basis of an X-ray structural analysis of zeolite "A" which will be published soon.

Zeolite "X," $Me_{86/n}[(AlO_2)_{86}(SiO_2)_{106}]\cdot 267H_2O$, is chemically different from, but structurally similar to, the mineral faujasite. The structure consists of a complex assembly of 192 tetrahedra in a large cubic unit cell 24.95 Å. on an edge. Adsorption measurements indicate that the effective pore diameter is 10 to 13 Å. The adsorption volume is about 0.35 cu.cm. per gram of dehydrated zeolite. Because of the large pore size this zeolite readily adsorbs almost all substances of appreciable vapor pressure. However, an adsorptive selectivity is exhibited for polar molecules, and, in fact, selectivity may occur for molecules with negligible dipole moment due to other more subtle molecular characteristics.

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ISOTOPIC EXCHANGE BETWEEN Pu(III) AND Pu(IV)[1]

Sir:

The exchange reaction between Pu(III) and Pu(IV) in perchlorate media is being investigated at this laboratory. This is the first report of exchange between the (III) and (IV) states of any actinide element.

It has been necessary to work in the region of 10^{-6} to 10^{-5} *f* plutonium to keep the half-times in the range of 1–5 min. No adverse "dilute solution" effects have been observed. However, it has been necessary to use redistilled water in preparing solutions and scrupulously cleaned glassware to avoid oxidation–reduction effects. Trivalent plutonium was freshly prepared before each run by hydrogen reduction in the presence of platinum black.[2] Tetravalent plutonium was also freshly prepared for each run by extraction with thenoyltrifluoroacetone (TTA) from 0.5 *f* $HClO_4$ followed by back extraction into a suitable stock solution.

The reaction is first order in each plutonium species within experimental error; actual values are Pu(IV) = +0.92 ± 0.14 and Pu(III) = +1.01 ±0.11. The rate of exchange at 0° in 0.5 *f* $HClO_4$ may be represented as: $R = k'(III)(IV)$ where $k' = 1.10 \pm 0.10 \times 10^4 f^{-1}$ min.$^{-1}$. The error limits given represent the 95% confidence level.

The isotope Pu^{238} ($t_{1/2}$ = 89.6 yr.,[3] E_α = 5.48 Mev.) is used as tracer in solutions of Pu^{239} ($t_{1/2}$ = 24,360 yr.,[4] E_α = 5.14 Mev.). The changes in tracer concentrations were determined using an alpha energy analyzer described elsewhere.[5]

Separation of the valence states was carried out at 0° by tributyl phosphate extraction of Pu(IV) from 6 *f* HCl. An aliquot of the exchanging solution was added to excess 6 *f* HCl–40% TBP/60% hexane mixture immediately prior to separation.

The Pu(III)–Pu(IV) system undergoes exchange more rapidly than either Eu(II)–Eu(III) or Ce(III)–Ce(IV). The europium system does not exchange in perchloric acid[6] and the cerium system exchanges fairly slowly[7,8] although high ionic strength environments were used in the cerium study. The rapid plutonium reaction may be due to increasing lability of the "surplus" electron in Pu(III).

A positive ionic strength dependence has been observed in the plutonium system. The hydrogen-ion dependence is complex. Work to date indicates that the rate as given above involves hydrolyzed species of Pu(IV), *e.g.*, $Pu(OH)^{+++}$. The rapidity of the plutonium exchange through a hydrolyzed Pu(IV) is compatible with the somewhat analogous Fe(II)–Fe(III)[9] reaction and also with recent theoretical considerations by Libby[10] and Zwolinski, *et al.*[11]

Systematic investigation of the various kinetic parameters of the plutonium exchange system is currently under way.

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[1] This work was sponsored by the United States Atomic Energy Commission.

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THE REACTION BETWEEN CHLORAMINE AND PYRIDINE

Sir:

It has been reported recently[1] that chloramine reacts with pyridine and α-picoline to yield ammonium chloride and decomposed heterocycle. We had found, in the course of other work, that passage of chloramine through pyridine at room temperature and atmospheric pressure gave, in addition, low yields of 2-aminopyridine and its hydrochloride. The structures of these products were established by use of mixed melting points with authentic base, hydrochloride, and benzenesulfonyl and *p*-dimethylaminobenzylidene derivatives, as well as by study of ultraviolet and infrared spectra. A continuing investigation has shown that the amination reaction is a general one for pseudoaryl heterocyclics. Even theobromine and caffeine have been converted—in very poor yields—to their (presumably) 8-amino derivatives. Of the single-hetero-atom systems studied to date, the best yields of α-amino derivatives have been obtained in the quinolines. Quinoline was converted to a 1:10 molar ratio of 2-aminoquinoline and its hydrochloride in slightly more than 40% of the theoretical yield. Raschig's work[2] has suggested that certain benzene derivatives undergo nuclear amination on reaction with chloramine; Coleman

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