

only about 50% complete. This marked difference in the reaction rates affords a new method for ascertaining the approximate amounts of the alpha and beta isomers in solution. Such data should be of value in the study of the mechanism of the oxidation reactions and also for determining whether a given crystalline form of a sugar consists of a single isomer or whether it is a mixture of the alpha and beta forms. The oxidation of the sugar containing a single isomer progresses uniformly, while the oxidation of a mixture of the alpha and beta forms progresses rapidly until one form, usually the beta, is used up, and then more slowly as the oxidation of the other form is continued. Inasmuch as homogeneous crystalline compounds containing the alpha and beta forms of a single sugar have been discovered recently by Hockett and Hudson [THIS JOURNAL, 53, 4455 (1931)] it is necessary to determine whether or not the known crystalline sugars are substances of this type. This problem may be attacked by determining the rates at which they are oxidized by bromine water.

Since a large number of the sugars are being studied under strictly comparable conditions, the results may be used also in correlating the rate of oxidation with the stereomeric structure of the sugars.

The writer is being assisted in this work by W. W. Pigman.

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THE NATURE OF ACTIVATED ADSORPTION

Sir:

In a recently published article [THIS JOURNAL, 54, 602 (1932)] Taylor and Sickman presented data on the low- and high-temperature adsorption of hydrogen by zinc oxide, from which some information on the two types of adsorption can be secured by statistical methods. From their Fig. 3 on page 612, it is found that equal amounts are adsorbed at 125°K. and 580°K. and 400 mm. pressure, while the heats of adsorption are 1100 and 21,000 cal., respectively. Writing statistical expressions for exp. $(-f/kt)$ (f : free energy at constant pressure in μ space), setting free energy of gas equal to that of adsorbate at each temperature and dividing the square of the expression for 125°K. by that for 580°K. the following equation results

$$e^{(2\Delta a_1/KT_1) - (\Delta a_1/KT_2)} = \frac{T_1^3 h^3}{T_2^{7/2} P^{1/2} \pi^{6/5} m^{1/5} k^{1/2} J} \frac{\Omega_{v_2}^3 N^2}{\Omega_{v_1}^2 S^2}$$

The assumptions underlying this expression are that in low temperature adsorption hydrogen molecules have freedom of motion over the surface (two dimensional ideal gas) and that their rotation is unchanged by

adsorption, while at high temperature hydrogen atoms are produced which are held by definite surface atoms. Further, m and J are the mass and the moment of inertia of hydrogen molecules, Ω_{v_1} is the phase space of vibration (in h units) normal to the surface in low temperature adsorption, Ω_{v_2} is the phase space of vibration of adsorbed atoms at higher temperature, P is the gas pressure, S is the surface available for the low temperature adsorption in sq. cm., while N is the number of surface atoms available for the high temperature adsorption. Assuming, in the first approximation, that the zero point energy changes $\Delta\epsilon_1$ and $\Delta\epsilon_2$ are equal to the measured heats of adsorption, the numerical calculation yields

$$\frac{N}{S} = 2 \times 10^{12} \frac{\Omega_{v_1}}{\Omega_{v_2}^3}$$

Since the ratio $\Omega_{v_1}/\Omega_{v_2}^3$ is hardly much larger than unity and the total number of surface atoms per sq. cm. is of the order of 10^{15} , it is seen that only a small fraction of the surface participates in the "activated" adsorption. Other assumptions regarding the state of adsorbed gases lead to still smaller fractions of the surface involved in high temperature adsorption. Thus, if in activated adsorption hydrogen molecules retain their identity and execute a rotational motion in addition to vibration as a whole (Ω_{v_2}) around their position of equilibrium, the expression is obtained

$$\frac{N}{S} = 2 \times 10^{11} \frac{\Omega_{v_1}}{\Omega_{v_2}^3}$$

If, finally, freedom of motion on the surface is accepted for activated adsorption, the ratio of surfaces involved in the two processes is found to be

$$\frac{S_2}{S_1} = 10^{-8} \frac{\Omega_{v_1}}{\Omega_{v_2}}$$

A larger fraction of surface involved in activated adsorption than calculated above, is obtained only if formation of multimolecular layers at low temperature is postulated. These calculations lead to the conclusion that activated adsorption is limited to particular surface atoms only, the adsorbate not forming a freely moving two-dimensional gas on the surface (*cf.* H. S. Taylor, "Catalytic Symposium," Faraday Society, 1931); they indicate at the same time a way for a detailed study of the structure of surfaces by measurements of heat changes in adsorption of varying amounts at low and high temperatures. It should be pointed out also that in calculations of the theoretical adsorption rate, correction must be made for the inactive surface.

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