

CLINICAL AND MATERIALS SCIENCES

Vapor Phase Adsorption of Water on Hydroxyapatite

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Water vapor adsorption isotherms were determined gravimetrically on three hydroxyapatite samples differing in preparation and with surface areas of 70.4, 22.5, and 3.0 M²/gm, respectively. Heats of adsorption for the first layer of water were found to be 13.3, 13.2, and 13.9 kcal/mole on these hydroxyapatites. From repeated thermal desorption and adsorption cycles of water, stepwise adsorption was observed which diminished with each outgassing cycle until it disappeared after the fourth cycle. Cross-sectional area of adsorbed water molecule on hydroxyapatite surface was estimated at 11.5 Å². Standard free energies, isosteric heats, changes in enthalpy, and entropy of adsorption of water on HAP samples outgassed at 300 C were determined.

J Dent Res 56(12): 1437-1448, December 1977.

The amount of water adsorbed as a function of the vapor pressure provides information about the surface structural details of hydroxyapatite and hard dental tissues. Although relatively little information is available on the chemical characteristics of tooth hydroxyapatite (HAP) surface, Beebe, Holmes, and co-workers¹⁻⁸ have over the last decade published information on the surface areas, heats of adsorption, and pore size distribution of bone mineral and HAP. Dry and Beebe³ showed there was a strong affinity of water and methanol for anorganic bone and synthetic HAP outgassed at 450 C, and through the use of adsorption and calorimetric data were able to separate the total adsorption of methanol into chemisorbed and physisorbed fractions. The high energy of adsorption of the first layer of methanol and water was attributed to hydrogen bonding to the exposed oxygen atoms on the surface.

Received for publication June 21, 1976.

Accepted for publication March 7, 1977.

This research was supported in whole by the National Institutes of Health, National Institute of Dental Research, Training Grant #T01 DE-00181.

This paper was presented in part at the IADR 50th General Meeting, Las Vegas, Nevada, March 1972.

Holmes and Beebe^{1,4} measured differential heats of adsorption of N₂ and A on bone mineral and HAP, that were outgassed at 450 C and those that were covered with a monolayer of chemisorbed methanol and water. The heats of adsorption for N₂ on bone surface of HAP started at 5.5 kcal/mole and decreased to 2.0 kcal/mole at monolayer coverage. The HAP surface covered with water had heats of adsorption for N₂ of about 3.3 kcal/mole at low surface coverage to 2.0 kcal/mole at monolayer coverage. For methanol-covered surfaces, the heat of adsorption for N₂ was about 2.7 kcal/mole which dropped to 1.7 kcal/mole at monolayer coverage. These effects were attributed to variations in surface polarity to which the polarizable nitrogens were attached. The values for A adsorption were less than for N₂.

Holmes, Beebe, and co-workers^{1,5} also evaluated the effect of outgassing temperature on the loss in weight and surface area of bone mineral. They found that the surface area increased about 15% with increasing degassing temperature up to 300 C, and decreased for successively higher degassing temperatures up to 500 C. However, because of the slight decrease in the slope of the weight loss versus temperature curve in the region of 350 to 450 C, they chose to use a 450 C evacuating temperature to produce the reproducible "bare" surface. They postulated that the observed decrease in area upon degassing above 300 C might be caused by sintering becoming more important than the loss of water. Later Holmes and Beebe^{7,8} reported changes in surface areas of both amorphous and crystalline HAP as a function of conditions of preparation, storage, time of aging at room temperature, and degassing temperature up to 500 C. They found (1) that the amount of water retained after outgassing at 20 C depended on the history of the sample and (2) that the amount retained after outgassing at 20 C but removed at 500 C was less than an adsorbed monolayer. It was also estimated that any loosely bound water with a

binding energy less than 14 kcal/mole would be removed by evacuation at room temperature.

Pore structure and surface properties of bone mineral and synthetic HAP were reported by Lobenstein.⁹⁻¹¹ He determined the differential pore size distribution from N₂ adsorption isotherms. Outgassing bovine femur shaft at 160, 300, and 450 C caused a considerable change in the pore size distribution. A large decrease in the volume of the small pores was compensated by a corresponding increase in the larger pores. In order to study the mechanisms and chemistry of surface forces by which tooth structure and adhesives interact, Lobenstein¹¹ determined heats of adsorption of NH₃ and CO₂ on anorganic whole teeth and dentin. He found collagen had a pronounced influence on the apparent surface areas of the samples, and the heats of adsorption were < 12 kcal/mole. He concluded that amine groups incorporated into adhesives should provide better bonding than carboxylic groups. Water vapor adsorption isotherms on tooth components, determined by Lobenstein,¹⁰ were Type II isotherms with well-developed hysteresis loops over the entire range of relative humidities.

Water vapor adsorption isotherms at 20 and 25 C were determined on the synthetic HAP samples outgassed at 300 C by Rootare and Craig.¹² The surface areas of the samples ranged from 3 to 70m²/gm. The corresponding heats of adsorption of first layer (E₁) of water on HAP ranged from 13.9 to 13.2 kcal/mole. The free surface energy change for water on two HAP samples was 361 ergs/cm² (3m²/gm sample) and 220 ergs/cm² (70m²/gm sample). A

portion of the water was irreversibly absorbed and was attributed to chemisorption.

The thermal desorption of water on HAP and the adsorption of water vapor on HAP are presented here along with values for the heats of adsorption and the isosteric heats. The changes in the free surface energy, enthalpy and entropy of adsorption of water on HAP will be presented later.

Materials and Methods

HYDROXYAPATITE SAMPLES. — The synthetic hydroxyapatites used, the methods of preparation, and their properties have been described by Craig and Rootare.¹³ Victor HAP (VIC-HAP), prepared commercially by precipitation from hot solution, had a surface area of 70.0 ± 0.1 m²/gm. A second sample, prepared according to a method used at the National Bureau of Standards (NBS-HAP) by precipitation at 100 C, had a surface area of 22.5 ± 0.3 m²/gm. The third sample was prepared according to the method described by the Tennessee Valley Authority (TVA-HAP) by a solid state reaction at 1200 C, and it had a surface area of 3.04 ± 0.03 m²/gm.

The hydroxyapatite powder samples were compacted in a 1/2-inch diameter steel die in a compression testing machine under a 4,450 N (1,000 lbs) load. The total time under load was two minutes. The compaction facilitated the use of the materials for adsorption measurements.

GRAVIMETRIC ADSORPTION APPARATUS. — The gravimetric adsorption apparatus consist-

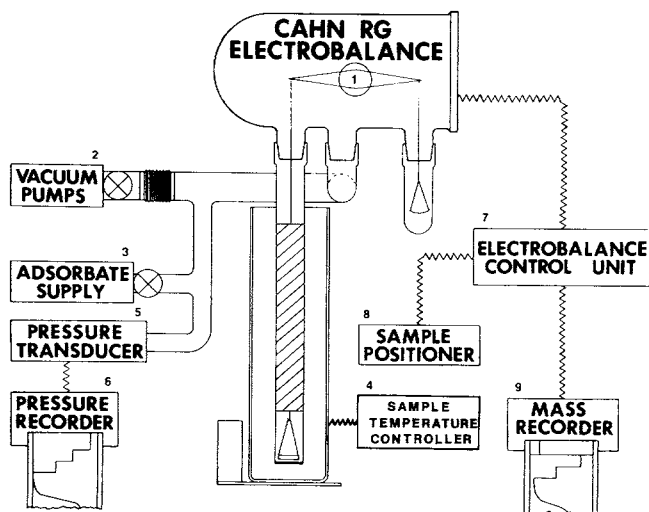


FIG 1. — Gravimetric vapor phase adsorption apparatus.

ed of a Cahn Recording RG Electrobalance* with a one-gram capacity and a sensitivity of 0.1 microgram. A schematic of the gravimetric adsorption apparatus is shown in Figure 1.

The electrobalance was mounted inside a Pyrex high vacuum bottle that had an aluminum cap on one end with electrical connections. An "O" ring provided a vacuum seal between the glass bottle and the cap. Compacted samples were suspended from the balance in a platinum pan by a 0.0004 inch diameter Nichrome[†] wire. The sample tube was a combination of Pyrex and Kovar.[‡] The sample tube was 48 cm long with an inside diameter of 1.6 cm. It had a flat Kovar disk at the base and a section of Kovar 28 cm long in the center. A ground glass joint (ST40/35) joined the tube to the vacuum bottle. A 3-cm section of Pyrex above the Kovar base permitted visual observation of the sample. Cutting¹⁴ has shown that this design of the tube insures that no significant radiation reaches the sample from the balance, and the Kovar provides thermal conduction so that the adsorbate vapor near the sample is at the same temperature as that of the constant temperature bath[§] surrounding the tube.

Dissipation of the heat liberated when the sample adsorbs vapor was accomplished by lowering the pan so that it was in contact with the Kovar bottom of the tube. Prior to an adsorption experiment the sample was outgassed under high vacuum with a furnace around the sample tube. A temperature-programmed controller was used to obtain linear heating rates and constant temperature for outgassing.

The adsorbate supply was connected to the sample tube through the glass envelope around the electrobalance. The end of the adsorbate tube was contained in the Lauda^{**} constant temperature bath which controlled the vapor pressure of the adsorbate. Especially purified¹⁵ adsorbate water was introduced into the adsorbate tube in a sealed evacuated ampule with a

break-off tip.

The temperature of the adsorbate was controlled with a relay controller and a platinum resistance thermometer. Temperatures from -65 to -30 C were maintained with a heat exchanger using dry ice and methanol, those from -30 to 25 C were maintained with a Neslab^{††} portable bath cooler immersion head in the Lauda constant temperature bath. Vapor pressure-temperature plots were made from published data^{16,17} and the vapor pressure for the isotherm was calculated from the temperature of the adsorbate bath.

The vacuum system consisted of a Cenco^{‡‡} 2-inch oil diffusion pump with a Hyvac 7 mechanical pump. Low pressures were measured by a cold cathode gauge, thermocouple gauge, and a Pirani[¶] gauge. A Bytrex[#] MPA-25 pressure transducer was incorporated for recording pressures above 1 mm of Hg to atmospheric.

Adsorption isotherms were obtained by measuring the vapor pressure of water and corre-

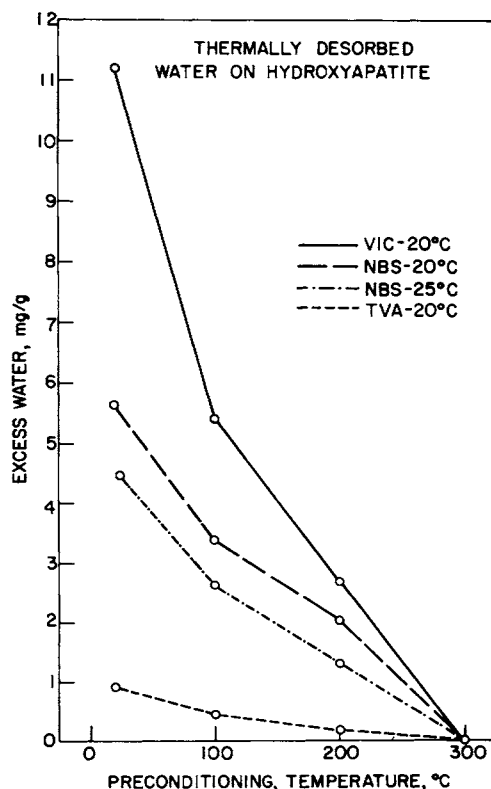


FIG 2. — Thermal desorption of water on hydroxyapatite as a function of preconditioning temperature.

*Ventron Instruments Corp., Cahn Div., 7500 Jefferson St., Paramount, Ca 90723.

§Haake Model FE Constant Temperature Circulator, Polyscience Corp., 2101 Dempster Street, Evanston, Il. 60201.

†Nichrome, trademark of Driver-Harris Co., NJ.

‡Kovar, trademark of Westinghouse Electric Company, Pa.

**Lauda Model B-20, Brinkmann Instruments, Inc., Catiaque Rd., Westbury, NY. 11590.

††Neslab Model PBC-4, Neslab Instruments, Inc., 871 Islington St., Portsmouth, NH. 02801.

‡‡Central Scientific Co., Division of Cenco Instrument Corp., 2600 S. Kostner Ave., Chicago, Il. 60623.

¶Type GP-140, Consolidated Electrodynamics, Rochester, NY.

#Bytrex Division, Tyco, 223 Crescent St., Waltham, Ma.

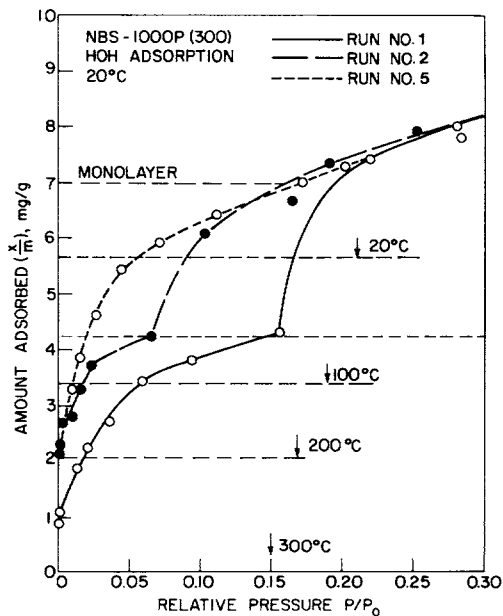


FIG 3. — Adsorption isotherms of water at 20 C and in the low vapor pressure region on NBS-HAP outgassed at 300 C. The horizontal broken lines and arrows indicate the level of water that can be removed in outgassing at that temperature under vacuum.

sponding equilibrium weights of adsorbed water on HAP. The weight of water adsorbed in milligram per gram (x/m) of HAP was plotted versus the log of relative vapor pressure of water, p/p_0 , where p is the actual water adsorbent vapor pressure and p_0 is the vapor pressure of water at the isotherm (adsorbate bath) temperature. The area under the Gibbs^{18,19} adsorption isotherm was integrated with a computer program¹⁵ to obtain the free surface energy changes for water on HAP,²⁰ the surface area, and the net heat of adsorption. Sufficiently large amounts of water were adsorbed in the

low pressure regions so that the main errors relate to control and measurement of temperature of the constant temperature bath.

The first adsorption point at -65 C required 3 to 5 hours and succeeding points about 2 hours until monolayer coverage had been reached. Longer times were required for equilibrium in the capillary condensation region of the isotherm. Desorption points required long times to reach equilibrium; the desorption isotherm of VIC-HAP required 46 days.

Results

THERMAL DESORPTION OF WATER ON HYDROXYAPATITE. — The thermal desorption of water from HAP samples is summarized in Figure 2; outgassing was started at 20 C except for NBS-HAP at 25 C. After outgassing to equilibrium at 300 C the adsorption isotherms for water on HAP were determined. The amount of water desorbed was a function of the surface area of the various HAP samples.

The adsorption isotherms at 20 C in the low vapor pressure region for NBS-HAP outgassed at 300 C are shown in Figure 3. The levels of thermally desorbed water are indicated as is the amount of water required for monolayer coverage. The first adsorption isotherm (Run No. 1) had a step or discontinuity in the curve at a (p/p_0) of about 0.16. The water was desorbed at 300 C and a second isotherm determined (Run No. 2) which also had a step at the same amount of adsorbed water (indicated by the broken horizontal line), but at a lower relative pressure of about 0.07. The third and fourth isotherms were run at 25 C (not shown in Fig 3). The third isotherm had a step at $p/p_0 = 0.045$, whereas the fourth had no step. Repeated outgassing and adsorption cycles established that the step in the isotherm disappeared after the fourth cycle. Similar steps were observed in adsorption isotherms for TVA- and

TABLE 1.
SURFACE AREA, NET HEAT OF ADSORPTION
AND HEAT OF ADSORPTION OF THE FIRST
LAYER FOR WATER ADSORBED ON HYDROXYAPATITE

HAP	Surface Area		Net heat of adsorption Q , kcal/mole	Heat of adsorption of first layer E , kcal/mole
	by water adsorption m^2/g	by N_2 adsorption m^2/g		
VIC	66.3 ± 0.2	70.03 ± 0.14	2.75 ± 0.09	13.29 ± 0.09
NBS	21.2 ± 0.1	22.50 ± 0.26	2.62 ± 0.04	13.16 ± 0.04
TVA	2.98 ± 0.02	3.04 ± 0.03	3.32 ± 0.07	13.86 ± 0.31

VIC-HAP and they too vanished after several adsorption-desorption cycles.

ADSORPTION ISOTHERMS FOR WATER ON HYDROXYAPATITE. — Surface areas. — The surface areas from gravimetric adsorption data for water on HAP were determined according to the B.E.T. (Brunauer, Emmet, and Teller) theory.^{21,22} Linear B.E.T. plots were obtained. The derived quantities (means of three determinations) and standard errors are listed in Table 1. The apparent thickness of the adsorbed monolayer is approximately 2.8 Å, if one assumes hexagonal packing of water molecules and 10.5 Å² as the area occupied by one water molecule. The surface areas of the solids derived from these measurements are slightly less than those reported for nitrogen adsorption, 70.0, 22.5, and 3.04 m²/gm, respectively (Table 1).

The net heat of adsorption, the average heat of adsorption of the first layer of water on HAP and their standard errors calculated with the use of B.E.T. equation and plots are reported in Table 1. The values of E_1 were calculated assuming the heat of adsorption of the second and successive layers was equal to the heat of condensation of water.

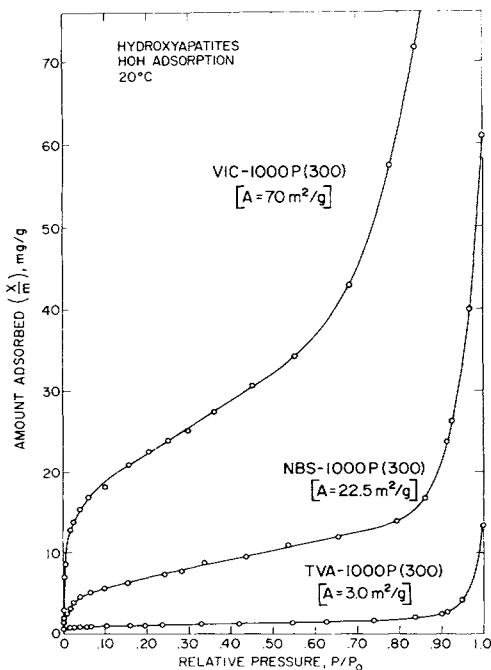


FIG 4. — Adsorption isotherms of water at 20°C on VIC-, NBS-, and TVA-HAP outgassed at 300°C.

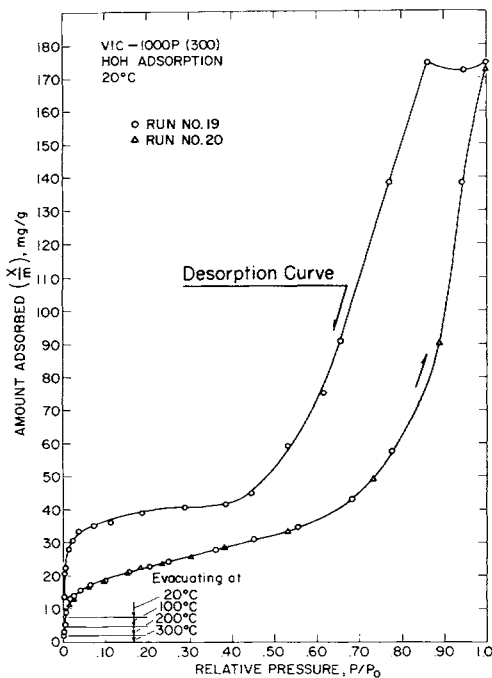


FIG 5. — Complete adsorption-desorption isotherm for water at 20°C on VIC-HAP outgassed at 300°C. The horizontal lines with arrows indicate the level of residual water on the surface of the sample when outgassed at the given temperature under vacuum.

ADSORPTION ISOTHERMS. — Typical adsorption isotherms for water on VIC-, NBS-, and TVA-HAP at 20°C are shown in Figure 4. All samples were outgassed at 300°C. The large differences in the amount of water adsorbed per gram of HAP were mainly the result of the differences in the surface areas of the three hydroxyapatites.

A complete adsorption-desorption isotherm for water on VIC-HAP at 20°C is shown in Figure 5. The data for two successive runs established that the adsorption and desorption curves were reproducible, but that hysteresis was observed.

The compacted HAP samples were porous and they did not completely fill with water at saturation. Total pore volumes of the compacts were determined by mercury porosimetry.¹⁵ The fraction of the total pore volume that filled with water at the saturation pressure ($p/p_0 = 1$) was 0.340, 0.158, and 0.038 for VIC-, NBS-, and TVA-HAP, respectively.

Equilibrium function and standard free energy of adsorption. — Surface characterization of physical adsorption systems as to the homo-

generity of the surface and adsorbate interactions were examined using Graham's²³ equilibrium function (E.F.) where

$$E.F. = \frac{\Theta}{(1 - \Theta)(p/p_0)}$$

and Θ is the fraction of surface covered from 0 to 1. The equation holds for the ideal case of monolayer coverage which is approached when adsorption is on uniform surfaces at low relative pressures and the interaction between adsorbed molecules is low. The equilibrium function, $E.F._0$, was determined from the lowest attainable adsorption point using the following relationship:

$$-\Delta F_{ideal} = RT \ln \frac{(1 - \Theta)(E.F._0)}{\Theta}$$

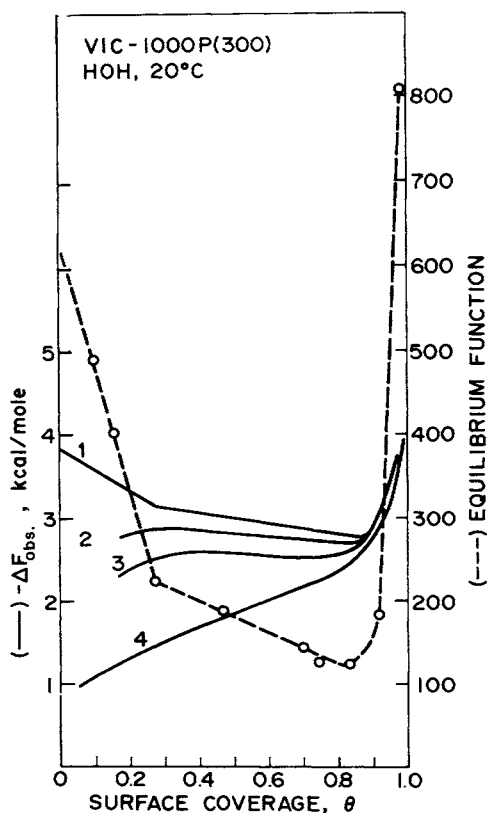


FIG 6. — Plots of $-\Delta F_{obs}$ and equilibrium function (E.F.) versus surface coverage, Θ , for water on VIC-HAP at 20°C.

TABLE 2.
STANDARD FREE ENERGIES OF ADSORPTION
OF WATER ON HYDROXYAPATITE

HAP	E.F. ₀	$-\Delta F_{obs}$, kcal/mole	$-\Delta F_{ideal}$, kcal/mole	$-\Delta F_{int}$, kcal/mole
VIC	636	3.04	3.90	-0.86
NBS	2218	3.50	4.50	-1.00
TVA	3940	4.90	4.90	0.0

For the actual system the observed differential free energy of adsorption, $-\Delta F_{obs}$, is calculated from

$$-\Delta F_{obs} = RT \ln (p_0/p)$$

Plots of $-\Delta F_{obs}$ and E.F. versus Θ for water on VIC-HAP at 20°C are shown in Figure 6. Curves 1, 2, 3, and 4 represent free energy changes for VIC-HAP outgassed at 300, 200, 100, and 20°C, respectively. The dashed line is a plot of E.F. versus Θ . The initial decrease in E.F. indicated a heterogeneous surface. At higher coverages, where Θ ranges from 0.25 to 0.85, lateral adsorbate interaction lowered the slope. Strong interactions at $\Theta = 0.85$ caused a sharp rise in the curve. For samples outgassed at temperatures from 20 to 200°C the initial sharp decrease disappeared, and the slope was positive.

The difference between the two differential free energies at the same surface coverage ($\Theta = 0.5$) for the actual and ideal system is attributed to the lateral interaction, $-\Delta F_{int}$.

$$-\Delta F_{int} = -\Delta F_{obs} - (-\Delta F_{ideal})$$

Values for $E.F._0$, $-\Delta F_{obs}$, $-\Delta F_{ideal}$, and $-\Delta F_{int}$ are listed in Table 2 for the three preparations. The strength of adsorption bonding may be related to the calculated values of $-\Delta F_{ideal}$, and for water on HAP is in the order $TVA > NBS > VIC$. The value for $-\Delta F_{int}$ for TVA-HAP is zero because half the available surface is covered at the first or second experimental adsorption point, and thus $-\Delta F_{obs}$ and $-\Delta F_{ideal}$ are the same.

Isoteric heat of adsorption of water on hydroxyapatite. — The heat of adsorption can be calculated from water adsorption isotherms at two different temperatures. The differential heat of adsorption, called the isosteric heat of adsorption, q^s , an analog of the Clausius-Clapeyron equation, is defined by the equation^{15,24}

$$q'' = \frac{dq}{d(x/m)} = RT^2 \left[\frac{d \ln p}{dt} \right] (x/m).$$

Integrating the above equation yields:

$$q'' = 2.303 \frac{RT_2 T_1}{(T_2 - T_1)} \left[\log \frac{(p/p_0)_2}{(p/p_0)_1} + \log \frac{(p_0)_2}{(p_0)_1} \right]$$

where R is the molar gas constant, and $(p/p_0)_1$ and $(p/p_0)_2$ are the equilibrium relative pressures at the same (x/m) surface coverage values at the two temperatures T_1 and T_2 , respectively. The isosteric heats of adsorption for water on VIC-, NBS-, and TVA-HAP versus the number of surface layers (L) (Fig 7) exhibited sharp increases in q'' at low surface coverages, with maximum values of 125 to 190 kcal/mole, before diminishing and approaching the heat of condensation of water ($E_L = 10.5$ kcal/mole) after about two or three statistical layers of water had been adsorbed. These maxima occurred at about the same coverage for TVA-HAP ($L = 0.66$) and NBS-HAP ($L = 0.58$) while the maximum for VIC-HAP occurred at a much lower coverage ($L = 0.22$). No significant capillary effect was observed in the condensation region since no peak was observed in the isosteric heat curves.

The enthalpy,¹⁵ $-\Delta H$, the free energy change, $-\Delta F$, and the entropy change, $-\Delta S$, were calculated by the following equations:

$$\begin{aligned} -\Delta H &= q'' - \Delta E_L, \\ -\Delta F &= RT \ln p_0/p, \\ -\Delta S &= \frac{\Delta H - \Delta F}{T} \end{aligned}$$

The enthalpy, free energy, and entropy changes decreased as the adsorption process caused increasing numbers of layers of vapor to condense on the adsorbents. The values of VIC-HAP are listed in Table 3.

Discussion

This study shows that a portion of the water is irreversibly adsorbed (chemisorbed) by HAP, and that it is removed only when the sample is heated to temperatures higher than the isotherm temperature. Similar observations have been made of water adsorbed on various metal oxides which form surface hydroxyl groups hydrated with water. Some examples are thorium oxide,²⁵⁻²⁹ hematite,^{30,31} titanium dioxide,³⁰ rutile,^{31,32} zinc oxide,^{31,32-35} sodium vermiculite,³⁶ and Cab-O-Sil.³⁷

The monolayer capacity of HAP for ad-

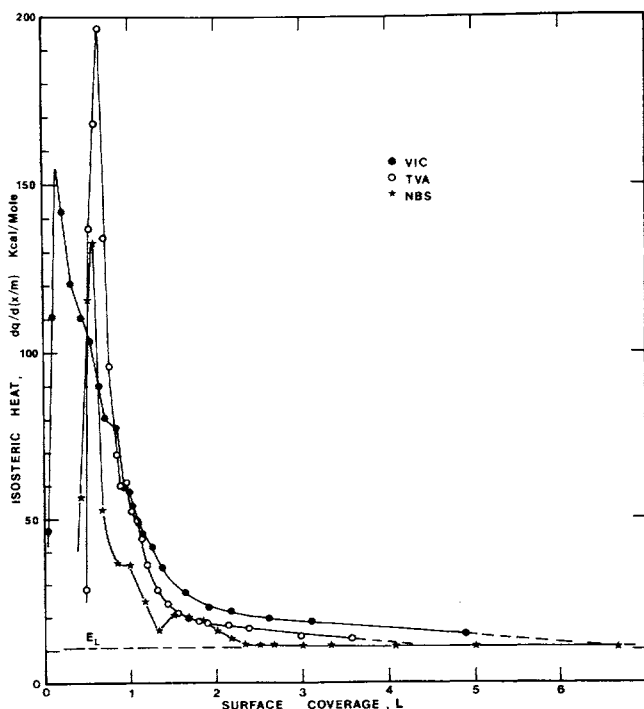


FIG 7. — Isosteric heats of adsorption for water on VIC-, NBS-, and TVA-HAP versus the surface coverage in statistical layers, L .

TABLE 3.
CHANGES IN ENTHALPY, FREE ENERGY AND
ENTROPY OF ADSORPTION OF WATER ON
VIC-1000P (300) HYDROXYAPATITE AT 20 C

Amount Adsorbed (x/m) mg/g	Surface Coverage L	Enthalpy Change - ΔH kcal/mole	Free Energy Change - ΔF kcal/mole	Entropy Change - ΔS cal/deg/mole
1.0	0.054	32.3	5.26	105.7
2.0	0.110	100.5	4.83	326.3
4.0	0.220	131.7	4.06	435.4
6.0	0.330	110.4	3.54	364.4
8.0	0.440	100.0	3.22	330.1
10.0	0.540	93.2	2.95	307.9
12.0	0.650	79.5	2.58	262.3
13.0	0.710	70.1	2.34	231.0
15.0	0.820	67.3	2.13	222.3
17.0	0.920	48.9	1.55	161.3
18.0	0.980	47.5	1.38	157.2
19.0	1.03	43.1	1.26	142.8
20.0	1.09	38.7	1.15	128.2
21.0	1.14	34.8	1.06	115.0
23.0	1.25	30.6	0.89	101.3
25.0	1.36	24.5	0.72	80.9
30.0	1.63	17.0	0.48	56.3
35.0	1.90	12.4	0.33	41.1
40.0	2.17	11.2	0.25	37.3
48.0	2.61	9.05	0.19	30.2
57.0	3.10	7.87	0.15	26.3
90.0	4.89	4.12	0.07	13.8

sorbed water calculated by the B.E.T. theory includes chemisorbed and physisorbed water. The chemisorbed water accounted for about a monolayer, whereas the physisorbed water was about eight, nine, and fifteen layers thick for VIC-, NBS-, and TVA-HAP, respectively. The pores of the HAP samples were not filled with water although the porosity was more than 50%. The pore volume filled with water was 0.34, 0.16, and 0.04 for VIC-, NBS-, and TVA-HAP, respectively. The variation is difficult to explain but two factors involved are the differences in surface area and pore size. Also, there may be some interaction of surface energies and interfacial tensions due to differences in solubility of one HAP sample versus another in the small capillaries that help control the amount of physisorbed water.

The monolayer adsorption was the same for the three hydroxyapatites, about 9.2, 9.3, and 9.2 water molecules per 100 A² of VIC-, NBS-, and TVA-HAP surface respectively. The calculations for chemisorbed water based on surface areas from water adsorption yielded 11.3, 11.5, and 11.2 molecules per 100 A² for VIC-, NBS-,

and TVA-HAP respectively. Since physisorption and chemisorption overlap, the monolayer capacity from the B.E.T. equation (about 10 molecules per 100 A²) appears to be a good estimate of the chemisorbed water.

The shapes of the adsorption isotherms indicate that the initial rapid rise is chemisorbed water and the later slowly rising straight line slope is characteristic of physisorbed water. If it is assumed that the clean surface, outgassed at 300 C, is completely dehydrated and free of chemisorbed water, the initial contact with water would result in formation of a chemisorbed hydration layer on the surface.

The hydroxyapatite surface at ambient conditions is totally covered with water. In order to understand what the surface is like beneath the bulk and physisorbed water, it must be removed in increments or layers determined by the relative affinity of the water molecules to the surface. The bulk and physisorbed water comes off the surface easily by lowering the relative vapor pressure of water at the surface. This removal is accomplished easily by evacuation of the sample at the temperature of the iso-

therm. However, there will remain a layer of water on the hydroxyapatite surface that cannot be removed by evacuation. This layer of water is strongly bound or chemisorbed water.

The chemisorbed water is removed only when the sample is heated and evacuated. In order to remove the adsorbed water from the surface of the hydroxyapatite, which includes the condensation of the surface hydroxyl groups, greater amounts of energy must be provided by heating the sample up to 1,000 C.¹² The data indicate that if the sample is heated to only about 300 C, the layer of water chemisorbed on the surface is stripped away, leaving the hydroxylated surface intact. If the surface areas of these surfaces, outgassed at 300 C, are measured by water adsorption, they are only 2 to 6% lower than the values obtained by nitrogen adsorption¹⁵ (see Table 1). This is very good agreement in view of the assumptions.

It is proposed that the chemisorption of the estimated 10 water molecules (HOH) per 100 A² takes place in two steps of 5 HOH molecules at a time. Starting with the hydroxylated surface as shown in figure 8 below.

The first five HOH molecules per 100 A² form a partially hydrated surface by a "bridging" structure, where one HOH bonds to two hydroxyls. When the next five HOH molecules per 100 A² are added, the "bridging" structure can no longer exist because of crowding of the water molecules. The additional water molecules will squeeze in and force the "bridging" molecules to give up one of the hydroxyls thus causing each chemisorbed water molecule to be associated or tied up with one hydroxyl group on the surface. After the surface is completely hydrated, subsequent water molecules would

encounter a much lower energy surface consisting of water molecules. It should be noted that while the above model represents a reasonable and probable mechanism, other mechanisms may also be consistent with the experimental results.

The first thermal desorption cycle at 300 C removed 10 to 11 water molecules per 100 A². The thermal desorption cycling caused some rearrangement or change on the HAP surface which resulted in about a 50% decrease in the chemisorbed water.

If the surface areas of HAP samples, based on the cross-sectional area of adsorbed nitrogen molecule of 16.2 A², reflect the true available surface area, the effective size of the water molecule can be calculated from the monolayer values (WM) of adsorbed water. A linear regression analysis was used to evaluate the data of WM(H₂O) versus surface area by nitrogen.¹⁵ A straight line relationship was obtained:

$$Y = 0.2605 \text{ mg/m}^2 X,$$

where Y is the monolayer capacity (WM,mg/gm) and X is the surface area from nitrogen adsorption (B.E.T.) data. The area occupied by one water molecule (A_m) on HAP surface was calculated from the above slope value by the following relationship:

$$A_m = \frac{MW \times 10^{23}}{N \times S} = \frac{18.016 \times 10^{23}}{6.023 \times 10^{23} \times 0.2605} = 11.48 \text{ A}^2/\text{molecule},$$

where MW is the molecular weight of water, N is the Avogadro's number and S is the slope

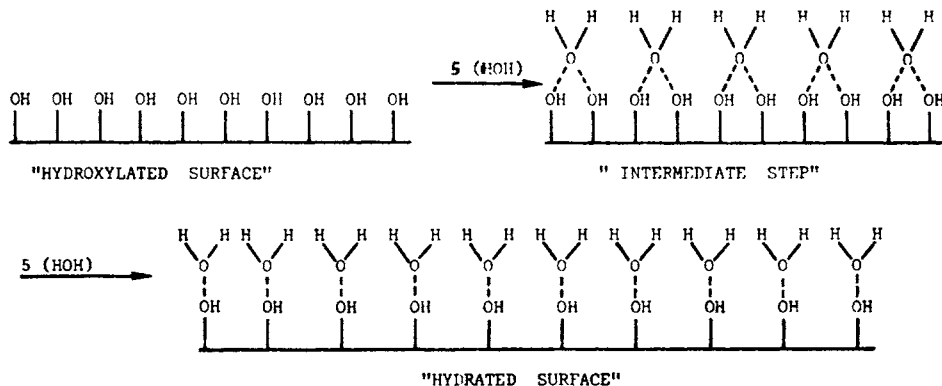


FIG 8. — Proposed model for the absorption of water by hydroxyapatite.

from previous equation. With appropriate conversion factors for units, 11.5 \AA^2 is obtained for the cross sectional area of the adsorbed water molecule on hydroxyapatite surface.

The size of the water molecule (A_m) can also be calculated from the liquid density (ρ) of the adsorbate at the isotherm temperature.³⁸ Assuming that the arrangement of water molecules on the adsorbent surface is the same as it would be on a plane surface covered with bulk liquid, the packing factor (f) is determined for the number of nearest neighbors. For twelve nearest neighbors in the bulk liquid and six on the plane (a common arrangement) the value of f is 1.091. Thus, the area occupied by one water molecule, calculated from the relationship:

$$A_m = 1.091 \left[\frac{M}{\rho N} \right]^{2/3} \times 10^{16},$$

where M is the molecular weight of water, ρ is the liquid density of water at the isotherm temperature and N is the Avogadro's number, is 10.5 \AA^2 at 20 C and 25 C. Thus, the packing of water on HAP is 10% less dense than in the bulk liquid. A variety of values is reported³⁹ ranging from 6.2 to 24.6 \AA^2 .

A stepwise adsorption isotherm is usually observed in multilayer adsorption of nonpolar gases on nonpolar surfaces that are energetically homogeneous. However, stepwise adsorption isotherms with water on polar surfaces have been observed as reported for thorium oxide²⁵⁻²⁸ and zinc oxide.³¹⁻³³

Gammage, Fuller, and Holmes²⁷ observed stepwise adsorption of water on clean ThO_2 outgassed, at 1,000 C. They claimed that unless the surface has been saturated with water, adsorption is irreversible. In addition to surface hydroxylation, a slow conversion of reversibly bound water to irreversibly bound water occurs. On successive cycles they also found that the step in the isotherm disappeared after the fourth cycle. The adsorption data on HAP similarly indicate the complex nature of the irreversible adsorption process as a function of thermal-desorption cycling.

The step in the adsorption isotherm may relate to a dual characteristic of the surface. Initially, the surface may consist of about equal portions of hydrophilic and hydrophobic areas. After cycling with water vapor adsorption, the hydrophobic areas may be reduced in the degree of hydrophobicity. The Ca-O and P-O bond sites vary in distance from the surface, and it is possible that hydroxylation of these sites may proceed at different energy levels; a

reorientation of these sites with respect to the surface composition of Ca-O and P-O bond distributions is possible, causing a shift in the step of water adsorption isotherm (Fig 3), and its elimination after several adsorption-desorption cycles. It has also been suggested that if the crystals were not perfectly stoichiometric, thermal cycling might drive Ca, PO_4 , or impurities to the surface, thus changing its character.

The isosteric heat of adsorption versus surface coverage curves all had initial sharp and large increases followed by decreases to the heat of liquefaction of water after about two layers of water had been adsorbed. The initial increase can be accounted for by chemisorption taking place on the dry, dehydrated HAP surface. On a highly active surface having a high degree of heterogeneity, the first water molecules to adsorb involve large energy changes. Once this initial adsorption has occurred, a less active surface with lower degree of heterogeneity is able to adsorb water with less release of energy. When all the active sites are covered, at a L of about 1.5, water molecules encountered a fairly homogeneous surface which is finally covered after two layers to become a two-dimensional, liquid-like surface upon which water condenses with little difference between it and a three-dimensional bulk liquid.

Conclusions

Vapor phase adsorption of water on hydroxyapatite showed that the amount of water adsorbed was a function of the outgassing temperature and the number of times the samples had been thermally outgassed. The adsorption isotherms of water showed steps in the low pressure region. These steps diminished with each repeated adsorption-desorption cycle by moving to progressively lower relative pressures with each cycle. However, the step occurred with each cycle at the same amount of adsorbed water until it disappeared after the fourth cycle. These steps and their disappearance were interpreted to result from a dual type of surface having hydrophilic and hydrophobic areas which changes to a more homogeneous hydrophilic surface after adsorption-desorption cycling.

The shape of the isotherms, free energy, enthalpy, and entropy of adsorption, and the equilibrium function as a function of the surface coverage, permit a characterization of the surface of hydroxyapatite. The initial adsorption of water resulted from chemisorption of water on highly active sites of the hydroxylated hydroxyapatite surface. These initial adsorp-

tions resulted in high free energy changes. Thereafter, less active sites adsorb water until the surface is covered with two layers of water. Further water is adsorbed on a two-dimensional, liquid-like surface which is similar to the bulk water.

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