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SURFACE AREAS OF URANIUM AND URANIUM HYDRIDE POWDERS

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The BET method¹ was successfully used to measure the surface areas of uranium and uranium hydride powders^{2,3}. Equation (1) shows the form of the BET equation that was applied.

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C-1}{U_m C} \cdot \frac{P}{P_0} \quad (1)$$

The symbols have their usual meaning¹. The total volume of gas adsorbed, V , on the powdered samples was determined both gravimetrically and volumetrically. If one assumes that all particles in the powder are spheres of the same size, the radius of this hypothetical particle can be calculated by use of Eq (2),

$$r = \frac{3}{(SA) \rho} \quad (2)$$

where r is the radius of the sphere, SA is the specific surface area, and ρ is the crystal density of the particle.

Figure 1 shows an example of the results of several argon isotherms, which represent a measurement of the BET surface area of powdered uranium by gravimetric means. It is notable that the intercept of the straight line is small, which implies that the heat of liquefaction of argon is about the same as the heat of adsorption of the first monolayer.

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Fig. 1. Example of BET isotherm argon on uranium, specific surface area, $0.243 \text{ m}^2/\text{g}$. $T = 75.2^\circ\text{K}$.

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URANIUM HYDRIDE

Measurements of the surface area of UH_3 by applying the BET method to N_2 isotherms at 75°K have been reported². In general, the surface areas can be placed into two categories. UH_3 samples prepared by a single hydriding of U with H_2 at 300°C had surface areas ranging from 0.3 to $0.6 \text{ m}^2/\text{g}$. Samples prepared by multiple hydridings and decompositions at 300°C had surface areas ranging from 0.8 to $1.1 \text{ m}^2/\text{g}$. Duplicate determinations with a volumetric apparatus were in agreement to within 7%. There is a practical upper limit of $\sim 1 \text{ m}^2/\text{g}$ to the surface area of UH_3 prepared at 300°C . The results indicate that a complete monolayer of N_2 on UH_3 at 75°K measures the total surface area of UH_3 .

A kinetic study of the reaction of ammonia with UH_3 convincingly shows that the integrated rate expression, Eq (3), describes the data well.

$$[\text{H}_2] = k \log \left[\frac{(\text{NH}_3)}{(\text{NH}_3)_0} (1 + t/t_0) \right] \quad (3)$$

A summary of the data is shown in Fig 2. The logarithmic rate law was derived by Landsberg⁴ on the assumption that chemisorption of the reactant is rate controlling.

It is notable that the straight line intercepts in Fig 2 do not extrapolate to the origin. This fact implies that the initial reaction is more rapid than indicated by Eq (3). A constant obtained by taking the ratio of the intercept, as shown in Fig 3, to the volume of N_2 adsorbed by a monolayer, V_m , on each sample suggests a monolayer of nitride is formed by the rapid process. The subsequent reaction then involves the chemisorption of NH_3 on the nitrified surface as the rate-determining step. The correlation between the surface area and the kinetic data is good.

Fig 2

Fig 3

URANIUM POWDER

A rate law for the nitridation of pyrophoric uranium powder with deuterioammonia was determined by Alire et al.³. The surface area of powdered uranium samples was measured by using argon isotherms at 75°K determined gravimetrically to $\pm 2\%$. Nitrogen was not used because it reacted with powdered U at 75°K.

The data in Table I indicate that multiple hydriding and decomposition of the same sample at 300°C will result in a maximum surface area of uranium of about $0.3 \text{ m}^2/\text{g}$. Surface areas as high as $\sim 0.6 \text{ m}^2/\text{g}$ can be obtained by keeping the decomposition temperature as low as 215°C. Temperatures for decomposition much below 215°C are impractical because the decomposition time is too long. However, a stable area is not generally achieved by low-temperature decomposition.

The area was found to decrease significantly by heating in vacuo. Figure 3 shows the results of heating a sample for varied time intervals at several temperatures and a pressure of about 10^{-5} torr. The phenomenon was attributed to sintering. Surprisingly, sintering was observed at temperatures as low as 200°C. To study the kinetics of uranium with deuterioammonia, it was necessary to sinter each sample at the experimental temperature for 15-24 h to achieve a stable area.

A rate law for the nitridation of pyrophoric uranium with deuterioammonia was established for the entire course of the reaction. The rate was determined to be a linear function of the initial BET surface area. An interpretation of the results was done in terms of a diffusion mechanism which assumes the diffusion of uranium atoms to the surface as the rate-determining step. The activation energy was measured to be $25 \pm 3 \text{ kcal/mole}$ of uranium reacted.

TABLE I

SURFACE AREAS OF POWDERED U

No. of Hydridings	Max Temp Dehydriding (°C)	Surface Area (m²/g)	Equivalent Sphere Radius (μm)	Comments
1	~ 300	0.037	4.29	
2	~ 300	0.200	0.79	
3	~ 300	0.251	0.63	
3	~ 300	0.230	0.69	
3	215	0.439	0.36	
3	220	0.380	0.42	
4	225	0.5250	0.30	
10	225	0.2270	0.70	Sintered
12	~ 300	0.2940	0.54	

The rate of reaction was described by Eq (4),

$$\frac{du}{dt} = K A(1-f_R) , \quad (4)$$

where du/dt is rate of reaction in moles of U/min. A is area and f_R is the fraction reacted. K is the rate constant of the reaction.

The data in Fig 4 illustrate the excellent correlation between the surface area and the rate constant. Perhaps the most significant revelation in this study is the fact that a stable area of uranium powder was achieved by heating in vacuum at the experimental temperatures.

The surface areas of UN_2 , UH_3 , and UO_2 have also been measured⁵. The results are shown in Table II. The formation of UN_2 from uranium powder by reaction with ammonia increases the area by about a factor of 10. Similar results are also obtained by forming UH_3 . The formation of UO_2 results in a much larger increase in area.

An experiment that attempted to measure the sintering effects of UH_3 was performed. A sample of UH_3 with an area of about $0.4 \text{ m}^2/\text{g}$ was heated at 400°C for 15 h with an atmosphere of H_2 . There was no change in surface area measured. This observation is surprising in view of the fact that the dissociation and reformation of UH_3 is a dynamic phenomenon. Good surface-area measurements can only be obtained in clean vacuum systems because UH_3 is a very reactive material and acts as a getter.

CONCLUSIONS

The BET surface area measurements have provided a frame of reference to study the effects of differences in surfaces on the reaction rates of uranium and uranium hydride with gases.

Fig 4. Experiments at 298°C, KSA or Q_{max} as a function of specific surface area. O , WT area; $\square$, present data; Δ , Q_{max} data.

TABLE II

SURFACE AREA CHANGE BY REACTION

<u>Initial Surface Area (m²/g)</u>	<u>Final Surface Area (m²/g)</u>	<u>Product</u>	<u>Comments</u>
0.23	2.13	UN ₂	not sintered
0.037	1.18	UN ₂	not sintered
0.20	1.73	UN ₂	sintered
0.127	7.47	UC ₂	sintered
0.120	6.32	UO ₂	sintered
0.04	0.3	UH ₃	not sintered

caused by differences in surfaces. It is not believed that these measurements represent absolute values of the specific surface area, but are a relative comparison of the different surfaces.

Good correlation between rate constants and the BET surface area was demonstrated. It is felt that any measurements made on powders of uranium or uranium hydride should include a BET surface area measurement of the starting material. Attempts to draw conclusions about the particle size or shape of powders from BET surface areas are generally not informative.

REFERENCES

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