THE ADSORPTION OF WATER VAPOR ON GERMANIUM AND GERMANIUM DIOXIDE

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Isotherms have been measured for water adsorbed on germanium and germanium dioxide at temperatures close to 300°K. These are compared with published data for water on silicon dioxide. The isotherms are all of the multilayer type and from these have been calculated free energies, heats and entropies of adsorption at various coverages. By comparing the experimental entropy values with figures calculated from various models, it is shown that the first layer is localized but that succeeding layers are mobile and have effectively the same properties as liquid water.

Introduction

It is well known that germanium surfaces are very sensitive to the presence of water vapor and experiments have been reported as to the effect humidity has on germanium junction devices.[1] No one, however, has investigated the basic process which must underlie this deterioration, namely, adsorption of water vapor on the surface. The only attempt to correlate electrical changes with the amount of water adsorbed on the surface was made by Christensen[2] who measured gravimetrically the adsorption isotherm for water on germanium dioxide.

In this paper results will be presented for the adsorption of water vapor on germanium at pressures above 0.5 mm. and the correlation between these results and electrical measurements on germanium devices discussed.

Experimental

The adsorption of water vapor on a germanium filament at very low pressures has already been studied using a mass spectrometer.[3] It was found that on heating the germanium

to 350° the water desorbed completely as a mixture of water and hydrogen presumably as a result of the reaction

$$Ge + xH_2O \rightleftharpoons GeO_x + xH_2$$
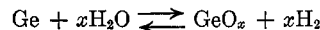
Therefore it should be possible to determine the adsorption isotherm by measuring the pressure change in a closed system on heating the germanium after adsorption. This would eliminate any dead space corrections which are required in the more usual type of constant volume adsorption apparatus. The accuracy of the pressure measurements was 10^{-2} mm. so that it was necessary that the pressure change on desorption was of the order of 1 mm. For this reason we had to use samples of crushed germanium with a surface area of about 300 cm.^{2}. The germanium dioxide available was already finely divided and had a surface area of several square meters per gram. The germanium dioxide powder was produced by Eagle Picher Co. and was high purity material of the "soluble" type. The germanium was originally a crystal of high resistivity n-type material, while the silicon was obtained from a low resistivity p-type crystal.

The apparatus used consisted of a water vapor source, an adsorption–desorption vessel (A-B), a differential manometer and a pumping system. The sample of crushed material was placed in the thermostated half (A) of a dumbbell shaped vessel. The other bulb (B) was made of quartz and attached to bulb A through a graded seal. Round B was wound a nichrome furnace, with a thermocouple embedded in the center.

The two bulbs were so arranged that the sample could be transferred from one bulb to the other by rotating the

(1) R. M. Ryder and W. R. Sittner, *Proc. I.R.E.*, **42**, 414 (1954).

(2) H. Christensen, *J. Applied Phys.*, to be published.

(3) J. T. Law and E. E. Francois, *Ann. N. Y. Acad. Sci.*, in press.

assembly about a standard taper joint. The advantage of winding the furnace directly onto the tube was that during a desorption measurement the temperature of only the germanium was changed and no desorption occurred from the glass walls of the apparatus.

A sample of distilled water was freed from gas by alternately freezing and melting under vacuum. The powdered solid was placed in B and degassed at 800° in a vacuum of 10^{-6} mm. for several hours. After cooling to 350° it was tipped into A and adsorption measurements started when it reached room temperature. Water vapor was admitted and left in contact with the solid for 30 minutes (no detectable change occurred if left for a further 18 hours). The sample was then tipped into the bulb B which had been maintained at 350°. The resulting increase in pressure was read by means of a travelling microscope on the wide arm (20 mm.) mercury manometer. The volume of the system had been determined by filling it with water so that the amount of gas desorbed could be determined. This however only gives the volume of gas desorbed from the whole sample and it is necessary to know its surface area before any useful figures can be calculated.

The surface area of the powder can be determined from the water isotherm at room temperature, by either the Hüttig[4] or the Brunauer, Emmett and Teller[5] (B.E.T.) method. A cross-sectional area for the water molecule of 10.6 Å.² at 295°K. was assumed. The areas (in cm.²/g.) obtained are listed in Table I where values are also quoted which were obtained from electron microscope pictures for germanium dioxide.

TABLE I

	Germanium, cm.²/g.	Germanium dioxide, cm.²/g.
B.E.T.	220	2.9×10^4
Hüttig	...	3.5×10^4
Electron microscope	...	$3.5\text{–}5.0 \times 10^4$

From these data the volume (V_m) required to form a statistical monolayer could be calculated and the adsorption results are presented in terms of V_{Ads}/V_m.

Results

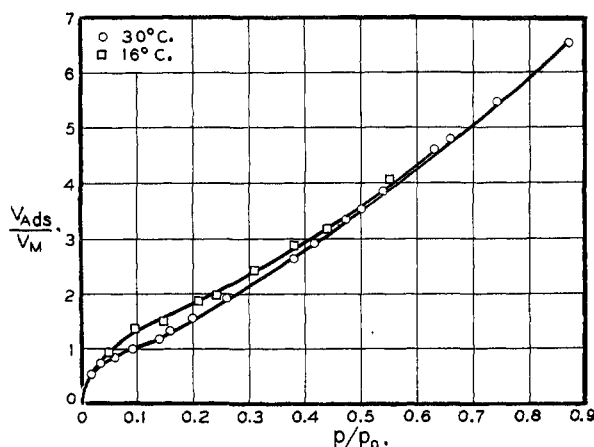**Germanium.**—The isotherms obtained for water on germanium at 16 and 30° are shown in Fig. 1.

Fig. 1.—Variation of volume of water adsorbed on germanium with p/p_0.

In Fig. 1 the amount adsorbed is plotted against p/p_0. The numbers on the ordinate represent layers in that the value V_m from the B.E.T. calculation was set equal to one. Thus it can be seen that the monolayer is filled at less than $0.1p_0$ and that multilayer adsorption then commences. Near the saturation vapor pressure something like 8–10

(4) G. F. Hüttig, *Monatsh.*, **78**, 177 (1948).

(5) K. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **59**, 1533 (1937).

layers are adsorbed. In Fig. 1 it can be seen that the curves for the two temperatures coincide above $0.5p_0$. This indicates that the heat of adsorption in this region is identical with the heat of condensation of water vapor, as would be expected in the high multilayer region.

Germanium Dioxide.—The adsorption isotherms on GeO_2 are shown in Figs. 2 and 3. Here again the monolayer is complete at quite low pressures and multilayer adsorption is found at higher pressures. At pressures above $0.3p_0$ the amount adsorbed is about half that found for germanium so that the surfaces clearly behave quite differently. The results obtained by H. Christensen[2] are also shown in Fig. 2 and seem to indicate that his surface was not completely degassed before the measurements. If it is assumed that a monolayer was already present on his surface his results are not too unlike those found in the present work.
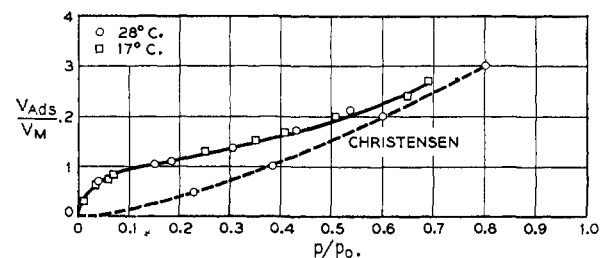

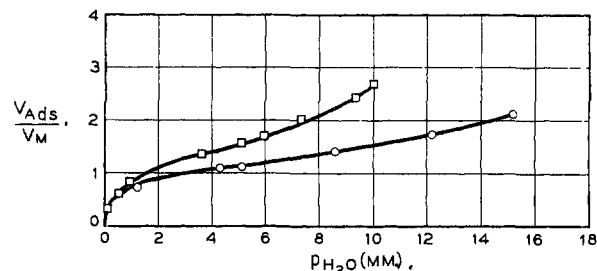Fig. 2.—Variation of volume of water adsorbed on germanium dioxide with p/p_0.

Fig. 3.—Variation of volume of water adsorbed on germanium dioxide with pressure.

Silicon.—Attempts were made to measure the isotherm for water adsorbed on silicon but the results obtained were identical with those described below for silica. For this reason it is felt that the surface was covered with a heavy oxide film. The sample was heated to 1320°K. in an effort to remove it but no marked improvement was obtained. This is not too surprising as the heating was done in a quartz tube where the following equilibrium must exist.

$$SiO_2 + Si \rightleftharpoons 2SiO$$
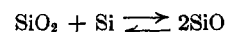
Silicon Dioxide (Silica).—The isotherm for silica that was taken from Livingston's[6] thesis appears to be practically identical with the one obtained for GeO_2 in the present work. It is shown in Fig. 4 together with the corresponding isotherms for germanium and germanium dioxide for comparison.

(6) H. K. Livingston, "Adsorption and Free Surface Energy of Solids," Ph.D. Dissertation, University of Chicago, 1941.
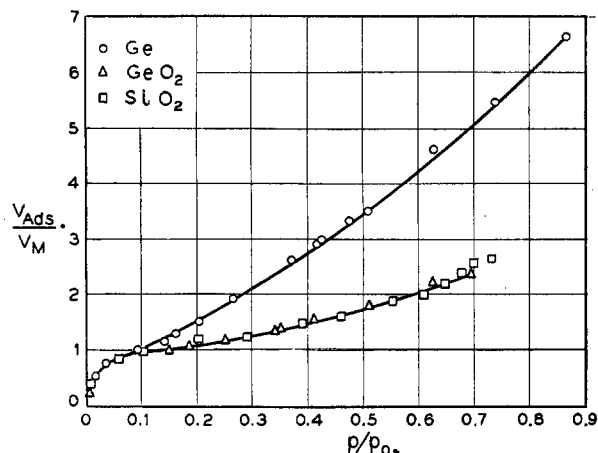
Fig. 4.—Comparison of adsorption isotherms for water on germanium, germanium dioxide and silicon dioxide.

Thermodynamics of Adsorption.—We will now confine our attention to germanium and germanium dioxide as these were the two materials most studied. In each case a multilayer isotherm was obtained which was reversible, *i.e.*, the adsorbed water could be removed by pumping. This was true until the monolayer region was reached when further water could only be desorbed by heating, thus indicating some form of chemisorption. The temperature required for desorption was not investigated carefully but is known to lie somewhere below 350°. During desorption the germanium surface was oxidized as a result of the reaction

$$Ge + xH_2O \rightleftharpoons GeO_x + xH_2$$
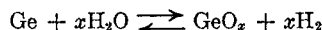
and if it was not cleaned by heating *in vacuo* before the next measurement lower values of the amount adsorbed were obtained. This indicates that if a germanium surface is sufficiently heavily oxidized it will behave much like GeO_2 and adsorb less water at a given pressure than a clean surface. From two or more isotherms at different temperatures it is possible to calculate heats, free energies and entropies of adsorption and so determine the degree of mobility of the adsorbed molecules. This is done by comparing the experimental figures with values calculated for different models, namely, fixed and mobile adsorption.

According to the mobile adsorption model, the adsorbed molecules behave as a two-dimensional gas, moving freely over the surface. Recently Kemball,[7] Everett[8] and deBoer[9] have studied the adsorption of various gases in this manner, their approach differing mainly in the choice of a standard state for the adsorbed species.

The differential heats of adsorption were evaluated using the Clausius–Clapeyron equation

$$\left(\frac{\partial \ln p}{\partial T}\right)_v = \frac{\overline{\Delta H}}{RT^2}$$

where V refers to the volume of vapor adsorbed, p the equilibrium pressure and $\overline{\Delta H}$ is the differential heat of adsorption.

(7) C. Kemball, "Advances in Catalysis," Vol. II, Academic Press, Inc., New York, N. Y., 1950, p. 233.

(8) D. H. Everett, *Trans. Faraday Soc.*, **46**, 453, 942 (1950).

(9) J. H. deBoer, *Koninkl. Nederland Akad. Wetenschap. Proc.*, **55**, 451 (1952).

The difference in free energy between the three-dimensional gas standard at temperature T and the adsorbed molecules in equilibrium with p was given by

$$\Delta G = RT \ln p/p_0'$$

The differential entropies were then calculated using

$$T\overline{\Delta S} = \overline{\Delta H} - \Delta G$$

The standard state in the gas phase (p'_0) was taken as 760 mm.

To facilitate the calculation of $\overline{\Delta H}$, V was plotted against log p, as shown in Fig. 6 for germanium.

$$\Delta H = 2.3RT^2 \frac{\Delta \log_{10} p}{T_2 - T_1}$$

The values obtained for $\overline{\Delta H}$ and $\overline{\Delta S}$ at 295°K. are shown in Fig. 5. Although they are not included in this figure, heats of adsorption were calculated from all possible pairs of curves in Fig. 6. The values at a given coverage never differed by more than 1 kcal./mole so that the average values shown were reproducible within ±0.5 kcal./mole.
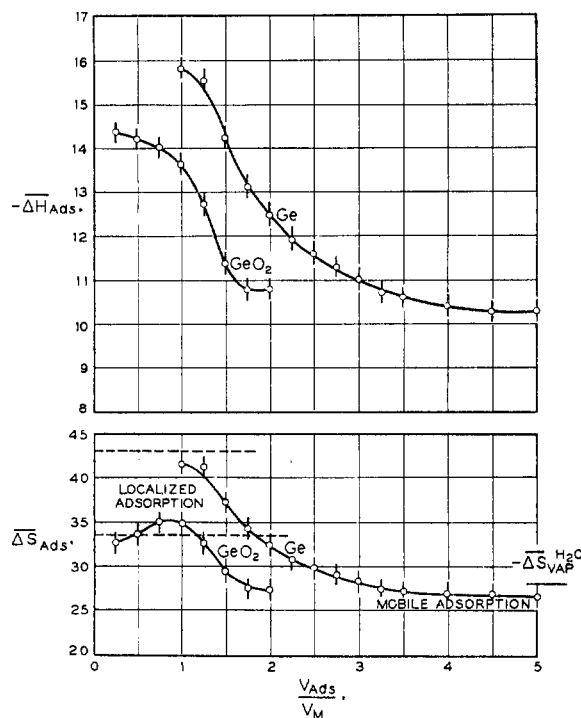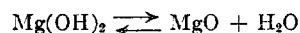

Fig. 5.—Variation of the heat and entropy of adsorption of water on germanium and germanium dioxide.

Accurate values of the entropy of water have been available for some time. Gordon,[10] neglecting the nuclear spin contribution, gave a figure of 45.1 e.u. at 298°K. and 1 atmosphere. Gordon's value was confirmed by Giauque and Archibald[11] using the reaction

$$Mg(OH)_2 \rightleftharpoons MgO + H_2O$$

The contributions of the vibrations to the entropy and the effect of the vibrations on the

(10) A. R. Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

(11) W. F. Giauque and R. C. Archibald, *J. Am. Chem. Soc.*, **59**, 561 (1937).
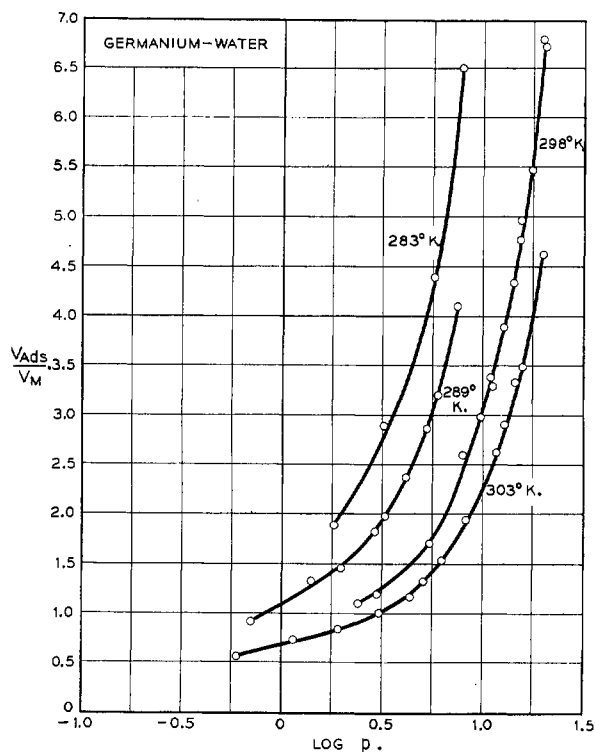
Fig. 6.—Variation of volume of water adsorbed on germanium with log p at various temperatures.

moments of inertia are small at room temperature and may be ignored. Using the moments of inertia given by Gordon[10] the sum of the translational and rotational entropy is found to be 45 e.u. compared with the accurate value of 45.1 e.u.

The rotational entropy was calculated from

$$S_R = 3/2R + R \ln \frac{8\pi^2}{\sigma h^3}(8\pi^3 ABC)^{1/2}(kT)^{3/2}$$

where A,B,C, are the principal moments of inertia and σ is the symmetry number. For water $S_R = 10.5$ e.u. at 295°K.

The translational contribution was obtained from the familiar Sackur–Tetrode equation and was found to be 34.5 e.u. at 295°K. From the total entropy in the gas phase and the experimental values of $\Delta \overline{S}_{Ads}$, the entropy values for the adsorbed molecules S_{Ads} were obtained. In Fig. 5 the experimental values of the heat and entropy of adsorption are plotted against the surface coverage. A striking feature about the differential entropies is the parallelism between the heat and entropy curves which is in agreement with the behavior noted by Everett.[8]

The general form of the entropy curve in Fig. 5 is that which has been described by Hill, et al.,[12] on the basis of the B.E.T. model. The maximum that occurs in the entropy curve for GeO$_2$ at $V = 0.75$ is indicative[12] of strong binding to the surface because of the small number of possible configurations of the system in the region of the monolayer. The initial increase in $\Delta \overline{S}_{Ads}$ has been shown[13] to be mostly due to the change in configurational entropy

(12) T. L. Hill, P. H. Emmett and L. G. Joyner, *J. Am. Chem. Soc.*, **73**, 5102 (1951).

(13) L. E. Drain and J. A. Morrison, *Trans. Faraday Soc.*, **48**, 316 (1952).

with concentration. The decrease in $\overline{\Delta S}_{Ads}$ for water on both germanium and germanium dioxide after the monolayer has been passed, reflects the building up of multilayers. In order to obtain more information about the freedom of the adsorbed molecules it is possible to compare the results with the calculated loss of entropy for water undergoing non-localized adsorption.

The experimentally determined entropies were differential quantities so that we need to obtain the differential entropy of a two-dimensional gas on the surface. The molecular partition function for an ideal two-dimensional gas is given by

$$Q = 2\pi mkTa/h^2$$

where a is the area available per molecule. We will define this area by

$$a = a_0(N_0 - N_s/N_s)$$

where a_0 is the cross-sectional area of the molecule, N_0 the number of molecules required to saturate a given area of adsorbent and N_s the number actually adsorbed at any stage.

Using the normal expressions for entropy in terms of partition functions and assuming a_0 is independent of temperature we obtain

$$N\overline{S}_s = R \ln \left[\left(\frac{2\pi mkTa_0 e}{h^2} \right) \left(\frac{N_0 - N_s}{N_s} \right) + 1 \right]$$

Using $a_0 = 10.6$ Å.^{2} for water, this gives the differential two-dimensional translational entropy per mole on a half covered surface as 10.6 e.u. at 295°K. On adsorption the third degree of translational freedom will be replaced by a weak vibration with which there will be associated an entropy of approximately 4 e.u.[7] If we assume that the rotational entropy of the water molecules is unimpaired by adsorption (which will almost certainly be true in the case of germanium when six layers are adsorbed) the differential entropy of adsorption will be

$$-\overline{\Delta S} = S^3{}_{Trans} - S^2{}_{Trans} - S_{Vibn}$$
$$= 34.5 - 10.6 - 4 = 20 \text{ e.u.}$$

which may be compared with the experimental value of 27.5 ± 2 e.u. The discrepancy between the calculated value of 20 and the experimental value of 27.5 e.u. is sufficiently great that the postulated model must be incorrect. The obvious reason is that we have assumed that in the multilayer region water behaves as a perfect two-dimensional gas. From what is known about the tendency of water to associate this is almost certainly not true. Any restriction resulting from association of the molecules will lead to an increase in the calculated value of $\overline{\Delta S}$. As a first approximation we are justified in taking the value of ΔS_{Vap} and comparing it with the observed entropy of adsorption. Wagman, et al.,[14] obtained a value of $\Delta S_{Vap} = 28.4$ cal./mole and it seems reasonable to say that for a mobile layer of water molecules $-\overline{\Delta S}_{Ads}$ will lie between 20 and 28.4 e.u. and probably much nearer the latter figure in agreement with the experimental value of 27.5 e.u. This agreement suggests that in the multilayer region on both germanium and germanium dioxide the water molecules are undergoing non-localized adsorption.

(14) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

Let us now consider the monolayer region where the adsorption may be localized. If all translational freedom is restricted there will remain the differential molar localisation entropy which is given by

$$N\bar{s}_s = R \ln \left(\frac{1 - \theta}{\theta} \right)$$

(where θ is the fraction of the surface covered) and the entropies associated with the two vibrations in the plane of the surface. The free rotation of the water molecules will probably be replaced by a restricted rotation about the germanium–oxygen bond: Surface $Ge-O_{-H}^{-H}$. At half coverage the configurational entropy term is zero so we have

$$-\overline{\Delta S} = S^3{}_{Rotn} + S^3{}_{Trans} - S^2{}_{Vibn} - S^2{}_{Rotn}$$
$$= 45.0 - 5 - 2 = 38 \pm 5 \text{ e.u.}$$

assuming reasonable values for $S^2{}_{Vibn}$ and $S^2{}_{Rotn}$. This value is close enough to the experimentally determined values of 41.6 for germanium and 34.9 for germanium dioxide that we are justified in saying that the monolayer region consists of localized adsorption.

Comparison of Adsorption Results and Electrical Deterioration of Germanium Units.—It has been shown[1] that the reverse current of a germanium p–n junction begins to increase rapidly when the unit is exposed to humidities of 40% or higher. By a comparison of Figs. 4 and 5 of the present work, it may be seen that this corresponds to the formation of a third layer in which the water molecules are quite mobile. It is quite striking that the electrical properties are not appreciably affected by the first localized layer or by the second transitional layer but that as soon as the water molecules have a high mobility the reverse current increases rapidly. This seems to indicate that a process of ionic conduction in the adsorbed film is either the cause of the high conductivity or an intermediate step in its occurrence. The electrical measurements like the adsorption isotherm are reversible upon removal of the water vapor even though the monolayer region must be unaffected by this treatment.