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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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) = $+0.92 \pm 0.14$ and Pu(III) = $+1.01 \pm 0.11$. 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.

[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).

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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

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

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

and Noyes[3] have demonstrated a similar reaction. Extensions of these investigations are being continued.

[3] G. H. Coleman and W. A. Noyes, THIS JOURNAL, **43**, 2211 (1921).

CHEMICAL RESEARCH DEPT.
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RECEIVED APRIL 12, 1956

CRYSTAL STRUCTURE AND MAGNETIC SUSCEPTIBILITY OF AMERICIUM METAL[1]

Sir:

We have obtained interpretable X-ray diffraction patterns of several small polycrystalline samples of americium metal of >99% purity, using Cu Kα radiation and a 4.5-cm. radius camera. The metal was prepared on a micro scale by reduction of the trifluoride with barium vapor, in a tantalum crucible system and subsequently was annealed by slowly reducing the temperature from 800 to *ca.* 25° over a period of ten hours.

The powder patterns have been indexed as double hexagonal close packed, $a = 3.642 \pm 0.005$ Å., $c = 11.76 \pm 0.01$ Å.

The space group is D_{6h}^4 and the atomic positions are: two Am in (0, 0, 0), (0, 0, $^1/_2$); two Am in ($^1/_3$, $^2/_3$, $^3/_4$), ($^2/_3$, $^1/_3$, $^1/_4$). The Am radius is 1.82 Å. and the calculated density 11.87 ± 0.05 g. cm.$^{-3}$.

Relative line intensities calculated for the proposed structure agreed with visual estimates of the intensities seen in the diffraction patterns, as shown in the accompanying table.

The density calculated for the metal agrees with that observed experimentally[2] (11.7 ± 0.3) within the error of the measurements. The metallic radius is 0.02 Å. smaller than that predicted by Zachariasen[3] for americium metal with three valence electrons per atom. This discrepancy may indicate a small error in the predicted value, or may be due to a slight admixture of americium (IV) in the metallic state. Measurements of the magnetic susceptibility of our samples gave $\chi_M = 1000 \pm 250 \times 10^{-6}$ cgs. units at 300° K., similar to the value of $\sim 1000 \times 10^{-6}$ c.g.s. units for AmF_3. The number of bonding electrons per atom appears to be quite close to three.

The decrease in the number of metallic bonds in going from uranium to americium affords a reasonable explanation of the corresponding decrease of some 50 kcal.[4,5] in the heat of vaporization.

It is interesting to note that americium is the first transactinium element which is rare earth-like in the metallic state.

Possible allotropy of the metal is now under investigation, and these studies, as well as a detailed description of the work outlined above, will be reported in a future publication.

TABLE I

DIFFRACTION DATA FOR AMERICIUM METAL[a]

hkl	$\sin^2\theta$ calcd.	$\sin^2\theta$ obs.	*I* calcd.	*I* obs.[b]
100	0.0597	0.0592	3	vw
101	.0640	.0640	18	m
004	.0687	.0692	14	ms
102	.0769	.0769	42	s
103	.0984	.0985	10	w
104	.1284	.1283	2	t
105	.1670	.1675	5	vw
110	.1792	.1792	11	m
106	.2142	.2144	9	m
200	.2389	....	0.4	..
201	.2432	....	3	..
114	.2479	.2471	13	ms
202	.2561	.2567	7	vw
107	.2700	.2698	2	t
008	.2747	.2755	2	vvw
203	.2776		2	
204	.3076	....	0.6	..
108	.3344	....	0.5	..
205	.3462	.3462	1	t
206	.3934	.3930	4	vvw
109	.4074	.4070	1	t
210	.4181	....	0.4	..
211	.4224	.4226	2	t
212	.4353	.4353	0.6	t
207	.4492	....	1	..
118	.4539	.4531	5	m
213	.4567		2	
214	.4867	.4878	0.6	vw
1,0,10	.4889		2.6	

[a] This list includes all planes up to $\sin^2\theta = 0.5$ for which the intensity was not calculated to be zero, by the symmetry of the special positions. [b] t, trace; vvw, very, very weak; vw, very weak; w, weak; m, moderate; ms, moderately strong; s, strong.

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RECEIVED FEBRUARY 27, 1956

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[1] This work was performed under the auspices of the AEC.

[2] E. F. Westrum, Jr., and L. Eyring, THIS JOURNAL, **73**, 3396 (1951).

[3] W. H. Zachariasen, *Acta Cryst.*, **5**, 660 (1952).

[4] E. G. Rauh and R. J. Thorn, *J. Chem. Phys.*, **22**, 1414 (1954).

[5] S. C. Carniglia and B. B. Cunningham, THIS JOURNAL, **77**, 1502 (1955).

SYNTHESIS OF FUSED-RING COMPOUNDS *VIA* ACYLATION OF KETONES

Sir:

A new method for synthesis of fused-ring compounds (II) has been found, which offers certain advantages over the well-known Pschorr,[1] Haworth,[2] Bardhan–SenGupta[3] and Bogert[4] procedures. The method consists of the reaction of cyclic ketones with phenylacetic anhydrides in the presence of boron trifluoride.[5] Acylation and cy-

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[1] R. Pschorr, *Ber.*, **29**, 496 (1896).

[2] R. D. Haworth, *J. Chem. Soc.*, 1125 (1932).

[3] J. C. Bardhan and S. C. SenGupta, *ibid.*, 2520 (1932).

[4] M. T. Bogert, *Science*, **77**, 289 (1933).

[5] C. R. Hauser, F. W. Swamer and J. T. Adams, in R. Adams, "Organic Reactions," Vol. 8, Chapter 3, pp. 59–196, J. Wiley and Sons, Inc., New York, N. Y., 1954.