sources and because of our assumptions; hence, they should be used for trend analysis only. The conclusion that we have reached here is that the HE samples behave very much as the binder material used with the TATB, and that the latter does not seem to greatly influence the transport of water by diffusion.

The relatively high vapor pressure of water over the TATB-6% Estane and TATB-9% Viton samples (see Figures 7 and 9) as a function of temperature, points out that in a closed system with relatively small volume, all of the water in the high explosive will be available as free water vapor, particularly if the temperature approaches 60°C.

The same observation applies to the TATB-10% Kel-F sample (see Figure 5), except that in this case the water vapor pressure is much lower. In any case, the total water content of the explosive formulations studied is rather low (see Table II).

Dimensional measurements of the specimens before and after testing revealed no significant change in diameter and a very slight change in height as shown in Table VI.

Table VI

TATB SAMPLES--DIMENSIONAL INSPECTION BEFORE AND AFTER TEST

	Initial Dimensions		Final Dimensions	
	Diameter	Height	Diameter	Height
	mm	mm	mm	mm
TATB + Kel-F	203.22 (8.001")	12.85 (0.506")	203.22 (8.001", 8.002")	12.75 (0.502" in 4 locations)
TATB + Estane	203.22 (8.001")	12.85 (0.506")	203.22 - 203.25 (8.0010", 8.0020")	12.751 - 13.271 (0.5020", 0.5020", 0.5025", 0.5025")
TATB + Viton A	203.22 (8.005")	12.85 (0.506")	203.33 (8.005" in 2 places)	12.700 - 12.789 (0.5000", 0.5020", 0.5035", 0.5010")

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