190. *Heats of Adsorption of Oxygen on Solid Solutions of Uranium Dioxide in Thorium Dioxide at* −183°.

By J. D. M. McConnell.

By use of a " cyclone microniser ", specimens of solid solutions containing 20 mole % and 10 mole % of uranium dioxide in thorium dioxide have been prepared having surface areas of about 12 m.^{2}/g. The initial heat of adsorption of oxygen on these solid solutions at −183° falls as the uranium content is decreased. A slow evolution of heat at partial coverage has been observed, but differs from that noted earlier on pure uranium dioxide.

During a study of the heat of adsorption of oxygen on uranium dioxide at −183°,[1] some work was carried out on a solid solution consisting of 75 moles % of uranium dioxide and 25 mole % of thorium dioxide. Firing at a high temperature is essential in preparation of such solid solutions,[2, 3] but yields a product having a small surface area (large particle size). At −183°, the reaction of oxygen is confined to the surface of uranium dioxide or its solid solutions in thorium dioxide. The small surface areas cause small uptakes of oxygen, and measurement of the differential heat of adsorption of oxygen by means of small increments of gas is difficult.

A " cyclone microniser " has now been developed[4] suitable for handling the small quantities in which solid solutions are generally available. Whereas previously the surface areas of solid solutions were of the order of 0·2 m.^{2}/g., products have been obtained from the microniser having surface areas in excess of 10 m.^{2}/g. This has made possible the study of heats of adsorption of fairly dilute solid solutions of uranium dioxide.

Previous studies on oxides having high surface areas have frequently been carried out on material treated at relatively low temperatures and thus of somewhat dubious composition. The present materials differ from the well-characterised starting material only in having been subjected to the purely physical process of grinding.

EXPERIMENTAL

Calorimeter.—The calorimeter was the instrument used previously.[1] The operation, including the method of evaluating heats of adsorption, was as before.

Solid Solutions.—Starting from thorium dioxide and hydrated uranyl nitrate, solutions in nitric acid were prepared containing respectively 20 mole % of uranium with 80 mole % of thorium (specimen TL8), and 10 mole % of uranium with 90 mole % of thorium (specimen TL9). The precipitate obtained by adding ammonia to the solution was dried in air at 150°, then heated in air at 900°. The product was ground in an agate mortar. *X*-Ray photographs confirmed that the products were single-phase.

Microniser.—The cyclone microniser, described in detail elsewhere,[4] consists of a loop of Pyrex glass tubing in the vertical plane round which the solid sample is blown by means of compressed air. After leaving the loop, the solid is crudely " fractionated " according to particle size in three separators in series. The surface area (measured by the B.E.T. method, with nitrogen at −195°) of specimen TL8 from the second separator was 11·7 m.^{2}/g.; that of specimen TL9, also from the second separator, was 12·7 m.^{2}/g. The silica contents of these specimens were 500 p.p.m.

Immediately before the calorimetric measurements, the specimens were reduced in static carbon monoxide at 600°/1 atm. for 1 hr., and transferred to the calorimeter *in vacuo*, this being chosen to minimise deposition of carbon on the oxide surface.[5]

---

[1] Ferguson and McConnell, *Proc. Roy. Soc.*, 1957, *A*, **241**, 67.

[2] Roberts, *J.*, 1954, 3332.

[3] McConnell and Roberts in "Chemisorption," (Chem. Soc. Symp.), July, 1956, Butterworths, London, 1957.

[4] McConnell, A.E.R.E., C/M 319.

[5] Roberts, Walter, and Wheeler, to be published.

RESULTS AND DISCUSSION

The change in differential heat of adsorption with uptake of oxygen by the oxide surface is shown in Fig. 1. The uptake of oxygen (expressed in terms of the " chemisorption limit " as defined by Roberts [2]) varies with the uranium content of the solid solution and, from Roberts's work, is 12% of V_m (the monolayer volume) for the 20% solid solution, and 6% of V_m for the 10% solid solution. On this basis, the coverages quoted in Fig. 1 and in the Table of several times the chemisorption limit still signify an uptake of less than a monolayer referred to the *total* solid surface.

Fig. 1 shows a steady decrease in the heat of adsorption with uptake of oxygen, as with pure uranium dioxide. The initial heat of adsorption decreases as the uranium content of the solid solution is reduced. It might have been expected that the true initial heat of adsorption, measured on an infinitely small increment, would be the same as on pure uranium dioxide, but that the rate of decrease of heat of adsorption with coverage would be greater on the solid solution. In these more dilute solid solutions, however, each uranium atom is in an environment composed largely of thorium atoms. Thus any process, such as the chemisorption of oxygen, which involves electron transfer will take place less readily on the solid solution than on pure uranium dioxide. The effect of diluting the uranium with " inert " thorium will be the more marked the more it involves the bulk of the uranium atoms and the less it is characteristic of individual atoms.

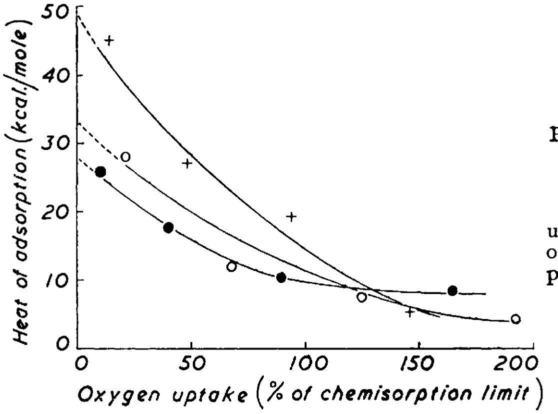

FIG. 1. *Change of heat of adsorption with surface coverage.*

Symbols refer to composition (mole % of uranium): + 75%, ○ 20%, ● 10%. (Results on the 75% solid solution are included for comparison.)

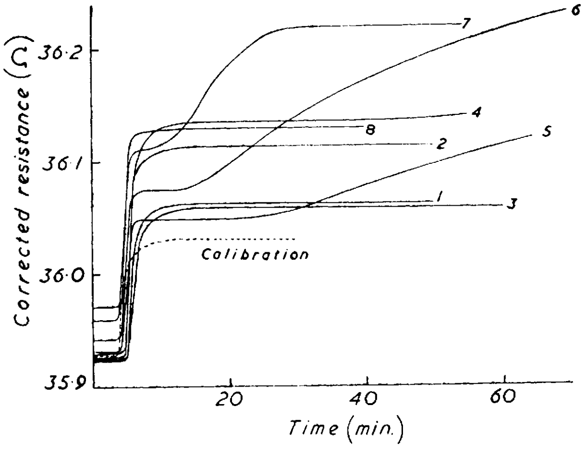

FIG. 2. *Corrected cooling curves for specimen* TL9.

Corrected cooling curves (see ref. 1) are shown in Fig. 2 for specimen TL9. Up to about

200% of the chemisorption limit (see also the Table), heat is evolved rapidly, and Newtonian cooling is established within less than 20 min., as in electrical calibration. Above 200% of the chemisorption limit, Newtonian cooling appears to be established, to be followed (curves 5—7, Fig. 2) by a further slow evolution of heat.

Specimen	Increment	O_2 adsorbed (mmoles)		Total coverage (% chemisorption)	Heat of adsorption (kcal./mole)
		incremental	total		
TL8	1	0·0604	0·0604	44	28·3
	2	0·0678	0·1282	93	12·1
	3	0·0915	0·2197	159	7·7
	4	0·0970	0·3167	229	(8·1) 4·5
	5	0·1118	0·4285	310	—
	6	0·1279	0·5564	410	4·1
TL9	1	0·0124	0·0124	22	26·1
	2	0·0241	0·0365	64	17·9
	3	0·0305	0·0670	118	10·6
	4	0·0541	0·1211	214	8·8
	5	0·0623	0·1834	324	(11·0) 4·4
	6	0·0784	0·2618	460	(9·2) 4·0
	7	0·0940	0·3558	630	6·4 3·7
	8	0·1090	0·4648	820	3·4

Monolayer volumes: TL8, 1·152 mmoles. TL9, 0·945 mmole.

This slow evolution differs from the slow reaction on pure uranium dioxide in two main respects. First, the second evolution of heat is very slow in increment 5, rather less so in increment 6 (and in neither of these increments was final establishment of Newtonian cooling observed), and complete after about 35 min. in increment 7. This is a reversal of the behaviour on pure uranium dioxide, where the slow reaction becomes increasingly slow with coverage. Secondly, it has been shown [2] that the chemisorption limit corresponds to reaction of oxygen with about half of the surface uranium sites. If all the surface uranium sites were to react, oxygen would be adsorbed up to 200% of the chemisorption limit. The further chemisorption of oxygen on a solid solution must involve the thorium atoms (since reaction with uranium atoms in the bulk of the solid at —183° is ruled out by arguments summarised elsewhere [6]), and the present slow evolution of heat must be a reaction of thorium atoms in the surface.

Heats of adsorption (3·5—4·5 kcal./mole) evaluated from the first parts of curves 5—7 for TL9 and curve 4 for TL8 are typical of physical adsorption. It has not been possible to evaluate accurate heats from the second parts of curves 5 and 6, but estimated heats are given in parentheses in the Table. (An estimated value is also quoted for increment 4 on specimen TL8.) Although these heats are low compared with values normally considered typical of chemisorption, they are nevertheless higher than the highest possible value (~5 kcal./mole) for physical adsorption. Very low heats of chemisorption have also been inferred from magnetic measurements on nickel on which hydrogen had been adsorbed.[7] Low-energy chemisorption has been discussed by Dowden.[8]

Whatever the significance of the slow evolution of heat at higher surface coverages of the solid solutions, the heats calculated from the first parts of two-part curves suggest that the first stage in the uptake of oxygen by the oxide is physical adsorption. An increasing body of evidence suggests that physical adsorption frequently, if not even always, precedes chemisorption. Changes in the resistance of evaporated nickel films have been interpreted as indicating that a considerable fraction of the total water vapour or carbon dioxide adsorbed is first attached to the surface in the physically adsorbed state.[9] Again, the behaviour of physically adsorbed molecules has been considered to depend on the relative values of two activation energies, one for desorption and the other for incorporation into

---

[6] Anderson, Roberts, and Harper, *J.*, 1955, 3946.

[7] Selwood, *J. Amer. Chem. Soc.*, 1956, **78**, 3893.

[8] Dowden in " Chemisorption," (Chem. Soc. Symp.), July, 1956, Butterworths, London, 1957.

[9] Suhrmann and Wedler, *Z. physikal. Chem.* (*Frankfurt*), 1957, **10**, 184.

the chemisorbed state.[10] (A somewhat similar picture has been invoked to explain the slow reaction observed on pure uranium dioxide.[1]) Evidence for a two-stage reaction has also been deduced from results on the adsorption of nitrogen on tungsten.[11]

It must be emphasised that although both pure uranium dioxide and solid solutions of uranium and thorium dioxides exhibit slow reactions and heats of low-energy chemisorption, these reactions must be quite different. In the former case, uranium sites must obviously be involved, whereas in the latter they cannot be.

The author thanks Dr. L. E. J. Roberts for many helpful discussions, and for criticism of this paper.

ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, NR. DIDCOT, BERKS.

[*Received, September 25th,* 1957.]

[10] Ehrlich, *J. Phys. Chem.*, 1955, **59**, 473.

[11] *Idem, J. Chem. Phys.*, 1955, **23**, 1543.