heated and worked up as described above in the preparation of VI. The yield of colorless product, recrystallized from ether–pentane, was 2.65 g. (61.8%), m.p. 113–114.5°, $[\alpha]^{27}D$ −51° (*c* 5.03, chloroform).

Anal. Calcd. for $C_{31}H_{33}O_{11}P$: C, 60.78; H, 5.43. Found: C, 60.80; H, 5.57.

2,3,4-Tri-*O*-acetyl-D-glucopyranose-6-deoxy-6-phosphonic Acid (IX).—A solution of 0.4 g. (0.65 millimole) of VII in 20 ml. of absolute ethanol was hydrogenated at a pressure of 40 pounds in the presence of 0.06 g. of Adams catalyst. The calculated amount of hydrogen was absorbed in 20 minutes, the catalyst was filtered, and the filtrate concentrated at 40° *in vacuo*. The residual viscous oil gave a positive Fehling test, and solidified on stirring with 5 ml. of pentane. It was recrystallized from ether–pentane. The colorless material darkened at 175° and had m.p. 187–191° dec. It contained two moles of ether of crystallization which could not be removed at 110° *in vacuo* without decomposition of the compound.

Anal. Calcd. for $C_{12}H_{19}O_{11}P\cdot 2(C_4H_{10}O)$: C, 46.33; H, 7.58. Found: C, 46.21; H, 7.60.

1,2,3,4-Tetra-*O*-acetyl-β-D-glucopyranose-6-deoxy-6-phosphonic Acid (VIII).—Hydrogenolysis of 1.5 g. (0.0027 mole) of VI in 40 ml. of absolute ethanol in the presence of 0.15 g. of platinum dioxide was carried out as described in the preceding experiment. The reaction required from 30–90 minutes. The product (0.92 g., 76%) crystallized slowly from absolute ethanol, m.p. 171–172° dec., $[\alpha]^{25}D$ +9.5° (*c* 3.27, chloroform). It was dried at 56° over phosphorus pentoxide.

Anal. Calcd. for $C_{14}H_{21}O_{12}P\cdot 2H_2O$: C, 37.50; H, 5.62. Found: C, 37.83; H, 5.77.

Further drying at 78° for four days removed all but 0.5 mole of water of crystallization.

Anal. Calcd. for $C_{14}H_{21}O_{12}P\cdot {}^1/_2H_2O$: C, 39.91; H, 5.27. Found: C, 39.94; H, 5.01.

The acid gave a lead salt insoluble in water, and a somewhat water-soluble barium salt.

D-Glucopyranose-6-deoxy-6-phosphonic Acid (X).—(a) To a solution of 1.1 g. (2.6 millimoles) of tetra-*O*-acetyl-β-D-glucopyranose-6-deoxy-6-phosphonic acid in 25 ml. of cold anhydrous methanol was added dropwise 5.2 millimoles of 1 *N* potassium methoxide in order to neutralize the compound. Cleavage of the acetoxy groups by addition of further 3.9 mmoles of potassium methoxide was accompanied by immediate precipitation of a colorless, hygroscopic *potassium salt*. After standing at −10° for 24 hours, the salt was centrifuged, washed four times with absolute methanol, twice with ether–methanol (1:1), and then with dry ether. The yield was 0.4 g. (*ca.* 50%), $[\alpha]^{26}D$ +28.7° (*c* 4.9, water).

Anal. Calcd. for $C_6H_{11}K_2O_8P\cdot H_2O$: C, 21.30; H, 3.87; P, 9.16. Found: C, 21.56; H, 4.21; P, 9.17.

From the combined mother liquors and washings of the potassium salt, 0.5 g. of a colorless barium salt was obtained with barium hydroxide, but some contaminating barium carbonate could not be separated.

Anal. Calcd. for $C_6H_{11}BaO_8P$: Ba, 36.20. Found: Ba, 35.47.

(b) A solution of 0.7 g. (1.6 mmoles) of VIII in 50 ml. of 0.65 *N* hydrobromic acid was heated on a steam-bath for 3 hours, cooled and neutralized to *p*H 3 with 50 ml. of 0.65 *N* sodium hydroxide solution. A mixture of 1.2 g. of phenylhydrazine hydrochloride, 1.8 g. of anhydrous sodium acetate and 1 ml. of a saturated sodium bisulfite solution was added, and the whole heated at 95° for 2 hours. A somewhat gelatinous yellow precipitate appeared on cooling. It was recrystallized from 75% ethanol to melting point 162–169°, and purified further by sublimation at 65° (1.5 × 10^{-4} mm.). **The osazone** melted at 170–172°.

Anal. Calcd. for $C_{18}H_{23}N_4O_6P$: N, 13.27; neut. equiv., 422. Found: N, 12.63; neut. equiv., 438.[24]

(24) The analyses of this osazone were performed by Dr. Claibourne E. Griffin.

CHARLOTTESVILLE, VIRGINIA

COMMUNICATIONS TO THE EDITOR

NEW SYNTHETIC CRYSTALLINE ZEOLITES

Sir:

The outstanding characteristic of some natural hydrated zeolites is their ability to undergo removal of water of crystallization with little or no change in crystal structure. The dehydrated crystals are then interlaced with regularly spaced channels of molecular dimensions in which adsorption may occur.

Because of the interesting adsorptive properties of these rare natural minerals, a research program was initiated in this laboratory in 1949 to study the synthesis and properties of zeolites. Between 1949 and 1953, twenty crystalline zeolites were synthesized. These included: synthetic counterparts of the minerals chabazite, gmelinite, erionite, and mordenite, a species very similar to gismondite, and a species isostructural with faujasite but quite different in chemical composition. In addition, fourteen zeolite species were synthesized which have no natural counterparts known to us.

These new synthetic zeolites have been the subject of intensive study in this and other laboratories, and a number of papers describing their properties in detail will appear shortly.

Chemically, these zeolites may be represented by the generalized formula: $Me_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot MH_2O$, where x/n is the number of exchangeable cations of valence n, and M is the number of water molecules, removal of which produces the characteristic pore system.

One of the new synthetic zeolites, designated as zeolite "A," which has no known natural counterpart has the composition: $Me_{12/n}[(AlO_2)_{12}(SiO_2)_{12}\cdot 27H_2O$. When Me is Na^+ or Ca^{++} the adsorption volume is about 0.30 cc. per gram of dehydrated zeolite. When Me is Na^+ the dehydrated zeolite readily adsorbs molecules having a critical dimension up to 4 Å., the critical molecular dimension being defined as the diameter of the smallest cylinder which will accommodate a model of the molecule constructed using the best available van der Waals radii, bond angles, and bond lengths. When $^1/_3$ of the sodium ions are exchanged for calcium ions, the effective pore diameter increases to about 5 Å. For example, straight-chain hydrocarbons are adsorbed readily whereas branched-chain hydrocarbons are excluded. Replacement of sodium by potassium decreases the effective pore diameter. These and other phenomena are explained on the

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.

RESEARCH LABORATORY OF
LINDE AIR PRODUCTS COMPANY
A DIVISION OF UNION
CARBIDE AND CARBON CORPORATION
TONAWANDA, NEW YORK

D. W. BRECK
W. G. EVERSOLE
R. M. MILTON

RECEIVED MARCH 19, 1956

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.

(1) This work was sponsored by the United States Atomic Energy Commission.

(2) R. E. Connick and W. H. McVey, "The Transuranium Elements," NNES-IV-14B, McGraw-Hill Book Co., New York, N. Y., 1949, p. 142.

(3) A. H. Jaffey and J. Lerner, ANL-4411 (1950).

(4) J. C. Wallman, UCRL-1255 (1951).

(5) C. W. Johnstone, *Nucleonics*, **11**, 36 (1953).

(6) D. J. Meier and C. S. Garner, THIS JOURNAL, **73**, 1894 (1951).

(7) F. R. Duke and F. R. Parchen, *ibid.*, **78**, 1540 (1956).

(8) J. W. Gryder and R. W. Dodson, *ibid.*, **73**, 2890 (1951).

(9) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

(10) W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952).

(11) B. J. Zwolinski, R. J. Marcus and H. Eyring, *Chem. Revs.*, **55**, 157 (1955).

LOS ALAMOS SCIENTIFIC LABORATORY
UNIVERSITY OF CALIFORNIA
LOS ALAMOS, NEW MEXICO

THOMAS K. KEENAN

RECEIVED MARCH 22, 1956

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

(1) G. M. Omietanski and H. H. Sisler, THIS JOURNAL, **78**, 1211 (1956).

(2) F. Raschig, *Z. angew. Chem.*, **20**, 2069 (1907).