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NOTE

This constitutes Chapters 1 through 10, inclusive, of the Survey Volume on Uranium Chemistry prepared for the Manhattan Project Technical Series. It is issued for purposes of review and criticism. It was decided in the Editorial Board meeting on June 11, 1946, that all comments must be communicated to the volume editors at the Argonne National Laboratory within one month after receiving this draft. The editors will appreciate prompt attention to expedite publication.

MD. 400.112. Gen
X. 416.2 Uranium

Date Circulated: 9/30/46

CLASSIFICATION CANCELLED
DATE FEB 12 1957 mcl
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Rabinowitch, E. I., and J. J. Katz (Argonne National Laboratory)

The Chemistry of Uranium (I); Manhattan Project Technical Series; Chapters 1 through 10.

xxxx Sept. 30, 1946. 336p.

Chapters entitled: Nuclear Properties of Uranium; Properties of the Uranium Atom; Uranium in Nature; Extraction of Uranium from Ores and Preparation of Uranium Metal; Physical Properties of Uranium Metal; Chemical Properties of Uranium Metal; Intermetallic Compounds and Alloy Systems of Uranium; The Uranium-Hydrogen System; Uranium Borides, Carbides, and Silicides; Uranium Nitrides, Phosphides, Arsenides, and Antimonides.

U7.63 Uranium - Properties; U9.0 UUranium Compounds; U7.55 Uranium - Ores;

2 X U7.04 Uranium - Alloys; U7.56 Uranium - Production; B25.85 Bibliographies.

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CHAPTER I

NUCLEAR PROPERTIES OF URANIUM

1. Isotopic Composition

2. Atomic Weight

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CHAPTER I

NUCLEAR PROPERTIES OF URANIUM

In its full sense a chapter on the nuclear properties of uranium should include all data on isotope separation, natural and artificial radioactivity, and fission. Therefore, in addition to other material, most of the work done on the Manhattan Project should be included. It is obviously impossible to present here even a short summary of all these subjects. Only a few fundamental data will therefore be given, particularly those pertaining to the isotopic composition and atomic weight of natural uranium.

1. Isotopic Composition

Natural uranium contains the three Isotopes U^{238} (UI), U^{234} (UII), and U^{235} ("actino-uranium," AcU). Several comparatively short-lived isotopes have been obtained artificially by various nuclear reactions involving Ac, Th, Pa, or stable U-isotopes as initial materials. The radioactive constants of the naturally occuring isotopes are given in Table 1.

TABLE 1

RADIOACTIVE CONSTANTS OF NATURAL URANIUM ISOTOPES

Mass Number	Radiation		Half-life (years)	Per cent in Natural Uranium
	Type	Energy (Mev)		
234 (UII)	α	4.75	2.69×10^5	0.006
235 (AcU)	α	4.31	$7\text{-}8 \times 10^{8*}$	0.7
238 (UI)	α	4.2	4.51×10^9	99.3

* See below page 7

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The isotopes U^{238} (UI) and U^{234} (UII) are members of a radioactive decay series, the so-called 4n + 2 series. $(UI \xrightarrow{\alpha} UX_1 \xrightarrow{\beta} UX_2 \xrightarrow{\beta} UII \xrightarrow{\alpha})$. They must therefore be present in a constant ratio equal to the ratio of their half-lives in all uranium sources in which radioactive equilibrium has been established.

According to Table 1, the equilibrium ratio of the isotopes UII and UI must be:

$$\frac{[U^{234}]}{[U^{238}]} = \frac{2.69 \times 10^5}{4.51 \times 10^9} = \frac{1}{16900} = 5.9 \times 10^{-5}$$

In other words, the percentage of U^{234} in natural uranium must be about 6×10^{-3} per cent. This is confirmed by mass spectograph analysis.

The result of the isotopic analysis of uranium by Nier (1939a) is illustrated by Fig. 1. The U^{234} peak is so low that only an approximate determination of the ratio $[U^{238}] : [U^{234}]$ is possible. A series of comparisons gave values between 13.0×10^3 and 18.4×10^3 with an average of 17,000 ± 10 per cent, which is in good agreement with the theoretical value. A new determination gave the same result and narrowed the limits of error:

$$[U^{235}] : [U^{234}] = 130 \pm 4, \text{ leading to } [U^{238}] : [U^{234}] = 17{,}000 \pm 3\%.$$

Actino-uranium, U^{235}, is not a member of the 4n + 2 series and its origin in natural uranium is open to speculation. Measurements show that its concentration is remarkably constant.

The first mass spectographic proof of the presence of U^{235} in natural uranium was given by Dempster, (1935), who estimated the concentration as less than 1 per cent. An exact determination was first made by Nier. (1939a). The following table shows the results obtained by Nier with different uranium minerals.

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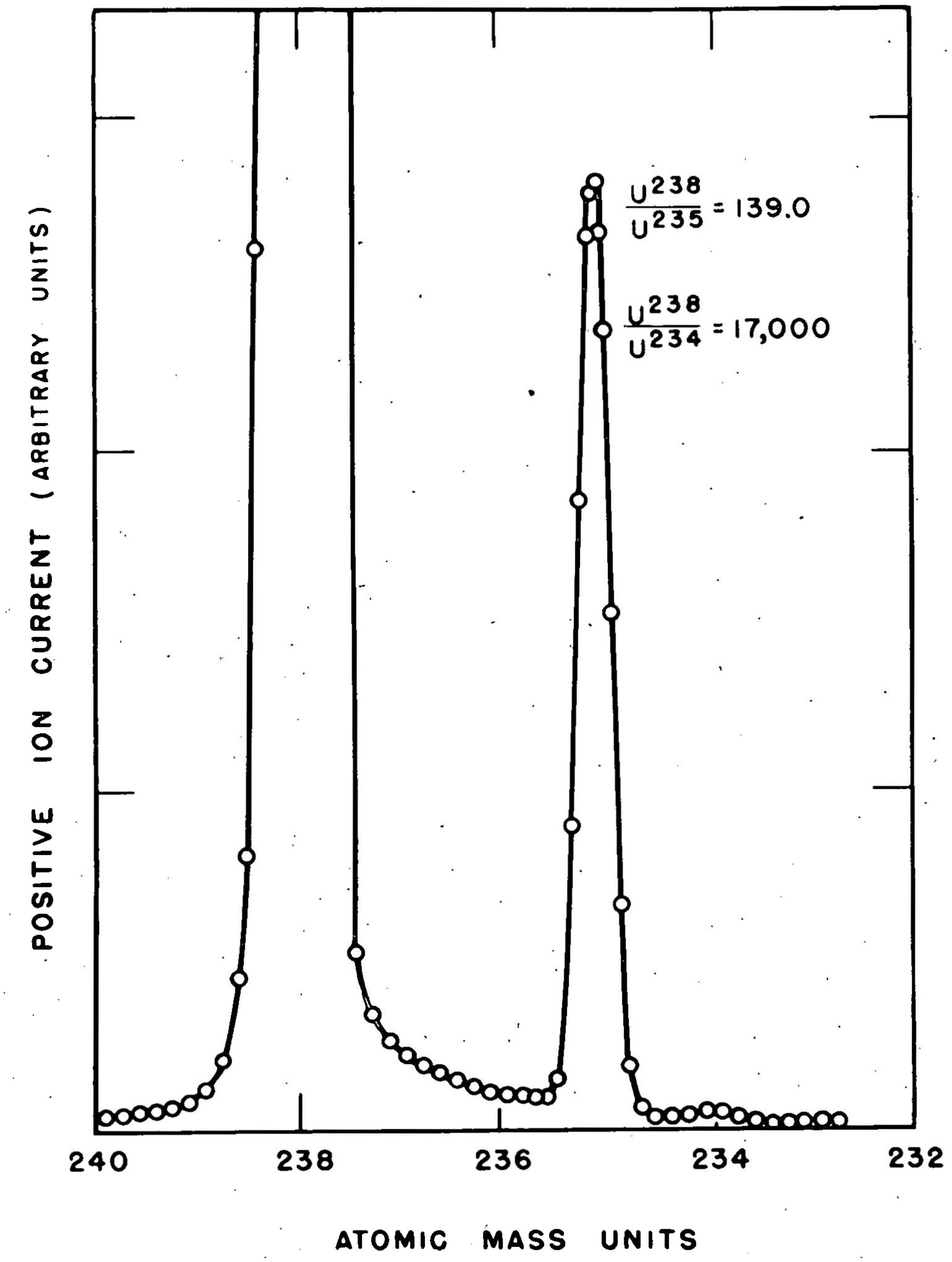

FIG. I. ISOTOPES OF URANIUM
(FROM A.O. NIER, PHYS. REV., 55, 151 (1939)).

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TABLE 2

ISOTOPIC RATIO $[U^{238}] : [U^{235}]$

Mineral	Age (years)	Ratio $[U^{238}] : [U^{235}]$ *	
		Limits	Average
Kolm (Sweden)	4×10^8	137.5 - 140.7	139.0
Uraninite (Ontario)	1.0×10^9	135.3 - 140.8	138.9
Dakeite	1×10^3	136.6 - 141.3	138.8

*Using UCl_4 and UBr_4 as ion sources.

Table 2 shows no noticeable effect of the age of the mineral. The ratio $[U^{238}] : [U^{235}]$ has been redetermined (SAM Columbia /). They used UF_5^+ and UF_6^+ ions from UF_6 in a standard source and U^+ ions in a surface ionization source. The results are shown in Table 3.

TABLE 3

ISOTOPIC RATIO $[U^{238}] : [U^{235}]$ DETERMINED WITH TWO DIFFERENT SOURCES

Source	$[U^{238}] : [U^{235}]$	
	Limits	Average
Standard	135.0 - 138.6	137.0 ± 0.7
Surface	137.9 - 139.0	138.0 ± 0.3

A cross check of two African ores, one Canadian ore, and a Colorado carnotite showed differences of no more than 0.03 per cent.

The values obtained with the two sources are barely reconcilable, if a ratio of 137.7 is assumed; this value is also just within the limits given by Nier (1939) ±1per cent. Perhaps an isotopic discrimination effect occurs in surface ionization due to different volatility of the two isotopes.

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The constant content of U^{235} in natural uranium minerals of varying age can be explained in two ways. One is to assume that U^{235} was present, in the natural isotope mixture as it existed at the time of formation of the "earth," in considerably large quantity relative to U^{238} than it is found now, and that its present concentration is in the nature of a residue from this initial "endowment." The other hypothesis is to assume that U^{235} has been formed (and may still be forming) from U^{238}, for example by the "pile reaction" $U^{238} + n \longrightarrow U^{239} \xrightarrow{2\beta} Pu^{239} \xrightarrow{\alpha} U^{235}$.

The first hypothesis can be checked by the determination of the ratio of urano-lead (RaG) and actino-lead (AcD) in uranium minerals of various age. This ratio is considerably higher than the present-day ratio of U^{235} to U^{238} (leading to a concentration of 5-10 per cent against 0.7 per cent) and increases with the age of the mineral. The values found by Nier (1939b) for minerals of age 2×10^8 years to 13×10^8 years could be fitted on a theoretical curve constructed with the values 0.046 for the present ratio of activities of the actinium series and the uranium series and 139 for the present ratio of concentrations of U^{238} and U^{235}. Using these constants Nier calculated the values which these ratios had in past geological periods:

TABLE 4

U^{238}/U^{235} RATIO IN THE PAST*

Years Ago	U^{238}/U^{235}	Activity of Ac-Series / Activity of U-Series
0×10^8	139.0	0.046
4×10^8	100.2	0.065
8×10^8	72.2	0.089
12×10^8	52.1	0.123
16×10^8	37.5	0.171
20×10^8	26.9	0.238

*After Nier, 1939.

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The values in the last column of Table 4 are not as large as the figures obtained in some earlier estimates, which were based on a higher value for the present ratio $U^{238} : U^{235}$ and a lower value for the relative activity of the actinium series. This indicates decrease in the importance of the actinium series in the thermal history of the earth.

In order to account as closely as possible for the $[Pb^{207}] / [Pb^{206}]$ ratios found by Nier in minerals of various age, he had to choose a value of 0.046 for the ratio of activities of the actinium series and the uranium series at the present time. (Fig. 2) Combining this figure with Nier's concentration ratio $[U^{235}] / [U^{238}] = 1/139$, and using a half-life of 4.51×10^9 years for U^{238}, one obtains for U^{235} a half-life of about 7×10^8 years. Direct measurements of the activity ratio, on the other hand, gave values close to 0.040, leading to a half-life of 8.1×10^5 years for U^{235}. As shown in Fig. 2, the observed values of the ratio $[Pb^{207}] / [Pb^{206}]$ are about 20 per cent higher than those calculated for an activity ratio of 0.040. The reason for this discrepancy, which can be interpreted either as an excess of actino-lead or as a deficiency of urano-lead, is as yet unclear. Nier's suggestion in 1939 was that the experimental value of the activity ratio might be too low.

In Table 1, $7 - 8 \times 10^8$ years was given for the half-life of U^{235} as the best estimate available in 1939. Since, on the whole, the results of the mass spectrograph analysis of U and Pb agree with the hypothesis of an initial U^{235} "endowment," the possibility of additional U^{235} formation during the life time of the earth remains an open question. This formation is inevitable whenever U^{238} atoms are exposed to neutrons; neutrons are always present in the earth from cosmic rays, spontaneous fission, and α, n reactions. There seems to be no reason why the U^{235}

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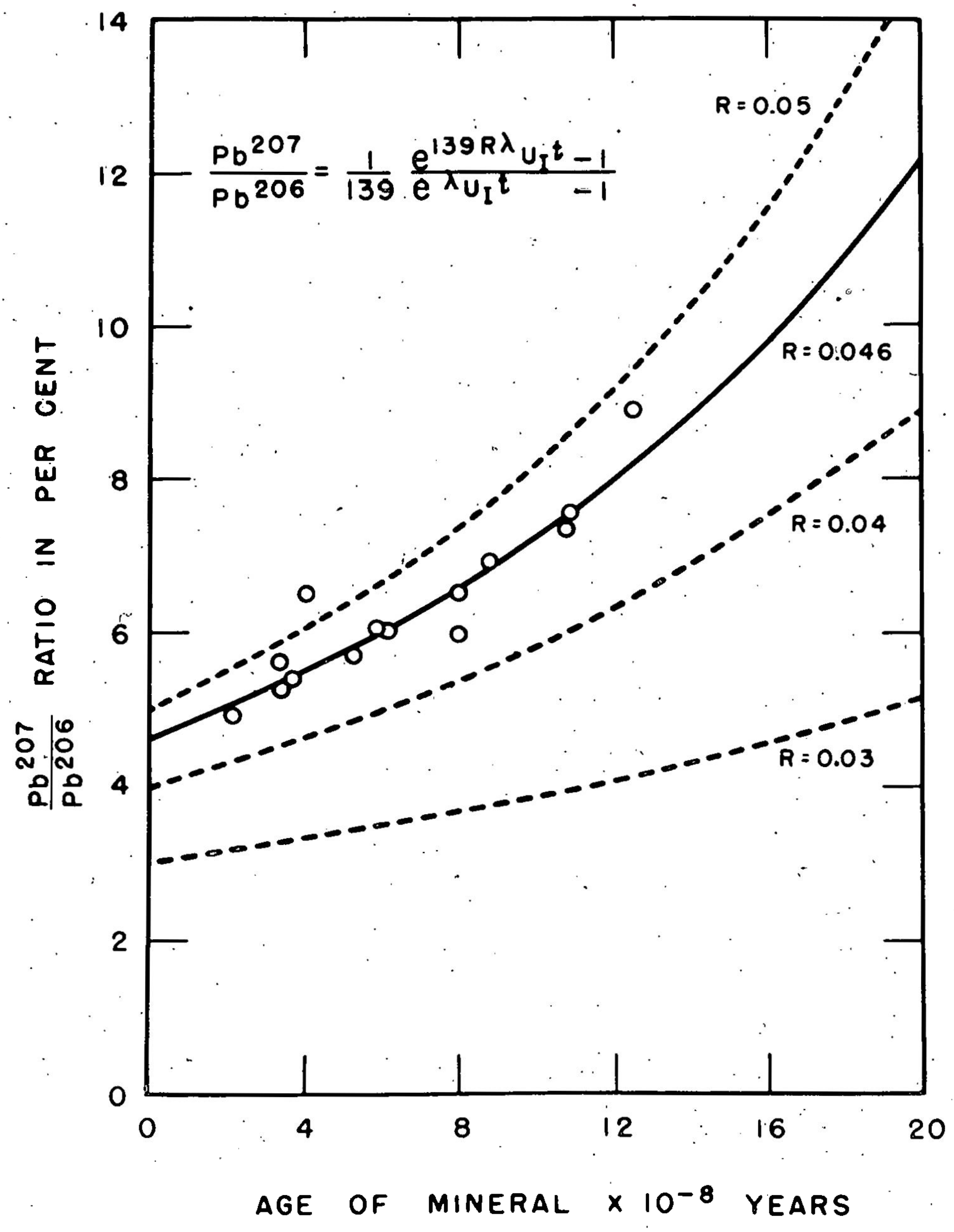

FIG. 2. Pb^{207}/Pb^{206} (CORRECTED FOR COMMON LEAD IMPURITIES) AS A FUNCTION OF THE AGE OF THE MINERAL FROM WHICH THE LEAD WAS EXTRACTED. THE CURVES ARE PLOTTED ACCORDING TO THE FORMULA IN THE DIAGRAM FOR VARIOUS ASSUMED VALUES OF R (THE RATIO OF ACTIVITIES OF THE ACTINIUM AND URANIUM SERIES). THE CIRCLES ARE EXPERIMENTALLY DETERMINED POINTS. (FROM A.O. NIER, PHYS. REV., 55, 157 (1939)).

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formation caused by these neutrons should be the same for uranium from various sources. Therefore, evidence of the production of U^{235} from U^{238} after the solidification of the earth's crust can be sought in small variations of the U^{235} content of various samples, rather than in the presence of an approximately constant amount of about 0.7 per cent in all of them.

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2. Atomic Weight

Precision measurements of the atomic weight of uranium have been carried out by Hönigschmidt and co-workers. These measurements were based on the determination of the ratios $UHal_4 : Ag$ and $UHal_4 : 4Ag\ Hal$, with Hal being either Br or Cl. The earlier determinations (Hönigschmidt 1915, 1916, 1928) gave for the atomic weight of uranium values between 238.13 and 238.18. A value of 238.14 was adopted as the most probable one by the International Committee for Atomic Weights in 1928. However, this value appeared too high in comparison with the independently known atomic weight of radium, and the newer determination of Hönigschmidt and Witner (1936) confirmed that it was erroneous. From eighteen determinations of the ratio $UCl_4 : 4\ Ag$ and twenty determinations of the ratio $UBr_4 : 4\ Ag$ (obtained by nephelometric titration), the two average values $U = 238.073$ and $U = 238.076$ were calculated, and a value of 238.07 was therefore generally adopted in 1936.

Since natural uranium contains 0.7 per cent U^{235}, an average atomic weight of 238.075 indicates that the atomic weight of the isotope U^{238} is 238.09_5. For the calculation of the packing fraction, this "chemical" atomic weight (related to natural oxygen = 16) must be multiplied by 1.000272 for conversion into "physical atomic weight," (related to $O^{16} = 16$). This leads to $U^{238}_{phys} = 238.16$ and gives for the packing fraction:

$$P = \frac{0.16}{238} = 0.00067.$$

Dempster (1938) constructed a curve of packing fractions based, in the region of high atomic weights, on the known energies of radioactive disintegrations and on the assumption that the packing fraction of Pb^{206} is 0.00023. This curve indicates a value of 0.00055 for U^{238} (see Fig. 3). Comparison of this value with the empirical value calculated above

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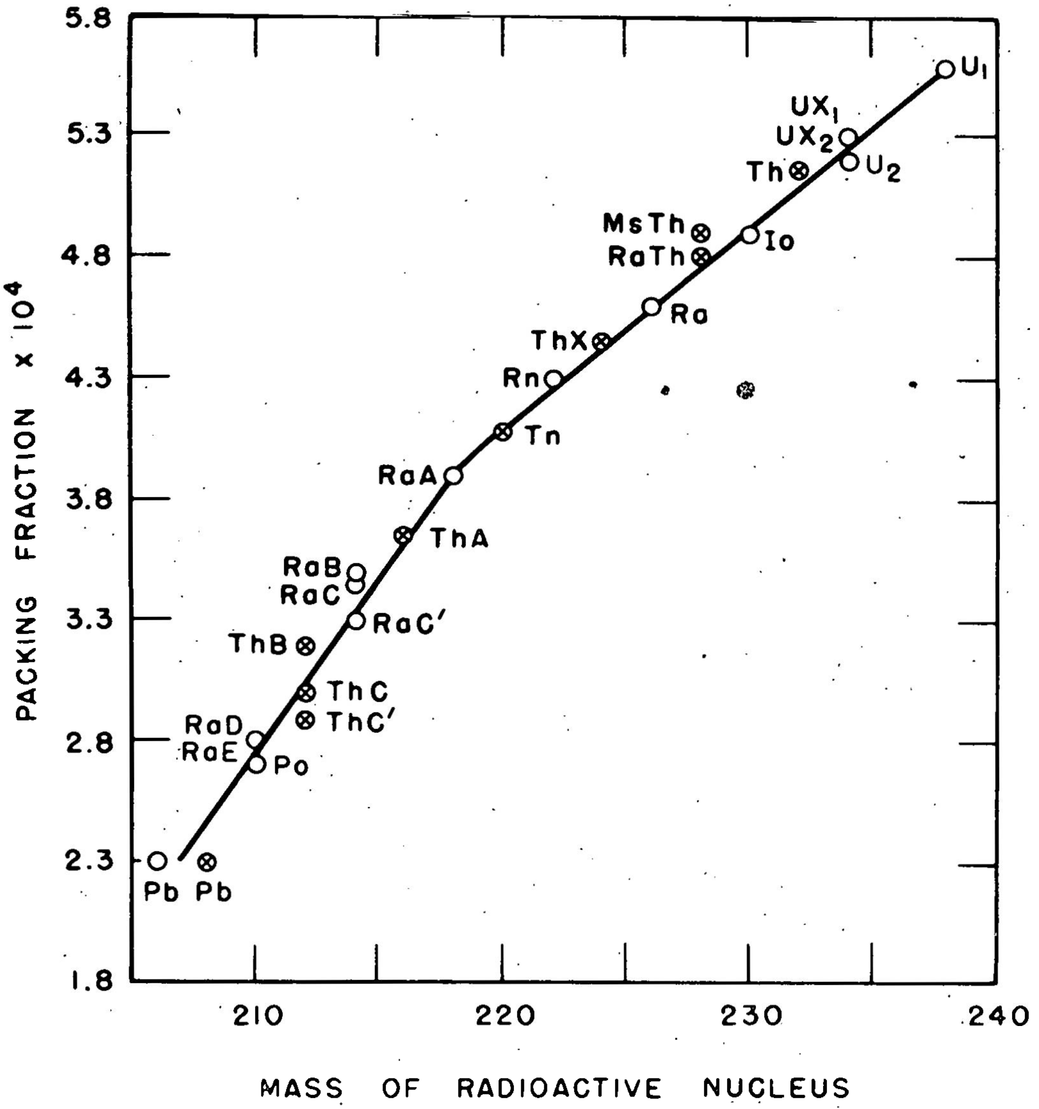

FIG. 3. THEORETICAL PACKING FRACTION CURVE FOR THE RADIO-ACTIVE ELEMENTS, COMPUTED FROM THE ENERGY OF DISINTEGRATION AND THE MASS OF HELIUM 4.0039, ASSUMING A VALUE FOR LEAD EQUAL TO 2.3 x 10^{-4}.
(FROM A.J. DEMPSTER, PHYS. REV., 53, 872(1938)).

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(0.00067) shows that the accepted atomic weight might still be somewhat high. Since the empirical P-value for Ra^{226} fits well on Dempster's curve, the experimental atomic weight of U^{238} is also somewhat high compared with that of Ra^{226}. Honigschmidt's latest determination of the atomic weight of radium gave $Ra^{226} = 226.05$. By adding the mass equivalents of the energies lost by radiation in the transportation of U^{238} into Ra^{226}, one obtains $U^{238}_{chem} = 238.07$; the corresponding packing fraction is

$$P_U = \frac{238.07 \times 1.00027 - 238}{238} = \frac{238.135}{238} = 0.00057.$$

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CHAPTER II

PROPERTIES OF THE URANIUM ATOM

1. X-Ray Spectrum
    1.1 Absorption
    1.2 Emission
    1.3 Photoelectric Effect
    1.4 Term System
2. Optical Spectrum
    2.1 Line Measurements
    2.2 Zeeman, Stark, and Pressure Effects
    2.3 Sensitive Lines
    2.4 Analysis of UI Spectrum
    2.5 Term Analysis of UII Spectrum
    2.6 Electron Configuration

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CHAPTER II

PROPERTIES OF THE URANIUM ATOM

1. X-Ray Spectrum

Uranium being one of the heaviest elements, has a most complex x-ray spectrum. The neutral uranium atom contains the fully occupied electron shells K (2 electrons), L (8 electrons), M (18 electrons), and N (32 electrons); and the partially occupied shells O (probably 21 electrons), P (probably 9 electrons) and Q (2 electrons). The distribution of the six outermost electrons between the groups 5f (O_{VI-VII}), 6d (P_{IV-V}) and 7s (Q_{I}) is not yet definitely known. These six electrons are the valence electrons of uranium and their excitation produces the optical spectrum. The other 86 electrons are "inner electrons" and their excitation produces the x-ray spectrum, which should thus contain the series K, L, M, N, O, and P. However, lines belonging to the last two "ultra-soft" series have not yet been observed.

1.1 Absorption. Table 1 gives a summary of the most recent measurements of the wave length of the absorption edges of uranium, made partly with uranium metal power and partly with uranium oxide as absorber. No effect of chemical binding has been noted.

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TABLE 1

ABSORPTION EDGES OF URANIUM

Designation	Position of the Edge		Width	Reference
	X.U.	ν/R	(X.U.)	
K_I	106.58	8550	--	Mack and Cook (1927)
L_I	568.0	1604.3	4.5	Sandström (1930)
	568.2	1603.7	--	Cauchois and Menescu (1940)
L_{II}	591.3	1541.0	4.3	Sandström (1930)
	590.7	1539.5		
L_{III}	720.8	1264.2	4.2	Sandström (1930)
	720.7	1264.3		Cauchois and Menescu (1940)
M_I	2228	408.9	--	Coster (1921a, 1922a,b)
M_{II}	2385	382.1	--	
M_{III}	2873	317.18	--	Stenström (1919)
	2877	316.7	--	Lindberg (1929)
M_{IV}	3326	273.99	--	Stenström (1919)
	3327	273.9	--	Lindberg (1929)
	3326	273.99	9*	Polaczek (1939)
M_V	3491	261.03	--	Stenström (1919)
	3491	261.03	--	Lindberg (1929)
	3491	261.03	13**	Polaczek (1939)

*3322-3331 X.U.

**3487-3500 X.U.

Earlier measurements of the absorption edges were carried out by Duane and co-workers (1920a,b,c: 1921), Siegbahn (1919), de Broglie (1916 a,b; 1919), Stoner and Martin (1925), and Dauvillier (1927).

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The fine structure of the absorption edges, which depends on chemical combination and the investigation of which is a means of analysis of the valence electron bands in crystals, has not yet been closely studied in the case of uranium. Dauvillier (1921a) reported the presence of a "white line" in the L_{III} edge; Cauchois and Menescu (1940) saw a similar line in both the L_{III} and the L_{II} edge of uranium metal (at 720.4 and 590.4 X.U. respectively); no white line was noticeable in the L_I edge. Polaczek (1939) could see no fine structure in the M_{IV} and M_V edges of uranium oxide.

The absorption coefficients of uranium for monochromatic x-rays of different wave lengths were measured by Stoner and Martin (1925) in the region of the L-absorption edges, and by Allen (1926) in the regions of the K-and M-absorption edges. Table 2 gives the results.

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TABLE 2

MASS ABSORPTION COEFFICIENT (μ/ρ)

OF URANIUM METAL FOR X-RAYS

λ (X.U.)	μ/ρ (cm^2/g)*	λ (X.U.)	μ/ρ (cm^2/g)***
64	1.80	108_0	150
72	2.25	124_0	190
98	3.90	145_0	285
107.5	4.65 K-edge	154_0	360
107.5	1.62	180_0	442
130	2.10	193_0	470
175	3.95	197_0	485
200	5.40	206_0	495
		218_0	516 M_I edge
λ (X.U.)	μ/ρ (relative units)**	224_0	525
		235_0	540 M_{II} edge
400	0.34	249_0	560
450	0.45	260_0	570 M_{III} edge
500	0.59	297_0	600
550	0.77 $L_{I,II}$ edges	304_0	600
600	0.64	318_0	600
631	0.73	322_0	600 M_{IV} edge
708	1.00 L_{III} edge	337_0	580
750	0.48	344_0	564 M_V edge
800	0.56	366_0	410
		374_0	424
		393_0	490

* Allen, after Compton and Allison (1935a). ** Stoner and Martin (1925). *** Allen (1926).

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The absorption coefficient increases by a factor of 2.9 at the K-edge (Allen, in Compton and Allison, 1935) and by an over-all factor of 3.52 at the three L-edges (Stoner and Martin, 1925; Küstner, 1932). Küstner gave the factors 1.11, 1.31, and 2.17 for the absorption increase at the three individual edges L_I, L_{II}, and L_{III}. Stephenson (1933) gave 2.27 for the absorption jump at the edge L_{III}, and Polaczek (1939) gave 2.4 for that at the edge M_V.

According to Allen (1926) the absorption coefficient of uranium is proportional to λ 2.92 in the N-region and λ 2.6 in the M-region.

1.2 Emission. Lines belonging to the four series K, L, M, N have been measured in the x-ray spectrum of uranium. Fig. 1 shows the interpretation of the most important lines of the first three series, according to Siegbahn (1931). Tables 3 to 8 contain the wave lengths of all the measured lines.

(a) K-Series.

TABLE 3

K – LINES OF URANIUM

Combination	Line Designation	Wave Length (X.U.)	Reference
$K_I L_{II}$	2	130.95	Rechou (1925)
L_{III}	1	126.40	
$M_{II,III}$	1,3	111.87	
$N_{II,III}$	2	108.42	

(b) L-Series.

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TABLE 4

L-LINES OF URANIUM

Term Combination	Line Designation	Wave Length (X.U.) after: Schror (1926)	Friman (1926)	Idei (1930)	Claesson (1936)	Relative Intensity after: Allison (1928, 1935)	Allison and Andrews (1931)	Stephenson (1933)	H Wi af Wil (1
L_IM_{II}	β_4	--	--	764.4	746.39	4.1; (3.2)	--	--	0.
M_{III}	β_3	--	--	708.79	708.81	4.2; (3.3)	--	--	0.
M_{IV}*	β_{10}	--	--	685.3	686.15	--	--	--	--
M_V*	β_9	--	--	679.5	679.6	--	--	--	--
N_{II}	γ_2	--	--	603.9	603.99	1.5; (1.1)	--	--	0.
N_{III}	γ_3	--	--	597.1	597.30	1.4; (1.1)	--	--	0.
N_{IV}*		--	--	--	569.7_7	--	--	--	--
N_V*		--	--	--	568.6_5	--	--	--	--
O_{II}	γ_4^1	--	--	575.3	575.45	0; (0)	--	--	--
O_{III}	γ_4	--	--	573.6	573.90	(0)	--	--	--
$O_{IV,V}$*		--	--	--	571.3	--	--	--	--
$P_{II,III}$	γ_{13}	--	--	568.9	569.4_1	--	--	--	--
$L_{II}M_I$	η	--	--	803.5	803.59	1.0 (0.83)	--	--	--
M_{III}*	β_{17}	--	--	--	743.4_7	--	--	--	--
M_{IV}	β_1	718.55	718.51	--	718.54	49.4; (40.5)	50.7	--	0.
N_I	γ_5	--	--	634.2	634.23	0	--	--	--
N_{III}		--	--		621.54	--	--	--	--
N_{IV}	γ_1	613.32	613.59	--	613.50	12; (9.7)	19.9	--	0.2

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TABLE 4 (Continued)

Term Combination	Line Designation	Wave Length (X.U.) After: Schrör (1926)	Friman (1926)	Idei (1930)	Claesson (1936)	Relative Intensity after: Allison (1928; 1935)	Allison and Andrews (1931)	Stephenson (1933)	Half-Width after Williams (1931
N_{VI}		--	--	--	601.9_3	--	--	--	--
O_I	γ8	--	--	599.7	600.00	--	--	--	--
D_{III}*		--	--	--	596.0_4	--	--	--	--
O_{IV}	γ6	--	--	593.4	593.61 592.8	2.2 (1.8)	--	--	0.233
$P_{II,III}$*		--	--	--	591.9	--	--	--	--
$P_{IV,V}$		--	--	--	590.8_1	--	--	--	--
$L_{III}M_I$	l	--	--	1064.77	1064.89	2.4 (2.4)	--	--	--
M_{II}*	t	--	--	1032.9	1032.5_4	--	--	--	--
M_{III}*	s	--	--	961.4	961.8_0	--	--	--	--
M_{IV}	α2	920.65	--	920.62	920.56	11.0 (11.0)		8.73	0.494
M_V	α1	908.91	908.7	--	908.69	10.0 (10.0)	100		0.439
N_I	β6	--	--	786.8	786.78	1.6 (1.6)	--	--	--
N_{II}*		--	--	--	778.4_8	--	--	--	--
N_{III}*		--	--	--	767.3_8	--	--	--	--
N_{IV}*	β15	--	--	755.1	755.10	--	--	--	--
N_V	β2	753.23	753.07	--	753.14	28 (28)	--	1.00	0.369
$N_{VI,VII}$*	β7	--	--	737.3	737.07	6	--	--	--
O_I	β7	--	--	734.6	734.64	0.4 (0.4)	--	--	--
O_{II}*		--	--	--	731.74	--	--	--	--
O_{III}*		--	--	--	729.3_6	--	--	--	--
$O_{IV,V}$	β5	--	--	724.85	724.84	6.4 (6.4)	--	--	0.252
P_I ××	--	--	--	--	723.7_1	--	--	--	--

[redacted]

TABLE 4 (Continued)

$P_{II,III}$	--	--	--	722.7_5	--	--	--	--
$P_{IV,V}$‡ †	--	--	--	720.9_0	--	---	--	--

* These are "forbidden" (quadrupole) lines ($\Delta l \neq 1$); they are not shown in Figure 1.

† See also Allison (1929) who gave $\Delta\lambda$ = 1.86 X.U. for the separation $\beta_2 - \beta_{15}$, and 11:1 for the intensity ratio of these two lines.

‡ The $P_{IV,V}$ electrons are valence electrons; the interpretation of the line 720.9_0 is thus uncertain (since conductance niveaus, as well as the terms $O_{VI,VII}$ and Q_1, may also be involved).

§ These values were corrected by extrapolation to infinite exciting voltage; the actual values measured at 52.8 kv are in parentheses.

γ Line found by Cauchois and Allais (1940).

γγ Interpretation by Hulubei (1937).

∘ Fluorescence Spectrum.

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In addition to the "diagram lines" listed in Table 4, several satellites have been observed, which are usually interpreted as "spark lines" (transitions following double ionization).

TABLE 5

SATELLITES IN THE L-SERIES OF URANIUM

Designation	Wave Length Idei (1930)	(X.U.) after: Richtmyer and Kaufman (1933)	Claëssen (1936)
α_3	905.5	905.35 (α^{IX})	905.45
β_2'	750.0	749.92	749.89
β_2''	748.9	748.93	748.93
--	--	--	723.71
μ	601.5	--	--

Earlier measurements of the L-emission lines were made by Coster (1921a,b; 1922a), Dauvillier and co-workers (1921 b,c; 1923) Siegbahn and Friman (1916 a,b,c) and summarized by Duane (1920c; 1922).

The width of L-emission lines of uranium was measured by Williams (1931). The results are shown in the last column of Table 4.

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29 a

(c) M-Series. The M-Series is not as well known as the L-series. The best available data are collected in Table 6.

TABLE 6

M-LINES OF URANIUM

Term Combination	Line Designation	Wave Length (X.U.) after: Hjalmar (1923)	Lindberg (1928,1931)	Purdom and Cork*(1933)	Hirsch (1931)
$M_I N_{II}$	--	2909	--	--	--
N_{III}	--	2750	2745	--	--
O_{III}	--	2299	--	--	--
P_{III}	--	2248	--	--	--
$M_{II} N_I$	--	3321	3322	--	--
N_{IV}	--	2815	2813	--	--
O_{IV}	--	2439	2440	--	--
$M_{III} N_I$	--	--	4322	--	--
N_{IV}	--	--	3514	--	--
N_V	--	3472	3473	--	--
O_I	--	3107	3114	--	--
$O_{IV,V}$	--	2927	2941	--	--
$M_{IV} N_{VI}$	--	--	5040	--	--
N_{III}	--	--	4615		--
$N_{VI,VII}$		3709	3708	3708.0	3708.0
$O_{II,III}$	--	3570	3570	--	--
$M_V N_{III}$	--	--	4937	--	--
N_{VI}	2	3913	3916	3916	3914.6
N_{VII}	1	3901	3902	3902	3901.0
P_{III}	--	3514	--	--	--

*Glass grating

30 A

Earlier wave length determinations by Hjalmar (1923) and Stenström (1918) were summarized by Duane (1920c,1922).

Satellites (sparklines) were measured in the M-series by Lindberg (1928, 1931) and Hirsch (1931).

TABLE 7

SATELLITES IN THE M-SERIES OF URANIUM

Designation	Wave Length (X.U.)	Reference
α'	3886	Lindberg (1928,1931)
β'	3698	
γ'	3463	
α I	3892.2	Hirsch (1931)
α II	3884.3	
α IV	3869.0	
β I	3701.1	
β II	3693.3	
β III	3683.1	
α''	3885	Hjalmar (1923)
β'	3684	
β''	3696	
β'''	3700	
γ'	3459	
γ''	3466	

Parratt (1932) has used six uranium M-lines in the measurement of half-width of lines reflected by a calcite crystal.

N-Series. The available measurements of Hjalmar (1923) and Dolejšek (1924) are rather uncertain, and the interpretations of the two investigators disagree in several cases. Siegbahn and Magnusson (1934) measured several "ultra-soft" lines in the region $\gg$ 30A.

TABLE.8

N-LINES OF URANIUM

Term Combination after Dolejsek (Hjalmar's interpretation in parentheses	Wave Length (X.U.) after:		
	Hjalmar (1923)	Dolejšek (1924)	Siegbahn and Magnusson(1934)
N_IO_{II} ($N_{II}O_{IV}$)	10385	--	--
O_{III}(N_IO_{III})	9619	9873	--
P_{II} (N_IP_{III})	8691	8704	--
P_{III}	--	8605	--
$N_{II}O_I$	--	1285_0	--
O_{IV}	--	1008_0	--
O_V ($N_{III}O_V$)	12874	--	--
$N_{III}O_V$	--	1270_0	--
P_I ($N_{III}P_2$)	12250	--	--
$N_{IV}N_{VI}$	--	--	3178_0
$N_VN_{VI,VII}$	--	--	3481_0
$N_{VI}O_{IV}$	--	--	4208_0
$N_{VII}O_V$	--	--	
$N_{VI}O_V$	--	--	4328_0

32.2

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(e) Fluorescence. The fluorescence emission of L- and M-lines in the uranium x-ray spectrum was studied by Stephenson (1933) and Hevesy and Lay (1934a, b). Stephenson found, for absorption in the L_{III}-niveau, a value of 0.67 for the yield of fluorescence. The ratio of intensities of the lines $L_{\alpha 1,2}$ and $L_{\beta 2}$ in fluorescence was 3.73 in agreement with the value found for the characteristic emission spectrum. Hevesy and Lay (1934 a, b) found a lower yield of fluorescence (0.45 in the L_{III} niveau and 0.06 in the M-niveaus).

1.3 Photoelectric Effect The electron emission from uranium under x-ray irradiation was observed by deBroglie (1922) and by Robinson (1925). Robinson analyzed magnetically the electrons emitted by uranium oxide irradiated by CuK radiation. He found ten electron groups attributable to the photoelectric effect in various electron groups of uranium:

TABLE 9

PHOTOELECTRIC EMISSION OF U-OXIDE IRRADIATED WITH Cu Kα X-RAYS*

Group	Intensity (1-6 scale)	Electron Energy (ν/R)	Energy Loss ($592.8-\nu/R$)	Corresponding X-term	
1	3	276.9	315.9	M_{IV}	317
2	4	318.8	274.0	M_{IV}	274
3	5	332.4	260.4	M_V	261
4	2	486.8	106.0	N_I	106
5	3	500.3	92.5	N_{II}	93
6	5	517.3	75.5	N_{III}	76
7	6	540.4	52.4	$N_{IV,V}$	57, 54
8	2-3	555.8	37.0	Oxygen K ?	
9	3	566.8	26.0	$N_{VI,VII}O_I$	27
10	2	577.1	15.7	$O_{II,III}$	18,15
11	2-3	589.9	2.9	$O_{IV,V}P$	7-2

*Energy $h\nu/R$ = 592.8

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1.4 Term System. Since the x-ray absorption edges are not sharp, the usual way of calculating x-ray terms consists of selecting one or a few precisely known absorption edges and combining them with the much more sharply defined frequencies of the emission lines. Values obtained in this way by Bohr and Coster (1923), Dolejsek (1924), Lindberg (1931), Siegbahn (1931a), Claësson (1936), and Cauchois (1940) are listed in Table 10. The basic values taken from absorption measurements are framed. Those taken from previous investigations and used as a basis for new calculations are bracketed. The two last columns contain term values calculated by Monk and Allison (MP Chicago 1) from general term equations, using the screening constants shown in Table 11, and the term values in electron volts derived by Ruark and Maxfield (1935) from a combination of x-ray line frequencies with optical term values. What optical values have been used in the case of uranium is not clear. The K-term in the last column is calculated from the absorption edge, since in this case the discrepancy between the result of direct absorption measurements ($\nu/R = 8550$, Table 1) and the value calculated from the L-edge and the K-emission lines ($\nu/R = 8477$) may be attributed to errors in the K-line measurements.

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TABLE 10

X-TERMS OF URANIUM +

Term	Missing Electron	Quantum Numbers of the Hole			Term Values (ν/R)						Theoretical Values by Monk and Allison, (MP Chicago 1)	Electron Volts (from Optical Terms and X-lines Ruark (1935)
					Calculated from X-ray Absorption Limits and Emission Line Frequencies by:							
		n	l	j	Bohr and Coster (1923)	Dolejsek (1924)	Lindberg (1931)	Siegbahn (1931a)	Claesson (1936)	Cauchois (1940)		
K	1s	1	0	½	8477.0	--	--	8474	--	--	8490	115790
L_I	2s	2	0	½	1603.5	--	--	1602.6	--	--	1596	21721
L_{II}	2p		1	½	1543.7	--	--	1542.7	--	1542.73	1535	20900
L_{III}				3/2	1264.3	--	--	1264.2	1264.2	1264.32	1264	17128
M_I	3s	3	0	½	408.9	--	--	408.5	408.7; 408.5	--	408.5	5537
M_{II}	3p		1	½	382.1	--	--	381.5	381.7; 381.6	--	379.5	5172
M_{III}				3/2	317.2	--	216.7	316.8	317.0 317.0	--	317.5	4296
M_{IV}	3d		2	3/2	274.0	--	273.9	274.2	274.5; 274.3	--	273.9	3721
M_V				5/2	261.0	--	261.0	261.2	261.7; 261.4	--	260.4	3546
N_I	4s	4	0	½	106.6	107.1	105.8	106.0	105.9; 106.0	--	--	1439
N_{II}	4p		1	½	95.7	96.0	93.1	93.5	93.8; 93.6	--	--	1271
N_{III}				3/2	77.1	77.4	76.4	76.6	76.9 76.6	--	--	1042
N_{IV}	4d		2	3/2	56.3	--	57.3	57.5	57.5; 57.3	--	--	783
N_V				5/2	53.6	--	54.2	54.3	54.5; 54.2	--	--	739
N_{VI}	4f		3	5/2	28.4	--	28.1	28.5	28.8; 28.9			391
N_{VII}				7/2	27.6	--	27.4	27.8	--; 27.9	--	--	382

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▨ Largely based on the values of Idei (1930).

* 7.6 from γ_6, 7.0 β_5; probably one value corresponds to O_{IV} and one to O_V.

∅ Although all $P_{II,III}$ lines are weak, the term value is definitely >2.

⊕ Line interpretation as $L_{II}P_{IV,V}$ and $L_{III}P_{IV,V}$ uncertain.

† The table given by Russell (Los Alamos 1) is a combination of Siegbahn's values for the K- and L-terms, with Claesson's values for the M-, N-, O and P-terms, with the addition of Cauchois' value for the P_I-term.

TABLE 11

SCREENING CONSTANTS OF URANIUM*

Term	L_I	$L_{II,III}$	M_I	$M_{II,III}$	$M_{IV,V}$
σ_2	2.0	3.49	6.8	8.5	13.0
σ_1	21.4	22.4	38.9	40.7	44.2

* After Monk and Allison (MP Chicago 1).

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Russell (Los Alamos 1) tried to use the term values given in Table 10 to find out which valence electron group, $P_{IV,V}$ or $O_{VI,VII}$, has the lower energy; in other words, whether the 6d or the 5f electron group is filled first in the uranium atom. He saw two arguments in favor of the assumption that in elements beyond thorium, the 5f electrons are bound stronger than the 6d electrons. In the first place, the term separation $O_I - O_{II}$(5s-5p) is only slightly larger in uranium than in thorium ($\Delta(\nu/R) = 4.9$ for Th and 5.0 for U). In the preceding period of the periodic system, the increase in the separation $N_I - N_{II}$ (4s - 4p) is somewhat larger and approximately constant (about 2 ν/R units per element) in the series Hf to Pt (where the 5d group is filled in), and is near zero and changing irregularly in the rare earth series, where the 4f group is completed. The inference is that the Th to U elements resemble the rare earth series more than the Hf to Pt sequence of elements. However, the data presented are quite insufficient to make this conclusion convincing.

The second argument is slightly better. Table 10 shows that the M_{IV} and M_V absorption edges (273.9 and 261.0) are smaller by about 0.5 ν/R units than the M_{IV} and M_V terms calculated from the L_{III} limit and the L-emission lines (274.5 and 261.6). The interpretation of this difference suggested by Russel is that the absorption in both the L_{III} and the $M_{IV,V}$ levels leads to electron transfer into the incomplete valence groups, rather than to complete ionization. According to the l-selection rule, $\Delta l = \pm 1$, L_{III} (2p) electrons ($l = 1$) can be transferred into the $P_{IV,V}$ valence group (6d, $l = 2$), while the $M_{IV,V}$ electrons (3d electrons, $l = 2$) can be transferred only into the valence group $O_{VI,VII}$ (group 5f, $l = 3$).

If electrons in the latter group are bound more strongly (by about 5 electron volts) than those in the 6d group, the absorption in the $M_{IV,V}$ group must require less energy than that calculated from the difference between the absorption energy in the L_{III} group and the energy of the $L_{III} M_{IV,V}$

emission line. Thus the above-mentioned difference between the calculated and the observed $M_{IV,V}$ term value can be explained.

However, even if this difference appears to be beyond the limits of experimental error, its interpretation is by no means certain. An analysis of the electron levels of a crystal, particularly a metallic crystal, on the basis of the electronic states of free atoms cannot carry much weight, because of the well-known transformation of these levels into "conductance bands" which belong to the crystal as a whole rather than to individual atoms.

It may be noted that the width of the M-absorption edges (Table 1) is such that the discrepancy between the calculated and the observed M_{IV} and M_V terms practically disappears if the term value is determined from the wave length at which the absorption reaches its maximum rather than from that at which the absorption begins to increase, or from the center of the edge. (See Polaczek, 1939).

The possibility of a measurable effect of nuclear spin on the x-ray terms of the heaviest elements was suggested by Breit (1930) who calculated that if uranium had a nuclear spin of 9/2 units, its K-level should be split into two components with a separation of 22.5 ev and its L_{II} level into components with a separation of 4 ev. Williams (1931) remarked that the natural breadth of the L_I line of uranium is much too large to reveal a splitting of this order of magnitude. The atom U_{238} whose atomic number and atomic weight both are even, probably has no nuclear magnetic moment; but the odd atomic weight nucleus U_{235} has a moment and possesses hyperfine structure, which has been resolved in some optical lines (p.   ) and may become apparent also in the x-ray spectrum.

Figures 1 and 2, taken from Siegbahn's monograph, show a scheme of the uranium terms and lines, on an arbitrary uniform scale in the first figure, and on the correct logarithmic scale in the second figure.

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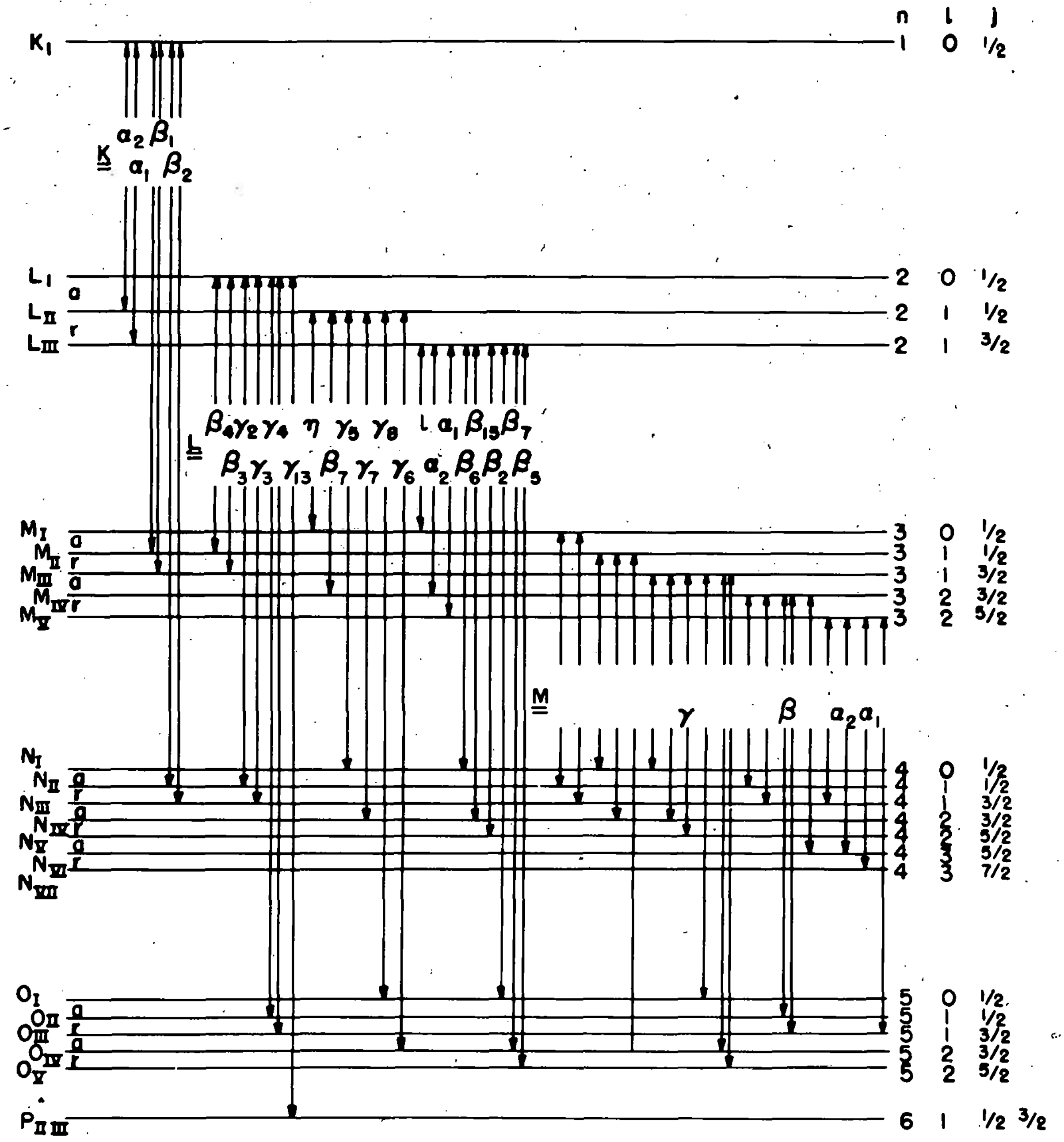

FIG. I. X-RAY TERM DIAGRAM OF URANIUM
(AFTER SIEGBAHN)

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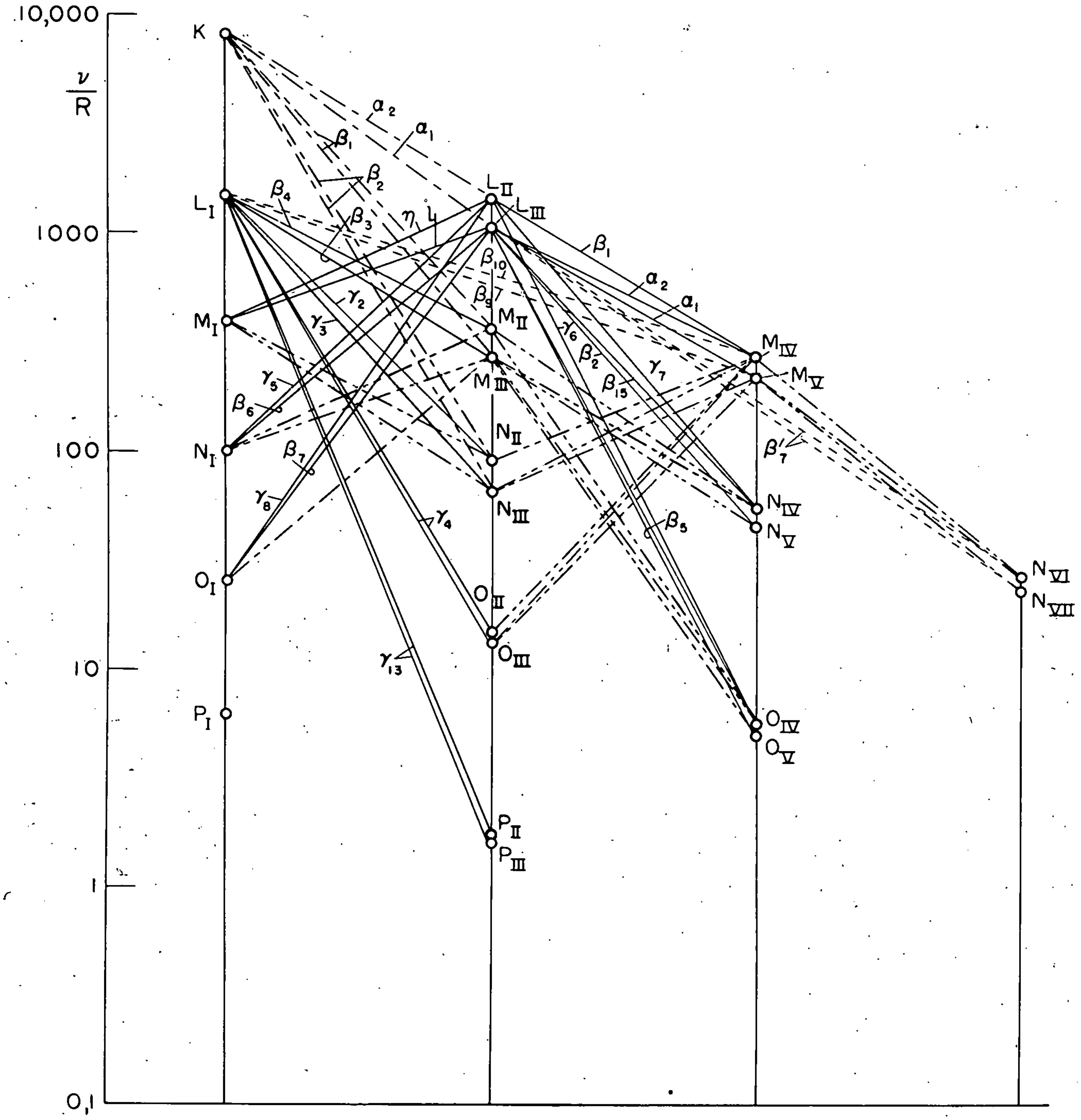

FIG. 2. X-RAY SPECTRUM OF URANIUM (AFTER SIEGBAHN). ORDINATES ARE PROPORTIONAL TO LOGARITHMS OF ENERGY LEVELS.

2. Optical Spectrum

2.1 Line Measurements. Table 11 shows the most important wave length measurements in the arc and spark spectra of uranium.

TABLE 11

WAVE LENGTH MEASUREMENTS IN URANIUM SPECTRUM

Observers	Wave Length Range	Number of Lines Measured
	Arc Spectrum	
Eder and Valenta (1910)	4642 - 7130	~600
Hasselberg (1910)	3583 - 5871	2200
Exner and Haschek (1911)	2264 - 6827	4960
Meissner (1916)	8223 - 8758	17
Kiess and Meggers (1921)	5500 - 9530	674
Harrison and co-workers (1939)	2000 - 10000	--
Kiess and co-workers (Nat. Bur. Standards 1)	3000 - 9000	7600
	Spark Spectrum	
Exner and Haschek (1911)	2195 - 6449	5632
Lang (1924)	374 - 2009	93
Harrison and co-workers (1939)	2000 - 10,000	--

Reproductions of the uranium arc and spark spectra are found in Eder and Valenta's atlas (1924).

A hyperfine structure, indicating a nuclear spin of 9/2, has been observed in British measurements (British 1) in the spectrum of the isotope U^{235}.

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2.2 Zeeman Effect. Stark Effect. Pressure Effect. The first measurements of the Zeeman effect of uranium spark-lines were made by Ross (1910). The MIT Spectroscopic Laboratory (MIT-1) has described Zeeman patterns for the lines 6876.75*; 5915.398, 5315.279, 5234.164, 5027.398, 4965.375, 4955.775, 4933.063, 4910.339, 4856.675*, 4393.598,* 3620.085*, 3566.598,* 3500.077*, 3439.434*, 3418.39*, 3400.467*, 3175.358*, and 2609.258A. The lines marked by asterisks may possibly be UII lines; the others belong to the UI spectrum.

Kiess and co-workers (Nat. Bur. Standards 1) have determined the Zeeman patterns of several thousand lines of the UI spectrum, but the results are not yet published.

The Stark effect of some uranium arc-lines was measured by Nagaoka and Sugiura (1924); the pressure shift by Humphreys (1897).

2.3 Sensitive Lines. Several tables of the most persistent uranium lines have been given.

TABLE 12

PERSISTENT LINES OF URANIUM

(A)	Hartley and Moss (1912	Meyer and Greulich (1921) (Spark)	Harrison 1939			Kiess (Nat.Bur. Standards 1)	Fred (MP Chicago 2)
			Arc Int.	Spark Int.*	Int.	Order of Appearance	Order of Appearance
3019	X	--	--	--	--	--	--
3090	X	--	--	--	--	--	--
3102	X	--	--	--	--	--	--
3552.172	--	--	8	12	--	--	--
3672.579	--	--	8	15	--	--	--
3859.58	--	--	--	--	--	--	(5)
3932.02	--	--	--	--	--	--	(1)
3966.57	--	--	--	--	--	--	(4)
4090.14	--	X	--	--	--	--	(2)
4241.669	--	--	40	50	--	--	--
4341.69	--	--	--	--	--	--	(3)
4620.22	--	--	--	--	600	(5)	--
5027.38	--	--	--	--	400	(4)	--
5915.40	--	--	--	--	500	(1)	--
5919.61	--	X	--	--	--	--	--
6395.42	--	--	--	--	200	(3)	--
6449.10	--	--	--	--	300	(2)	--

45e

2.4 Analysis of the UI Spectrum. Only preliminary reports are available on the analysis of the UI spectrum at the National Bureau of Standards (Nat.Bur.Standards 1,2). They give a list of low odd levels, which correspond to the valence electron configurations $5f^36d7s^2$ (155 terms, 377 components) and $5f^36d^27s$ (1122 terms). The terms shown in Table 13 have been given tentative designations on the basis of g-values derived from Zeeman patterns. They include the stable and the most important low metastable terms of the free uranium atom.

A second list, Table 13, gives a series of even terms which correspond to the valence electron configurations f^3dps, f^3ps^2 and f^3d^2p. About 300 term components have been determined so far and identified by arbitrary numbers with the addition of the quantum number J determined from combination rules.

TABLE 13 A

LOW ODD TERMS OF UI

Term	Value (cm^{-1})	Term	Value (cm^{-1})	Term	Value (cm^{-1})
$^5L_6$	0.0	$^7K_5$	5762.0	A_3	3868.4
$^5L_7$	3800.8	$^7K_6$	7005.5	B_3	7103.9
$^5L_8$	7645.6	$^7K_7$	10347.3		
$^5K_5$	620.3	$^7M_6$	6249.0	A_4	4453.4
$^5K_6$	4275.7	$^7M_7$	8118.6	B_4	5991.3
$^5K_7$	7326.1				
$^5K_8$	10685.7				

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TABLE 13 B

EVEN TERMS OF UI

Term Symbol*	Term Value (cm^{-1})
179(3)	17968.7
185(3)	18530.8
227(3)	22774.1
161(4)	16121.9
174(4)	17468.2
191(4)	19192.4
197(4)	19740.7
205(4)	20469.2
215(4)	21545.1
220(4)	22038.0
225(4)	22584.5
231(4)	23186.9
256(4)	25653.3
116(5)	11614.0
134(5)	13463.4
157(5)	15720.7
169(5)	16929.8
179(5)	17908.2
184(5)	18406.2
189(5)	18932.8
196(5)	19647.5
210(5)	21078.7
216(5)	21637.0
233(5)	23325.2
235(5)	23486.7
252(5)	25255.4
146(6)	14643.9
156(6)	15638.4
165(6)	16505.8
170(6)	17070.5
173(6)	17361.9
187(6)	18759.2
197(6)	19783.4
202(6)	20218.8
206(6)	25661.5
212(6)	21265.1
215(6)	21584.7
218(6)	21768.0
220(6)	22056.3
224(6)	22464.3
227(6)	22754.1
235(6)	23572.0
253(6)	25349.0
267(6)	26715.5
156(7)	15631.9
169(7)	16900.4
199(7)	19885.5
204(7)	20464.5
207(7)	20766.5
223(7)	22368.4
226(7)	22633.2
229(7)	22918.6
231(7)	23197.0
235(7)	23543.5
240(7)	24066.6
241(7)	24185.8
243(7)	24333.8
245(7)	24560.4
262(7)	26208.8
266(7)	26608.5
278(7)	27887.0
282(7)	28285.8
194(8)	19489.0
205(8)	20528.9
227(8)	22789.8
239(8)	23926.7
245(8)	24581.2
253(8)	25388.9
259(8)	25918.1
264(8)	26454.1
265(8)	26597.0
269(8)	26979.3
271(8)	27086.4
274(8)	27477.6
278(8)	27818.5
309(8)	30986.3
238(9)	23843.7
295(9)	29550.3

* Figures in parenthesis are J-values.

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TABLE 14

SOME CLASSIFIED STRONG LINES OF THE UI SPECTRUM

Wave Length	Intensity	Wave Number	Term Combination	Wave Length	Intensity	Wave Number	Term Combination
8710.76	40	11476.91	$B_4-174(4)$	7631.72	250	13099.61	$^5L_7-169(7)$
8607.96	600	11613.97	$^5L_6-116(5)$	7619.34	300	13120.89	$^5L_8-207(7)$
8574.59	30	59.17	$^7M_6-179(5)$	7609.16	100	38.44	$^5K_7-204(7)$
8570.52	120	64.70	$^7M_7-197(6)$	7533.91	250	13269.68	$^5L_7-170(6)$
8567.	40	68.53	A4-161(4)	7425.50	150	13463.41	$^5L_6-134(5)$
8557 32	30	82.70	$^5K_8-223(7)$	7396.98	40	13515.33	$A_4-179(3)$
8540.19	100	11706.15	$^7K_5-174(4)$	7130.05	40	14021.28	$^7K_5-197(6)$
8496.09	100	66.89	$^7M_7-199(7)$	7128.89	200	23.57	$^5K_5-146(6)$
8450.02	400	11831.04	$^5L_7-156(7)$	7074.78	80	14130.83	$^5K_6-184(5)$
8445.37	400	37.56	$^5L_7-156(6)$	6826.91	400	14643.88	$^5L_6-146(6)$
8441.20	80	43.41	$^5L_8-194(8)$	6820.76	80	57.09	$^5K_6-189(5)$
8389.16	40	11916.87	$B_4-179(5)$	6818.29	50	62.39	$A_3-185(3)$
8381.86	120	27.25	$^7K_6-189(5)$	6741.36	50	14829.73	$^7M_6-210(5)$
8346.75	80	77.43	$B_4-179(3)$	6683.38	40	14858.38	$^5L_7-187(6)$
8262.05	150	12100.21	$^7M_7-202(6)$	6620.52	50	15100.39	$^5K_5-157(5)$
8230.83	40	46.11	$^7K_5-179(5)$	6518.94	80	15335.70	$^7M_6-215(6)$
8223.09	200	57.54	$^7M_6-184(5)$	6464.97	150	15463.72	$^5K_7-227(8)$
8174.30	250	12230.11	$^5K_6-165(6)$	6449.16	300	15501.63	$^5K_5-161(4)$
8137.21	30	85.85	$^7K_7-226(7)$	6395.42	200	15631.88	$^5L_6-156(7)$
8097.61	40	12345.94	$^7M_7-204(7)$	6392.74	80	15638.43	$^5L_6-156(6)$
8034.79	40	12442.46	$^7K_7-227(8)$	6389.77	80	45.69	$B_4-216(5)$
7991.30	40	12510.17	$^7M_6-187(6)$	6372.43	200	88.27	$^5L_7-194(8)$
7970.46	100	42.88	$^7M_7-206(6)$	6359.28	100	15720.71	$^5L_6-157(5)$
7918.79	50	12624.73	$^5K_6-169(7)$	6298.53	40	15872.34	$A_3-197(4)$
7900.39	40	54.13	$^5K_6-169(5)$	6293.32	60	85.47	$^5K_5-165(6)$

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TABLE 14 (continued)

Wave Length	Intensity	Wave Number	Term Combination	Wave Length	Intensity	Wave Length	Term Combination
7881.91	400	83.80	$^7M_6$-189(5)	6268.66	50	15947.97	$^7M_7$-240(7)
7868.73	100	12705.05	$^5L_7$-165(6)	6215.37	100	16084.71	$^5L_7$-199(7)
7784.13	500	12843.13	$^5K_5$-134(5)	6175.38	200	16188.86	$^5K_6$-204(7)
7761.84	50	80.01	$^7K_6$-199(7)	6174.37	60	91.52	$^7K_6$-231(7)
7639.52	200	13086.22	$^5K_6$-173(6)	6171.85	250	98.12	$^5L_8$-238(9)
6164.50	80	16217.43	$^5K_7$-235(7)	5297.44	150	71.81	A_4-233(5)
6153.66	50	46.00	$^5K_7$-235(6)	5280.38	300	18932.78	$^5L_6$-189(5)
6152.25	60	49.73	$^7K_7$-265(8)	5272.01	100	62.85	$^5L_8$-266(7)
6129.72	100	16309.47	$^5K_5$-169(5)	5270.62	100	67.82	$^7M_7$-271(8)
6077.29	200	16450.15	$^5K_5$-170(6)	5259.90	80	19006.48	$^7M_6$-252(5)
6062.30	80	90.84	$^5K_6$-207(7)	5234.16	120	99.95	$^7M_6$-253(6)
5997.31	150	16669.54	$^7M_6$-229(7)	5216.92	80	19163.06	$^5K_5$-197(6)
5986.10	150	16700.75	A_3-205(4)	5164.14	200	19358.93	$^7M_7$-274(8)
5976.32	200	28.07	$^5L_7$-205(8)	5088.29	120	19647.52	$^5L_6$-196(5)
5971.50	250	41.58	$^5K_5$-173(6)	5063.77	150	19742.66	$^5L_7$-235(7)
5956.86	60	82.74	B_4-227(3)	5027.38	400	19885.54	$^5L_6$-199(7)
5933.82	60	16847.90	$^5K_5$-174(4)	5011.41	120	19948.90	$^5K_5$-205(4)
5915.40	600	16900.36	$^5L_6$-169(7)	4967.33	120	20125.93	$^5L_7$-239(8)
5898.78	80	47.96	$^7M_6$-231(7)	4955.78	120	72.83	$^5L_8$-278(8)
5836.03	80	17130.19	$^7K_7$-274(8)	4944.52	80	20218.80	$^5L_6$-202(6)
5780.59	100	17294.49	$^7M_6$-235(7)	4928.44	100	84.74	$^5K_6$-245(7)
5758.14	40	17361.94	$^5L_6$-173(6)	4910.35	120	20359.49	$^7M_6$-266(7)
5640.30	40	17724.63	$^7K_5$-235(5)	4885.15	120	20464.51	$^5L_6$-204(7)
5634.38	80	43.26	$^5L_8$-253(8)	4842.48	80	20644.82	$^5K_5$-212(6)
5621.51	100	83.89	$^5L_7$-215(6)	4810.90	100	20780.36	$^5L_7$-245(8)
5620.78	200	86.21	$^5K_5$-184(5)	4777.67	80	20924.86	$^5K_5$-215(4)
5616.58	80	99.51	$^7M_7$-259(8)	4756.81	120	21016.64	$^5K_5$-216(5)
5610.89	150	17817.56	$^7M_6$-240(7)	4715.68	120	21199.93	A_4-256(4)
5573.59	60	17936.80	$^7M_6$-241(7)	4663.75	120	21435.98	$^5K_5$-220(6)
5573.07	60	38.47	$^7M_7$-282(7)	4631.62	100	21584.67	$^5L_6$-215(6)
5564.17	300	67.16	$^5L_7$-218(6)	4620.23	300	21637.88	$^7M_6$-278(7)
5527.98	80	18084.80	$^7M_6$-243(7)	4576.64	80	21843.97	$^5K_5$-224(6)
5511.49	250	18138.88	$^5K_6$-187(6)	4516.73	80	22133.72	$^5K_5$-227(6)
5502.18	60	69.57	A_3-220(4)	4469.32	100	22368.51	$^5L_6$-223(7)
5496.43	150	88.59	$^5K_6$-224(6)	4383.27	50	22807.62	$^5L_7$-266(7)

TABLE 14 (Continued)

Wave Length	Inten-sity	Wave Number	Term Combination	Wave Length	Inten-sity	Wave Number	Term Combination
5452.41	40	18335.44	$^{7}N_{7}$-264(8)	4371.76	100	67.66	$^{7}N_{7}$-309(8)
5431.35	50	18406.54	$^{5}L_{6}$-184(5)	4362.05	300	22918.58	$^{5}L_{6}$-229(7)
5410.24	80	78.34	$^{5}K_{6}$-227(6)	4355.75	80	51.74	$^{5}K_{5}$-235(6)
5406.87	100	89.86	$^{7}M_{7}$-266(7)	4313.13	100	23178.50	$^{5}L_{7}$-269(8)
5385.54	100	18563.10	$^{5}L_{8}$-262(7)	4246.26	100	23543.52	$^{5}L_{6}$-235(7)
5382.94	100	72.07	$^{5}K_{5}$-191(4)	4222.36	150	23676.76	$^{5}L_{7}$-274(8)
5375.76	80	96.86	$^{7}M_{7}$-267(6)	4152.97	150	24066.58	$^{5}L_{6}$-240(7)
5341.50	120	18716.14	A_{3}-225(4)				
5336.54	120	33.55	A_{4}-231(4)				
5329.26	150	59.14	$^{5}L_{6}$-187(8)				
5315.27	150	18808.51	$^{5}L_{8}$-264(8)				
5308.54	300	32.34	$^{5}L_{7}$-226(7)				
5300.57	120	60.68	$^{7}M_{7}$-269(8)				
5299.44	100	64.69	$^{5}K_{8}$-295(9)				

50N

Table 14 gives a list of 141 strongest UI lines in the visible and infrared which were identified between the odd and even terms listed in Tables 13A and B.

The ground term 5_L could belong either to the configuration f^3ds^2 or f^3d^2s; in any case, its occurrence points to the presence of three f electrons in the ground state of the free uranium atom and makes its electronic structure analogous to that of neodymium ($4f^35d6s^2$). The lowest term of the configuration d^4s^2 (present in tungsten and postulated until recently also for uranium) is 5_D.

2.5. <u>Term Analysis of UII Spectrum</u>. The only available data are contained in a communication from the MIT Spectroscopical Laboratory (MIT-2). It gives a list of twelve low levels with their g-values (from Zeeman effects) and the total quantum numbers J (Table 15), also a list of 140 high levels (17392 - 41317 cm^{-1}) with J-values for all and g-values for some of them (Table 16). The low terms are tentatively identified as belonging to the configuration $5f^26d^27s$. The ground term $^6I_{9/2}$ could conceivably belong to the configuration f^4s since, according to Hund's rules, the deepest term of the configuration f^2d^2s should be ^6L. However, Harrison suggested that the term component $^6I_{9/2}$ is an f^2d^2s level situated below $^6L_{11/12}$ only by an accidental perturbance. If this is so, the center of gravity of the $^6I^+$ term will be found above those of the terms ^6L and ^6K.

In any case, the simply ionized uranium atom U contains at least two 5f electrons in its ground state.

TABLE - 15

LOW TERMS OF UII*

Term	Value (cm^{-1})	g Measured	g Theoretical for LS-coupling
^6I 9/2	0.00	0.826	0.727
^6L 11/2	289.05	0.615	0.651
^6K 9/2	914.77	0.546	0.605
L 13/2	1749.13	0.851	0.863
^6K 11/2	2294.72	0.839	0.870
^6I 11/2	4420.88	1.035	0.973
^4L 13/2?	4585.47	0.800	0.780
^6H 5/2 ?	4706.32	0.286	0.473
^4H 7/2 ?	5401.55	0.667	0.694
$6H_7$/2	5667.34	0.825	0.737
^4L 11/2 ?	5790.69	0.769	0.849
- 13/2	6283.47	--	0.785

* Probably belonging to the configuration f^2d^2s.

TABLE 16

HIGH TERMS OF UII

Term Value (Cm^{-1})	J	g (meas.)	Term Value (cm^{-1})	J	g (meas.)
39108.95	11/2		32535.12	13/2	.997
38968.45	11/2		32028.40	7/2	1.023
38903.29	7/2		31784.81	7/2	.934
38898.43	11/2 13/2		31670.35	9/2	
38681.86	7/2		31219.24	13/2	1.040
38579.87	9/2		30900.66	9/2	
38128.90	11/2 13/2		30860.13	11/2	.977
37931.77	9/2		30374.10	11/2	
37869.85	9/2 11/2		30341.70	15/2	1.019
37789.18	9/2		30240.43	11/2	
37684.33	11/2		30085.80	11/2 13/2	
37659.53	9/2 11/2		30061.77	11/2	1.017
37377.10	9/2 11/2		30000.16	11/2 13/2	
37341.79	9/2 11/2		29827.46	9/2	
37149.71	9/2 11/2		29557.93	11/2	
36782.70	9/2 11/2		29388.69	9/2	
36679.45	9/2 11/2		29349.25	9/2 11/2	
36351.21	9/2		29303.92	11/2	
36273.86	9/2 11/2		29205.40	9/2 11/2	
36253.41	9/2		29162.10	11/2	.977
36150.57	9/2		28636.89	13/2	1.064
36132.82	9/2 11/2		28507.96	11/2	1.020
36105.39	9/2 11/2		28484.51	11/2	
36089.84	9/2 11/2		28444.52	11/2	
36070.31	[illegible]/2 ✓		28159.68	9/2 11/2	
36029.20	9/2 11/2		28154.47	11/2	.885
35960.19	9/2		27930.1	11/2	.997
35903.18	11/2		27912.14	11/2	
35899.45	11/2 13/2		27725.03	11/2	
35372.90	9/2 11/2		27698.04	9/2	1.012
35324.38	9/2 11/2		27583.35	7/2	.730
35234.08	9/2 11/2		27499.42	11/2	1.036 (.662)
35214.41	9/2 11/2		27446.36	9/2	
35110.22	9/2 11/2		27357.30	11/2	
34949.12	9/2		27290.26	7/2	.93 (.54)
34923.62	11/2 13/2		27143.74	11/2 13/2	
34885.51	11/2	1.004	27126.11	9/2	1.012
34612.86	9/2	0.958	26716.74	13/2	.990
34678.05	11/2	(.562)	26415.19	11/2	
34663.67	13/2		26285.19	11/2	
34607.01	7/2		26191.35	13/2	.900
34402.25	11/2 13/2		26084.82	11/2	
34392.34	11/2		25986.35	13/2	.979
34199.47	11/2		25967.70	7/2	.855
34049.54	11/2 13/2		25737.60	5/2	.923
33795.02	7/2	0.977	25714.06	13/2	1.010
33648.16	7/2		26397.90	13/2	1.035
33104.43	11/2 13/2		251[illegible].93	13/2	1.030
33018.87	11/2				

TABLE 16 (Continued)

Term Value (cm⁻¹)	J	g (meas.)
25906.06	9/2 11/2	
25764.67	7/2	1.05
25495.45	7/2	.958
25492.96	11/2	.993
25437.54	9/2	.94
24923.59	13/2	1.088
24684.16	9/2	.918
24608.17	11/2	.904
24453.46	9/2	1.100
25342.24	7/2	.763 (.625)
24305.62	9/2	.974
24293.16	13/2	1.019
24288.01	11/2	1.012
24159.73	13/2	.959
24152.82	11/2	.906
24019.26	11/2	
24010.46	11/2	.969
23911.66	9/2	1.056
23778.15	11/2	.865
23 41.32	7/2 9/2	
23635.94	13/2	.912
23554.01	11/2	1.033
23315.09	9/2	.874
23241.36	11/2	.957
22917.46	11/2	.849
22764.92	11/2	.980 (.760)
22642.49	9/2	.872
22429.86	9/2	.929
22165.18	9/2	.885 (.621)
21975.59	13/2	1.029 (.697)
21831.04	9/2	.890
21710.76	13/2	.907
21555.28	9/2	1.023
21320.22	7/2	.827
21021.40	7/2	.885
20961.72	7/2	.865
20353.99	11/2	1.00
18827.02	11/2	.94
18200.08	9/2	.774
17434.37	11/2	.810
17392.22	9/2	.783 (.405)
41317.04	11/2	1.059

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2.6 Electron Configuration. The chemical properties of the elements Th to U remind one of the series Zr, Cb, Mo rather than of the series La, Ce, Pr. In other words, they appear to indicate a gradual completion of a d-electron groups, rather than the filling of an f group which is characteristic of the rare-earth family. The first theoretical stability calculations by Sugiura and Urey (1926) seemed to confirm this conclusion by indicating a stronger binding of 6d as compared to the 5f electrons. However, subsequent calculations of Wu and Goudsmit (1933), who used the Wentzel-Kramer-Brillouin approximation method, led to the conclusion that at $Z = 92$ (uranium) the 5f electrons may be almost as strongly bound as the 6d electrons and that $Z = 93$ at least one 5f electron is likely to be found in the ground state. Similarly, Mayer (1941) estimated by the Thomas-Fermi statistical approximation method that the 5f groups should begin to fill up at $Z = 91$ or 92.

Ephraim and Mezener (1933a, b) pointed to the analogy between the absorption spectra of rare-earth compounds with their sharp lines and the spectra of uranium compounds, some of which also exhibit very narrow absorption bands. This can be taken as indicative of states in which the role of optical electrons is played by well-shielded f electrons. The effect of anions on the cation spectrum also is similar in the rare-earth salts and in uranium salts. However, the spectra in question are those of ions (U(III), U(IV), and highly charged ions always have a stronger tendency to choose electron arrangements without vacant inner shells than neutral atoms. Therefore, Ephraim's suggestion that two f electrons are present in the neutral U atom and that a "thoride" series in which the 5f shell is filled begins with thorium, was only a guess. Positive information about this point is provided by the analysis of the spectrum.

As discussed above, this analysis shows that the ion U^+ contains at least two, and the neutral atom U as many as three, 5f electrons in the ground state:

$$U^+ \ldots 5f^2 6d^2 7s, \quad (6_I \text{ or } 6_L)$$

$$U \ldots 5f^3 6d 7s^2, \quad (5L).$$

If this assignment is correct, the transition from U^+ to U involves the addition of one 5f electron and the transfer of one electron from the 6d to the 7s group.

Recent chemical experience tends to support the view that something similar to the rare-earth series does exist in the last period of the periodic table, even though the progressive increase in valency which is limited in the "lanthanide series" to the first two elements (LaIII and CeIV), is much more extended in the "actinide series" (AcIII, ThIV, PaV(?), UVI). However, the filling of an f group need not necessarily produce a series of elements as closely similar chemically to each other as the rare earths are. The close similarity of these elements is due to the narrow range of changes in ionization potentials and ionic radii, a quantitative phenomenon which does not necessarily follow from the qualitative analogy in electron distribution.

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CHAPTER III

URANIUM IN NATURE

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CHAPTER III. URANIUM IN NATURE

1. General Survey

1.1 Igneous Rocks. Uranium is a ubiquitous element. The reason that we are better aware of its wide distribution in nature than we are of the distribution of many other elements is that the radioactive properties of uranium (and of its disintegration products, such as radium, which are always associated with it in nature) make it easy to detect and estimate even minute quantities of this element. The usual method of determination of uranium in minerals is indirect. It consists in measuring by means of an electroscope the amount of radium emanation evolved by a given weight of material. From this the amount of radium present can be derived, and the amount of uranium can in turn be calculated by assuming the existence of radioactive equilibrium between this element and its transmutation product radium (Kirsch, 1928). The constancy of the ratio of uranium to radium (2.84 x 10^6:1) in unweathered rocks expected on theoretical grounds has been established experimentally by numerous independent workers.* Recently the uranium content of various minerals and rocks has been determined directly by a fluorescence method which provides an exceedingly sensitive analytical procedure (Urry, 1941; Umovskaja, 1940). See section 2.6, and Vol.__. Igneous rocks containing excess silicic acid ("persilicic" rocks, often designated as "acid") are found to contain significantly higher proportions of uranium than the "subsilicic" rocks (often called "basic"). This is shown in Table 1 in which rocks are listed roughly in order of decreasing SiO_2 content.

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*In some cases the Ra:U ratio differs from that derived from the laws of radioactive equilibrium. This has been attributed to weathering and selective leaching. (Starik, 1936, 1937; Segel, 1938).

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TABLE 1

RADIOACTIVE CONTENT OF IGNEOUS ROCKS

Type of Rock	1 Metric Ton (1000Kg) of Rock Contains U(g)	Th(g)	K(kg)
Granite	9.0	20.0	34
Grano-diorite	7.7	18.0	25
Diorite	4.0	6.0	17
Central basalts			
Continental	3.5	9.1	19
Oceanic	3.6	7.1	18
Plateau basalt	2.2	5.0	8
Gabbro	2.4	5.1	7
Eclogite	1.0	1.8	4
Peridotite	1.5	3.3	8
Dunite	1.4	3.4	0.3

In addition to U and Th the table lists K, which is the third radioactive constituent of the earth of considerable geophysical importance.

The best available estimate of the mean uranium content in the surface of the earth's crust is 4×10^{-6} gram per gram of rock. The concentration varies in normal rocks between about 0.2×10^{-6} and 25×10^{-6} g/g. These values of Hevesy (1930, 1932) were accepted by V. M. Goldschmidt (1938; see also Evans and Goodman, 1941) as the best available estimates.*

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*A word of caution is needed regarding some data in the frequently quoted standard work of Clarke and Washington (1924). Owing to a mathematical error and the use of an obsolete value for the ratio of uranium to radium, these authors gave for the average abundance of uranium a value which is too large by a factor of twenty.

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The abundance of certain metallic elements in rocks is shown in Table 2. This table serves to illustrate the fact that metals such as cadmium, bismuth, mercury, and silver, which are not considered excessively rare, are present in the earth's crust in much smaller average amounts than uranium. There is, however, no simple relationship between the mean concentration of an element in the earth's crust and the probability of finding economically important deposits of that element.

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TABLE 2*

ABUNDANCE OF SOME ELEMENTS IN IGNEOUS ROCK

Element	Grams per Metric Ton (1000 Kg)	Atoms per 100 Atoms Si	Element	Grams per Metric Ton (1000 Kg)	Atoms per 100 Atoms Si
Li	65	0.091	In	0.1	0.000007
Be	6 (1)	0.0067	Gd	6.36(1)	0.000394
Na	28300	12.4	W	69.	0.0038
Al	81300	30.5	Pt	0.005	0.00000027
Si	277200	100	Au	0.005	0.00000026
Cr	200	0.039	Hg	0.5(1)	0.000025
Cu	100	0.016	Pb(2)	16	0.00080
Zr	40	0.0062	Bi	0.2	0.000009
As	5	0.00067	Th	11.5(3)(1)	0.00050
Ag	0.10	0.000009	U	4	0.00016
Cd	0.5	0.000045			

*Adapted from Goldschmidt (1938b).

(1) Value based on sedimentary rock analysis.

(2) For an interesting estimate of the age of the sun based on the terrestial Pb/U ratio, see S. Meyer (1937).

(3) This value refers to analyses based mostly on sedimentary rocks. The ratio of thorium to uranium has been studied by a number of workers. Based on a hundred determinations, an average value of 3.2 may be assumed for this ratio (Keevil, 1938, 1944) in normal igneous rocks, exclusive of typical thorium or uranium minerals. The geochemical distribution of thorium appears to be somewhat different from that of uranium (Meyer, 1937a; Kirsch and Hecht, 1938).

S. Meyer (see footnote 2) has derived an average Th/U ratio of 6.5 to 7 for the whole of the earth. Since a ratio of 3.2 is found near the surface, the concentration of Th in the core of the earth must be much higher.

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The question arises of the uniform distribution of uranium throughout the earth's crust, that is, whether the mean concentration found near the surface can be considered typical of the earth's crust as a whole. The answer is that the upper part of the crust probably is enriched in uranium. As mentioned above, uranium is known to occur preferentially in persilicic igneous rocks. Since the main components of the deeper regions of the earth's crust are comparatively poor in silica, uranium would be expected in less abundance there than near the surface. Another argument in favor of this assumption can be derived from an analysis of the thermal balance of the earth. Radioactive disintegration produces heat. If it is assumed that radioactive elements uranium and thorium are present in concentrations found near the surface of the earth down to a depth of 16 km and potassium is distributed fairly uniformly in the whole lithosphere, the heat produced by radioactivity would offset all the heat losses caused by thermal radiation from the earth into space. If significant amounts of uranium or thorium existed below this depth, the fact that the earth is in an approximately steady thermal state becomes incomprehensible (Holmes, 1926a, b).

It should not be thought, however, that the deeper layers of the earth's crust are entirely devoid of radioactive elements; indeed, the presence of uranium in these layers was postulated by Joly (1909) to account for the occurrence of geological revolutions (periods of volcanism and mountain growth) in the history of the earth. It appears reasonable to assume that while the bulk of uranium is contained within a depth of 16 or 20 km from the surface of the earth, some uranium may exist down to a depth of 40-48 km, which is the assumed thickness of the lithosphere.

The weight of the earth's crust to a depth of 20 km has been estimated at about 3.25×10^{19} tons. If an average uranium content of 4×10^{-6} g/g is assumed, the weight of uranium contained in this crust must be about 1.3×10^{14} tons.

The main quantity of uranium is contained in the silica-rich igneous rocks which comprise continental shields. Only relatively small quantities are probably present in the igneous rocks (mostly of the subsilicic type) which form the floors of the oceans.

1.2 Sedimentary Rocks. Igneous and metamorphic rocks constitute 95 per cent of the weight of the outer 16 km of the earth's crust. The sedimentary rocks (shales, etc.) make up the balance. Except for the carnotites of Colorado and Utah, the sedimentary rocks appear to contain much less uranium than the igneous rocks (on the average perhaps only one-half as much).

1.3 Oceans, Rivers, Thermal Springs. Uranium is present in measurable concentration in the water of the oceans. The older values (see Gmelin, 1936, for literature citations) for the uranium concentration in sea water were based on determinations of radium. However, it is by no means certain that radioactive equilibrium between uranium and radium is maintained in the oceans. On the contrary, there is positive evidence that the radium concentration in sea water is perhaps only one-tenth of that which would be present in equilibrium. This is not unexpected, since a large proportion of radium produced by disintegration of dissolved uranium is likely to be lost from sea water by precipitation as sulfate or carbonate. Therefore, the older data for the uranium concentration in sea water which were derived from the radium content are of little value. Recent applications of direct fluorescence analysis gave for the uranium content of sea water values from 0.36×10^{-6} to 2.3×10^{-6} g/l (Hernegger and Karlik, 1935). The uranium content was found to vary in proportion to the total salinity. Ocean water of 3.5 per cent salinity contains about 2×10^{-6}g uranium per liter and equal (2×10^{-9} g/g) (Föyn and co-workers, 1939), or about one two-thousandth as much uranium as is present in an equal weight of rock. Assuming the volume of the oceans to be about 2 x 10^9, the total uranium content of the oceans must be of the order of 4 x 10^9 tons, or 0.003 per cent of that of the earth's crust (1.3 x 10^{14} tons).

Numerous thermal springs are known to be radioactive. The activity, however, appears to be due mainly to radium; little is known of the uranium content of these waters. The uranium content of rivers is, on the basis of very fragmentary evidence, thought to be of the same order of magnitude as that of sea water.

A number of investigations have been carried out to determine the uranium content of oceanic sediments (Piggot and Urry, 1942; Hoffmann, 1942). No radioactive equilibrium exists in these sediments; their uppermost layers in particular contain excessive amounts of radium. The reason for this was mentioned above; the precipitation of insoluble radium sulfate and carbonate from sea water. Consequently, the amount of uranium present in the sediments cannot be correctly evaluated from determinations of radium. Roughly, it has been estimated that a total of 10^6 tons of uranium is present in the oceanic sediments, a negligible quantity by comparison with that contained in continental rocks.

1.4 <u>Living Matter.</u> Uranium is a constituent of living matter (the "biosphere" of Vernadsky), but the biological significance of the apparently universal distribution of uranium in plants and animals is not discussed here (see the biological volume of this series). Uranium appears to be a normal component of protoplasm (Diobkov, 1937). It has been estimated that uranium occurs there in concentrations varying from 10^{-4} to 10^{-9} per cent by weight (Hoffmann, 1941a; 1942a,b; 1943a,b). The fixing of uranium by algae may have had some significance in the formation of certain uranium deposits (Hoffmann, 1941b). (See p.).

1.5 <u>Extra-Terrestrial Occurrence.</u> Numerous analyses of meteorites show that they contain uranium (Paneth, 1928, 1930, 1931; Quirke, and Finkelstein, 1917; Noddack, 1930; Hoffmann, 1941c). However, in conformity with the rule that subsilicic terrestrial rocks in general have a low uranium content, it is found

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that stony meteorites (called aerolites), which have less SiO_2 than even the highly subsilicic terrestrial rocks, contain only about 3.6×10^{-7} gU/g. (This is an average value based on analyses of 20 aerolites). The uranium content of iron meteorites (siderites) is even smaller. It has been established that meteorites contain on the average as little as 9×10^{-8} gU/g, that is, only about one-half percent of the uranium content of igneous rocks. This, too, is in agreement with our knowledge of the geochemical distribution of uranium, since the iron core of the earth is probably almost free of uranium.

Spectroscopic observation has as yet been unable to establish with any certainty the presence of uranium in the sun or other stars.

The important application of the radioactivity of uranium to the determination of the age of rocks cannot be discussed here. We refer in this respect to the reviews by Lane (1924 and subsequent years), Kirsch (1928), Ellsworth (1932), and Holmes (1931 and 1937). The discovery of fission has brought new aspects into the problem of the role of radioactive elements in geochemistry and geophysics. For the first analysis of these aspects, we refer to the review by Goodman (1942), "Geological Applications of Nuclear Physics," which contains an excellent bibliography.

2. Occurrence and Composition of Uranium Minerals

At the present time, it is difficult to give a completely coherent picture of the origin of the bewildering array of uranium minerals found in nature. The difficulty arises from a variety of circumstances. In the first place, most of these minerals are so complex and exhibit such variability in composition that even the chemical constitution is known with any certainty for only a few of them. Furthermore, crystal structure analyses of most uranium minerals are as yet either fragmentary or non-existent. Finally, certain aspects of the chemistry of uranium itself are only now becoming clear. This is particularly true of the uranium-oxygen system, a knowledge of which is important for understanding the nature of

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uraninite and pitchblende minerals.

Most uranium minerals are found in pegmatites, particularly granite pegmatites. The chief exceptions are pitchblende (which occurs in veins and seams), carnotite, and certain uranium deposits associated with carbonaceous matter, such as kolm (a kind of oil shale found in Sweden). The presence of uranium in granite pegmatites can be accounted for by applying the geochemical principles of V. M. Goldschmidt (1923). According to his views, as the uniformly molten earth cooled its matter became separated into one vapor and three concentric condensed phases. The elements are supposed by Goldschmidt to have concentrated in the various phases in the way shown in Table 3.

TABLE 3

DISTRIBUTION OF THE ELEMENTS IN THE VARIOUS ZONES OF THE EARTH*

Elements of the Siderosphere Iron Phase	Elements of the Chalkosphere Sulfide Phase	Elements of the Lithosphere Silicate Phase	Elements of the Atmosphere Gaseous Phase
Fe, Co, Ni P, C Mo, (W?) Pt, Ir, Os(?), (Pd) Ru, Rh	((O)), S, Se, Te Fe, (Ni), (Co), Mn(?) Cu, Zn, Cd, Pb (Sn?), Ge, (Mo?) As, Sb, Bi	O, (S), (P), (H) Si, Ti, Zr, Hf, Th F, Cl, Br, I B, Al, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tu, Yb, Lu, Li, Na, K, Rb, Cs. Be, Mg, Ca, Sr, Ba. (Fe), V, Cr, Mo, ((Ni)), ((Co)) Cb, Ta, W, U, Sn (C)(1)	H, N(2), (C), (Cl?) Ne, Ne, A, Kr, Xe

*( ) Indicated minor amount; (( )) indicates very small amount.

(1) as carbonate

(2) Perhaps also as nitride in siderosphere under high temperature and pressure.

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The siderosphere constitutes the earth's core; the chalkosphere forms an intermediate shell; and the lithosphere forms the outer crust of the earth. The elements which concentrated in the lithosphere were those possessing the most stable oxides. Uranium is one of these. As the liquid silicate magma cooled, the high-melting solid phases containing the main components of the mixture began to crystallize out. Where solid solubility between the crystallizing species and a minor constituent existed, the latter was co-precipitated at an early stage. In cases where crystallochemical constants prevented the entry of a rare element into the lattice of the main crystallizing phase, a progressive concentration of this element in the residual liquid phase took place. In the third column of Table 3 are listed elements whose crystallochemical properties must have prevented their entry into the crystalline rocks formed from the bulk of the silicate magma. These elements are: the rare earths, zirconium, thorium, hafnium, titanium, columbium, tantalum, tungsten, tin, lithium, beryllium, boron, and uranium. These rare elements must have become concentrated in the last portion of the liquid magma. Rocks formed from this residual silicate magma are well-defined geological entities rich in feldspar and are designated as pegmatites.

Thus a rational explanation is found for the presence in pegmatites of combinations of uranium with thorium, tantalum, columbium, zirconium, hafnium, and the rare earths. Where most of the elements listed above were absent, practically pure uranium dioxide crystallized out and formed the mineral uraninite. In pegmatites containing phosphorous, complex uranium phosphates were sometimes formed instead of oxide.

Many secondary reactions must have occurred after the primary deposition of uranium minerals from the magma. Oxidation was an ever present probability. Selective leaching of the pegmatite could have occurred, or the pegmatite could have been suffused with hot solutions of various compounds.

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In this way, many original minerals could have undergone considerable change. Consequently, unraveling the geological history of any particular uranium mineral often is a complicated problem; and only in isolated instances has anything been obtained which resembles a clear picture. However, with renewed interest in the subject the situation may improve.

In addition to the uranium minerals found in pegmatites, there are two other types which require special attention because of their economic importance. One is carnotite, a unique mineral which is examined in detail below. The other is pitchblende, veins of which have been found in Canada, Bohemia, and the Belgian Congo. The pitchblende veins are thought to be dreived from the same residual magmas as the pegmatites. These magmas might have contained appreciable quantities of water; consequently, in addition to the fractions which crystallized out as pegmatites, these magmas may also have produced aqueous fractions. In these high temperature, high pressure solutions, most of the elements in the second column of Table 3 which were present in the magma must have been concentrated, as well as uranium (many compouhds of which are readily soluble in water). Streams of these hot solutions impinging on igneous rocks underwent chemical reactions which resulted in precipitation and the formation of so-called "hydrothermal" vein deposits. In this way uranium became associated in pitchblende veins with copper, bismuth, silver, tin, and gold. Most of these elements were precipitated as sulfides; but, in accordance with its chemical properties, uranium was almost always deposited as oxide.

2.1 <u>Classification of Uranium Minerals</u>. The paucity of good x-ray crystallographic data makes any classification of the uranium minerals rather arbitrary.

In the older minerology the terms uraninite and pitchblende were applied indiscriminately to almost any uranium-oxygen mineral. This should be avoided, since very distinct differences between the two minerals exist, and considerable confusion results from the use of the two terms as synonyms. Uraninite is found only in pegmatites and invariably contains significant quantities of thorium and rare earths. Pitchblende is found only in veins of hydrothermal origin and usually contains no thorium and only traces of rare earths. Uraninite probably was originally pure uranium dioxide, UO_2; all hexavalent uranium found in uraninite probably arose from subsequent oxidation. Pitchblende, however, probably had a composition close to U_3O_8 even when first formed. Uraninite is crystalline (generally metamist); pitchblende is always amorphous. In the following presentation, the term uraninite is used only for crystalline uranium oxide found in pegmatites. (See Van Aubel, 1927).

The classification adopted for this discussion is as follows: (compare with Tyler, 1930)

- A. Uranium Minerals in Pegmatites
  - 1. Uraninite
  - 2. Uranium-bearing Columbates and Tantalates.
- B. Non-Pegmatitic Uranium Minerals
  - 1. Pitchblende
  - 2. Oxidation Products of Pitchblende (often identical with those formed from uraninite)
  - 3. Secondary Uranium Minerals
    - (a) Uranates, Silicates, Carbonates, Sulfates
    - (b) Uranium "micas," of the type $M(II)(UO_2)_2(XO_4)_2$ $M = Ca, Cu, Fe, Pb, Mn, UO_2$; $X = P, V, As$
    - (c) Carbonaceous Uranium-bearing substances

Secondary minerals resulting from oxidation or other chemical reactions may occur in both pegmatites and pitchblende veins. In the next section some important members of these groups will receive more detailed discussion.

In order to facilitate an understanding of the composition of the uranium minerals, the ionic radii of a number of elements of frequent occurrence in uranium minerals are given in Table 4. A general rule is that ions whose radii differ by not more than 15 per cent are interchangeable in crystal (provided that certain restrictions, such as the requirement of conservation of charge, are not violated). For limitations and applications of this rule see Goldschmidt (1938).

TABLE 4

IONIC RADII FOR SOME ELEMENTS OF COMMON OCCURRENCE IN URANIUM MINERALS*

Ion	Ionic Radii (A)°	Ion	Ionic Radii (A)°	Ion	Ionic Radii (A)°
U(IV)	1.05	Cb(V)	0.69	P(V)	0.3 -0.4
Th(IV)	1.10	Ta(V)	0.68	V(+V)	~0.4
Er(III)	1.02	Ti(IV)	0.64	As(V)	0.4
Yb(III)	1.00	Mo(IV)	0.68	V(V)	~0.4
Y(III)	1.06	Fe(III)	0.67	Cr(VI)	0.3-0.4
Ca(II)	1.06			S(VI)	0.34

For Coordination number 6.

*Selected from Evans (1939).

2.2 <u>Uraninite.</u> Uraninite (Dana, 1944a) may be considered the primary uranium mineral. It is found in granite and syenite pegmatites, where it is associated with zircon, tourmaline, monazite, mica, feldspar, etc. It is also often closely associated with minerals containing rare earths and columbium or tantalum. Uraninite was first shown to be essentially uranium dioxide, UO_2, by Goldschmidt and Thomassen (1923), who examined natural uraninite crystals from southern Norway by X-rays. According to these observers, uraninite is isomorphous with CeO_2 and ThO_2; it possesses a fluorite type cubic structure.

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Its lattice constant is 5.460 A. (MP Chicago 1) Similar results were obtained by Schoep (1934), who found that natural uraninite gives the same x-ray pattern as synthetic uranium dioxide. Uraninites from different occurrences have been found to be crystallographically identical. The first column in Table 4 indicates what substituting ions are likely to occur in uraninite. It shows that similarity of ionic radii accounts to a certain extent for the invariable presence of rare earths in uraninite crystals.

As might be expected from the chemical properties of uranium dioxide, natural uraninite is always more or less strongly oxidized, so that its actual composition lies between UO_2 and $UO_{2.67}$ ($\cong U_3O_8$), with tetravalent uranium usually predominant. This oxidation may be the result of weathering, but it may also result from the liberation of oxygen within the crystal in sequence of radioactive disintegration of uranium to lead:

$$UO_2 \rightarrow PbO + \tfrac{1}{2}O_2 \ (+6\ He)$$

The amount of oxygen presumably liberated by radioactive disintegration and bound in the crystal has been found experimentally to correspond very closely to the amount of PbO (RaG Oxide) (Bakken and Gleditsch, 1939). Radioactivity thus plays an important role in the variations in composition of uranium oxide minerals. This is also proven by their generally metamist character.

Weathering effects in single crystals of uraninite have been studied by determining the U(IV)/U(VI) ratio in several layers of cleveite crystals as a function of the distance from the surface. The ratio increases towards the core (Bakken and Gleditsch, 1938; see also Malter and Kipp, 1936). The analytical work also indicates that uraninite may be subject to selective leaching, which particularly affects the radium and lead content of the crystals. The mineral becomes black by alteration; least altered specimens are iron-grey. More pronounced alteration leads to a coating of scarlet, orange, yellow, green, grey, or brown decomposition products. Attempts have been made to reproduce the process of weathering of uraninite (Føyn, 1939a). When specimens

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TABLE 5

URANINITE MINERALS

Mineral	Structure	Per Cent Uranium	Optical and Crystallographic Properties	Typical Occurrences
Uraninite	Essentially UO_2 with UO_3 present as a result of oxidation. Fluorite structure, isomorphous with ThO_2, CeO_2. Density: 8.0-10.0g/cc.	65.2-74.5%	Crystalline. Opaque. Octahedral or cubic isotropic crystals. Color variable, may have semimetallic luster. Least altered specimens iron-grey	Karelia, USSR. Masaki, Japan. Gaya, India. Grafton Center, N. H. Portland, Conn. Bedford, N. Y. Mitchell County, N. C. Pennington County, S. D. Quebec, Canada. Cape Province, South Africa.
Bröggerite	$(U,Th)O_2$. Contains Th in substitution for U to at least 14% ThO_2. This variety is restricted to Th > (Y, Ce, etc.) Rare earth content: 0-8%.	48.7-74.9	Isotropic crystals	Anerrod Peninsula, Norway.
Cleveite	$\{U(IV), R.E. (III)\}O_2$ Rare earth content: 5.17%, with U, Er, Ce, La present. UO_2:UO_3 varies from 0.5-0.7	53.3-66.4	Crystalline.	Norway.
Nivenite	$\{U(IV), R.E.(III)\}O_2$ Rare earth content: 11.2-11.8% Y, Er, Ce, L La present. UO_2:UO_3 ratio about 2.5. Density: 8.29 g/cc	57.	Crystalline.	Llano County, Tex. pegmatite on Honshu, Japan. Issaka
Thorianite	$(Th(IV), U(IV))O_2$ ThO_2:U_3O_8 varies from 6:1 to 2:1. Density: 8-9.7 g/cc	9.5-28.2	Cubic Crystal yellowish brown to black. Refractive index ≥ 1.8	Ceylon & Japan (?), Madagascar. Boshogoch River, Siberia. Easton, Pa.

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of cleveite and bröggerite were heated in an autoclave with water to 200°C cleveite (With a high $UO_3:UO_2$ ratio) underwent little change, whereas bröggerite(with a low $UO_3:UO_2$ ratio) showed extensive decomposition.

A number of typical analyses of uraninite minerals are given in Table 6. Numerous other analyses may be found in Doelter's Handbuch (1929). An examination of the data reinforces Kirsch's view that all these minerals are products of alteration and ion-substitution in originally pure UO_2 (designated by Kirsch as ulrichite, a term sometimes applied in the literature to slightly weathered specimens of uraninite).

TABLE 6
PER CENT CHEMICAL COMPOSITION OF SOME URANINITE MINERALS

	Bröggerite (a)	Nivinite(b)	Cleveite(c)	Uraninite(d)	Uraninite(e)
CaO	0.37%	0.32%	0.86%	1.01	0.46
MnO	--	--	--	0.03	0.001
PbO	9.04	10.08	10.92	10.95	16.42
MgO	trace	--	0.14	0.08	0.01
$(Y,Er)_2O_3$	1.11	9.46	9.99	2.14	1.01
$(Ce,La)_2O_3$	--	--	2.25	1.88	--
La_2O_3	0.27	2.36	--	--	0.80
CeO_2	0.18	0.34	--	--	0.265
UO_2	46.13	44.17	23.07	39.10	48.87
U_3O_8	--	--	--	--	--
UC_3	30.63	20.89	40.60	32.40	28.582
ThO_2	6.00	6.69	4.60	10.60	2.15
ZrO_2	0.06	0.34	--	--	0.22
SiO_2	0.22	0.46	--	0.19	0.055
Al_2O_3	--	--	--	0.09	--
Fe_2O_3	0.25	0.14	1.02	0.43	0.30
CO_2	--	--	--	--	--
H_2O	0.74	1.48	4.96	0.70	0.44
Insoluble	4.42	1.47	2.34	0.15	0.15
Remainder	0.19	0.08	--	0.31	0.39
Total	99.61%	98.28%	100.75%	100.06%	100.123%
Density	8.893 g/cc	8.29 g/cc	7.49 g/cc	9.062 g/cc	9.182 g/cc

(a) From Gustav's Mine, Annerød, Norway, F. W. Hillebrand, U. S. Geol. Survey Bull. 78, 43, (1891).

(b) From Barringer Hill, Llano Co., Texas. F. W. Hillebrand, Am. J. Sci., 42, 390 (1891)

(c) From Arendal, Norway. Hidden and MacIntosh, Am. J. Sci. 38, 474 (1889); recalculated by Hillebrand in reference (a) above.

(d) From Wilberforce, Halliburton Co., Ontario. H. V. Ellsworth. Nat. Research Council, Ann. Rep., App. H. Exhibit A, 1929-30.

(e) From Ingersoll Mine, Pennington Co., S. D. Davis, Am. J. Sci., 11, 201 (1926).

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2.3 Other Uranium Minerals of Pegmatitic Occurrence: Columbates, Tantalates, and Titanates. Perhaps the most frequently occurring uranium minerals in pegmatites are the uranium-bearing columbates, tantalates, and titanates. Columbium, tantalum, and titanium are among the elements which crystallize during the last stages of magma solidification (see p.   ). The ionic radii in Table 4 indicates the substitutions which may be encountered in the compounds containing these elements. The structure and composition of these minerals are not discussed here in detail but can be found in Dana's "System of Mineralogy" (1944). It is sufficient to indicate that these minerals are oxides of the isodesmic type and have the rutile structure. Since crystallographic data are for the most part lacking, these minerals can at present be classified only by chemical criteria. The chemical constitution of most of them can be expressed by the formula $A_mB_nO_{2(m+n)}$; where m:n is between 1 and 0.5. A = Rare Earths, U, Ca, Th, Fe(II), Na, Mn, or Zr; and B = Cb, Ta, Ti, Sn, W(?), Zr(?), or Fe (IIIO. In Table 7 are listed the more important uranium-bearing minerals of this type.

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TABLE 7

PEGMATITIC Cb, Ta, Ti MINERALS CONTAINING URANIUM

A. PYROCHLORE - MICROLITE SERIES

$A_2B_2O_6$ (O, OH, F)

A = Na, Ca, K, Mg, Fe(II), Mn(II), Pb(?), Ce, La, Di, Er, Y, Th, Zr, U.

B = Cb, Ta, Ti, Sn(?), Fe(III)(?), W(?).

Mineral	Composition and Structure	Per Cent Uranium	Optical and Crystallographic Properties	Occurrence	Described in	
					Doelter (1929)	Dana (1944)
Pyrochlore	Essentially $NaCaCb_2O_6F$	2.5-8.1%	Lustrous, glassy to resinous. Brown to nearly black.	In Nepheline, Syenite & Pegmatite. Urals and Caucasus, USSR	III$^1_,$95	I, 748
Microlite	Essentially $(Na,Ca)_2Ta_2O_6(O,OH,F)$	0.-5.3	Small octahedrons golden-yellow to brown	Sweden, Virginia, Greenland, W. Australia, Mass.	III$^1_,$250	I, 748
Hatchettolite	Uranium pyrochlore.	10-15	Transparent, isotropic octahedra; lustrous, resinous. N = 1.98±	Hybla, Ont. Mitchell Co., N.C. Madagascar	III$^1_,$	I, 754
Ellsworthite	High uranium calcium-iron pyrochlore. Strongly altered. Related to Hatchettolite	15-17	Massive. Amber Yellow to choclate brown. Isotropic n = 1.89±	Hybla, Ont. Halliburton, Ont.	IV$^2_,$955	I, 755

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TABLE 7 (continued)

B. FERGUSONITE SERIES

ABO_4
A = Y, Er, Ce, La, Di, U(IV), Zr, Th, Ca, Fe(II)
B = Cb, Ta, Ti, Sn, W

Mineral	Composition and Structure	Per cent Uranium	Optical and Crystallographic Properties	Occurrence	Described in	
					Doelter (1929)	Dana (1944)
Fergusonite	Essentially a columbate of Y, Er.	0.2-8.16%	Tetragonal, C = 1.4643. Pyramidal crystals, very dark brown.	Greenland. Sweden. Norway. Mass. Llano Co., Texas. Ceylon. Terek River, Caucasus. Mitchell, Co., N. C.	III, ^{1}252	I, 757
Risorite	A Ti fergusonite.					
Yttrotantalite	Essentially an iron-yttrium-uranium-columbium-tantalate.	1.4-3.96	Rhombic, a:b:c = 0.5556:1.0:0.5173. Prismatic. Yellowish brown to black. Isotropic, n = 2.15 ± 0.02	Norway. Sweden. Miask, Urals Alabama.	III, ^{1}256	I, 763
Ishikawaite	Essentially a uranium (IV)-iron-rare earth columbate. Analagous to samarskite.	20	Tabular, orthorhombic crystals with a:b:c = 0.9451:1:1472. Color black. Waxy luster. Density: 6.2-6.4	Iwaki Province, Japan		I, 766
Rutherfordite	Altered fergusonite.			Rutherford Co., N. C.		I, 762
Brannerite	$(U,Ca,Fe,Y,Th)_3Ti_5O_{16}$	40	Isotropic, N = 2.30 ± 0.02. Black, transparent in thin splinters.	Custer Co., Idaho		I, 774

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TABLE 7 (continued)

C. AB_2O_6 SERIES

A=Y, Ce, Ca, U, Th, Er, La, Pb
B=Ti, Cb, Ta, Fe(III), Sn, W, Zr(?)

Mineral	Composition and Structure	Per Cent Uranium	Optical and Crystallographic Properties	Occurrence	Described in	
					Doelter (1929)	Dana (1944)
Euxenite Polycrase	(Y,Ca,Ce,U,Th) (Cb,Ta,Ti)$_2$O$_6$ The high Ti end of this series of minerals is polycrase.	2.3-14.5%	Orthorhombic. Very dark brown in color.	Woodstock. W. Australia. Nipissing. Ont. Norway. Caucasus. Swaziland. Greenland. N. C. S. C. Brazil. Madagascar.	III^1, 102	I, 787
Priorite Blomstrandinite	(Y,Er,Ca,Fe(II), Th,U(IV)) Ti,Cb)$_2$O$_6$	1-5	Similar to euxenite	Norway. Swaziland Wolhynia USSR.	III^1, 106	I, 793
Samarskite	(Y,Er,Ce,U,Ca, Fe,Pb,Th) (Cb,Ta,Ti,Sn)$_2$O$_6$	0.5-14.0	Orthorhombic a:b:c=0.5456:1:0.5178 Yellowish-brown to black. Isotropic n=3.20±0.05	Minsk, Ural Mts. Berthier Co. Quebec. Baltimore, Md. Mitchell Co., N.C. Colorado. Caucausus. Madagascar.	III^1,	I, 787
Wiikite	Titanium-rich samarskite	3.0-7.8	Orthorhombic. Color, Gold to dark grey	Lake Ladoga, USSR.	III^1,	I, 801
Toddite	Probably a mixture of columbite and euxenite	10	Pitch Black. Submetallic luster. Isotropic.	Sudbury, Ont.	IV^2,	I, 785

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TABLE 7 (continued) [redacted]

D. $A_mB_nX_x$ m:n=1.3

A=U. Ca, Th, Pb, Ce, Y, Er,
B=Ti, Cb, Ta, Fe(III), Al (?)

Mineral	Composition and Structure	Per Cent Uranium	Optical and Crystallographic Properties	Occurrence	Described in	
					Doelter (1929)	Dana (1944)
Betafite	$(U,Ca)(Cb,Ta,Ti)_3O_9 \cdot mH_2O$.	20-26%	Greenish-brown Isotropic, n=1.925±.01	Betafo, Madagascar.	III^1,97	I,803
Samirésite	High lead betafite.	15-20	Yellow, octahedral.	Samiresy, Madagascar.	III^1,98	I,803
Blomstrandite	Variety of betafite.	16-21	Octahedral.	Tongafeno, Madagascar.	III^1,98	I,803
Ampangabéite	Oxide of Cb with rare earths and uranium. Formula unknown. Probably like betafite.	10.17	Orthorhombic, isotropic, n=2.13±0.03. All shades of brown	Ampangabé, Madagascar	IV^2,557	I,806
Delorenzite	An oxide of Ti Y, U, Fe, and Sn, possibly AB_3O_8.	~ 10	Rhombic, black. a:b:c=0.3375:1:0.3412	Caravaggio, Italy.	III^1,52	I,808

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In section 2.2 and 2.3, a number of the more important uranium minerals occurring in pegmatites have been discussed. Despite their wide distribution, these minerals have practically no economic importance. Or, perhaps more correctly, they have had no such significance up to the present. Only two of these minerals have been mined to a very limited extent for their uranium content; betafite in Madagascar and euxenite and polycrase in Western Australia. This situation may change in view of the new importance of uranium. Thus, by way of example, the Iasaka pegmatite in Honshu, Japan contains about 100 g uraninite per ton of rock; while unattractive for the extraction of radium, it may be worthy of exploitation for its uranium content (Iimori, 1941).

2.4 Pitchblende and its Alteration Products. Pitchblende is the most important uranium mineral from the point of view of richness of deposits. Its composition is variable, but in the absence of severe weathering conditions its formula approximates U_3O_8. Pitchblende occurs in metalliferous veins, together with sulfides and arsenides of Fe, Cu, Pb, Co, Ni, As, and Bi. It is found in high-temperature hydrothermal (so-called hypothermal) tin veins as colloform crusts, associated with cassiterite, pyrite, galena, and Co-Ni-Bi-As minerals, especially at Cornwall, England. Another and more important mode of occurrence is in "mesothermal" Co-Ni-Bi-Ag-As veins (hydrothermal veins) formed at moderate temperature. There the pitchblende is associated with pyrite, chalcopyrite, barite, fluorite, native bismuth, native silver, and Co-Ni-As compounds. The deposits at Joachimov (Joachimsthal) in Bohemia, Johanngeorgenstadt in Saxony, and Great Bear Lake in Canada, all are of this type. Pitchblende is also found as colloform crusts with pyrites, sphalerites, etc. in hydrothermal sulfide veins formed at moderate temperatures in which Co-Ni minerals are absent. The deposit in Gilpin County, Colorado examplifies this last type of occurrence. The pitchblende deposits of the Great Bear Lake and the Belgian Congo receive detailed consideration in Section 3.

As stated before (p.   ), the formation of pitchblende deposits was associated with the formation of mineralized veins of the chalkosphere and siderosphere elements of Table 3. The chemical reactions involved in the transport of uranium by hot aqueous streams and its precipitation as U_3O_8, which must have occurred in the last stages of magma crystallization, are as yet unknown. As already noted, pitchblende is found in association with sulfide deposits, but the uranium itself is present in the form of oxide.

Pitchblende always occurs as an amorphous, characteristically black material which shows no signs of macroscopic crystallinity. The oxygen content is variable, although in many cases it is well approximated by the formula U_3O_8. These variations can be understood on the basis of crystallographic studies of the uranium - oxygen system. These studies (see Chapter X) have shown that the U:O ratio can range between about $UO_{2.5}$ and UO_3 without phase transformation. Small amounts of iron, manganese, aluminum, calcium, magnesium, silicon, etc. together with lead and helium from radioactive disintegration are usually found in pitchblende. A very important difference between pitchblende and uraninite is that pitchblende contains practically no thorium and less than 1 per cent rare earths. The uranium content of pitchblende varies between 40 and 76 per cent of the mineral. For numerous analyses, the compilations of Doelter (1929a) and Hintze (1930) should be consulted.

The chemical properties of pitchblende are substantially those of the uranium oxide, U_3O_8 (see Chapter   ). The mineral liberates helium on heating (Hillebrand, 1889). Pitchblende from the Belgian Congo has been reported to yield also on heating a sublimate of selenium (Steinkuhler, 1923). All varieties of pitchblende are soluble in sulfuric or hydrochloric acid.

A considerable number of oxidation products of pitchblende are known. These occur either in complex mixtures of minerals or as alteration zones in pitchblende or uraninite. In most cases the analyses are not very satisfactory, and in the case of ianthinite they are almost certainly wrong. This circumstances makes it

TABLE 8

OXIDATION PRODUCTS OF PITCHBLENDE

Mineral	Composition	Per Cent Uranium	Optical and Crystallographic Properties	Occurrence	Described in	
					Doelter (1929)	Dana (1944)
Becquerelite	($2UO_3 \cdot 3H_2O$?) Formula uncertain; water lost at 500°C.	74	Orthorhombic plates. Canary yellow to orange.	Kasolo, Katanga, Belgian Congo. Wölsendorf, Bavaria.	IV^2, 937	I, 625
Schoepite	($4UO_3 \cdot 9H_2O$?) Complete analyses are lacking, water lost at 325°C. May be identical with Becquerelite.	65-70	Small yellow crystals, orthorhombic, $a_0=14.40$, $b_0=16.89$, $c_0=14.75$. $a_0:b_0:c_0=$ $0.852:1:0.873$. Each unit cell contains $U_{32}O_{96} \cdot 72\ H_2O$(?)	Kasolo, Katanga, Belgian Congo.	IV^2, 939	I, 627
Ianthinite	($2UO_2 \cdot 7H_2O$) This must be incorrect. Alters readily to Becquerelite and Schoepite.	~70	Orthorhombic, violet-black. Semi-metallic luster.	Chinkolobwe. Kasolo, Katanga, Belgian Congo.	IV^2, 941	I, 633

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TABLE 8 (continued)

Mineral	Composition	Per Cent Uranium	Optical and Crystallographic Properties	Occurrence	Described in	
					Doelter (1929)	Dana (1944)
Gummite	$(UO_3 \cdot nH_2O)$ (See text p.)	40-70	Yellow, orange, red, reddish-brown to black.	Found at many occurrences of uraninite and pitchblende. Bohemia, Saxony, Belgian Congo, N.C., Conn., Quebec, etc.	IV^2, 950	I, 622
Clarkeite	A Gummite. Essentially a hydrous uranium oxide with Pb, alkalis, alkaline earths.	~80	Reddish-brown.	Mitchell Co., N.C.		I, 625
Fourmarierite	Perhaps $PbO \cdot 4UO_3 \cdot 5H_2O$	60-70	Orthorhombic. Red to brown.	Kasolo, Katanga, Belgian Congo.	IV^2, 944	I, 628
Curite	A hydrated oxide of lead and uranium, perhaps $2PbO \cdot 5UO_3 \cdot 4H_2O$ The water is completely lost at 450°C.	~60-70	Orange-red. Orthorhombic a_0=12.52, b_0=12.98, c_0= 8.35. Unit cell contains $Pb_6U_{15}O_{51} \cdot 12H_2O$	Kasolo, Katanga, Belgian Congo	IV^2, 942	I, 629

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impossible to assign a definite constitution to these minerals. In Table 8 is listed a number of hydrated oxides which may have been formed by oxidation of pitchblende <u>in situ</u>. Since these minerals have been exposed to extensive leaching, small proportions of other elements are usually present. All of these elements except lead are considered to be admixtures rather than essential components of the mineral.

The pitchblende deposits of the Belgian Congo are particularly rich in alteration products. In these deposits the minerals listed in Table 8 are found in complex mixtures. Although the exact relationships are unknown, these minerals represent various stages of oxidation. The term gummite is applied to minerals which are essentially hydrated oxides of uranium of unknown composition and probably represent the final stages of oxidation and hydration of pitchblende. Small percentages of alkali metals, alkaline earths, rare earths, alumina, silica, etc. are commonly present, but these appear to be extraneous gangue materials. The physical and chemical properties of gummite vary widely.

2.5 <u>Secondary Uranium Minerals.</u> (For references and details see Gmelin, 1936a). The formation of uranates (as well as silicates, carbonates, phosphates, vanadates, arsenates, and sulfates of uranium) presumably involved the complete solution of uraninite or pitchblende and the subsequent deposition of the secondary compounds. Many of these secondary minerals must have formed in aqueous solutions near the critical temperature of water; but little is known at present about chemical reactions which take place under such conditions.

<u>Silicates and Uranates.</u> For convenience (and following Ellsworth's classification) these two classes of minerals are treated together. Their composition is often ill defined. A number of characteristic minerals of these types is described in Table 9.

TABLE 9

URANATES AND URANIUM SILICATES

Mineral	Composition	Per Cent Uranium	Optical and Crystallographic Properties	Occurrence	Doelter (1929)
Vandenbrandite (Uranolepidite)	$2CuO \cdot 2UO_3 \cdot 5H_2O$	~60	Triclinic crystals, dark green to black. $n_\gamma = 1.80$, $n_\alpha = 1.77$.	Kalongwe, Katanga along with kasolite, sklodowskite, etc.	
Uranospharite	$(BiO)_2U_2O_7 \cdot 3H_2O$	~50	Yellow rhombic crystals. Optically positive, $n_\alpha = 1.955$, $n_\beta = 1.985$ $n_\gamma = 2.05$	Schneeberg, Saxony, with walpurgin, trogerite, zeunerite, uranospinite.	
Soddyite	$12UO_3 \cdot 5SiO_2 \cdot 14H_2O$ or $5UO_3 \cdot 2SiO_2 \cdot 6H_2O$	~70	Yellow rhombic crystals, a:b:c= 0.7959:1:1.6685 Some prismatic crystals show strong pleochroism, dark violet along β axis, violet along γ axis, colorless along α axis.	Kasolo, Katanga, Belgian Congo along with kasolite.	IV^2, 946

TABLE 9 (continued)

Mineral	Composition	Per Cent Uranium	Optical and Crystallographic Properties	Occurrence	Doelter (1929)
Uranotile (Uranophane) (Lambertite)	$CaO \cdot 2UO_3 \cdot 2SiO_2 \cdot 7H_2O$	~ 50	Green or yellow rhombic, a:b:c=0.3075:1:1. Optically negative. Pleochroic.	Schneeberg, Joachimsthal; Rubelstadt, Silesia; Arendal, Norway; Villeneuve, Canada; Mitchell Co., N.C.; Katanga, Belgian Congo; Madrid, Spain; Pennsylvania.	II^2, 164
Sklodowskite (Chinkolobwite)	$MgO \cdot 2UO_3 \cdot 2SiO_2 \cdot 7H_2O$ A variety, cuprosklodowskite $CuO \cdot 2UO_3 \cdot 2SiO_2 \cdot 6H_2O$ is also found.	~ 50-60	Rhombic yellow crystals. n_α =1.613; n_β=1.635; n_γ =1.657. Pleochroic. a:b:c= 0.3114:1:1.0554	Kasolo, Katanga.	IV^2, 947
Kasolite	$3PbO \cdot 3UO_3 \cdot 3SiO_2 \cdot 4H_2O$	~ 40	Monoclinic yellow. a:b:c= 1.8566:1:1.0811 β =103°40'. n_α =1.89, n_β =1.90, n_γ =1.967	Kasolo, Katanga	IV^2, 949
Pilbarite	$PbO \cdot UO_3 \cdot ThO_2 \cdot 2SiO_2 \cdot 4H_2O$	~ 27%U ~ 30%Th		Pilabara Goldfield, Australia.	

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Recently the structure of uranotile, $CaO.2UO_3.2SiO_2.6H_2O$. has been determined by X-ray investigation, and it has been shown that uranotile forms rhombic crystals which are isomorphous with sklodowskite (Billiet, 1936).

Carbonates. For the most part, these minerals are poorly characterized. Uranothallite appears to be the most common mineral of this class. Little is known of their genesis; but it is likely that these minerals are not formed by a simple weathering process but rather by precipitation from aqueous solution. In Table 10 is listed a number of uranium carbonate minerals. The chemical formulae of these minerals are uncertain.

Sulfates. Minerals of this type (sometimes termed uranium ochers) are of rather frequent occurrence but are usually encountered only in very small amounts. Many of these minerals are water soluble and undergo alteration readily, which has made the assignment of chemical formulas difficult. The chemical identity of the minerals listed in Table 11 is therefore doubtful. Uranopillite appears to be the principal member. It is not unlikely that uraconite, voglianite, uranochalcite, and zippeite represent minor modifications of this mineral.

Uranium "Micas." A large number of uranium minerals of secondary (probably hydrothermal) origin has a composition which can be expressed by the general formula $M(II)(UO_2)_2(XO_4)_2$; where M=Cu, Fe, Pb, Mu, or UO_2, and X=P, As, or V, (See Table 4). It would appear reasonable for sulfates to be members of the same class, but the analytical data available do not allow this classification at present. For convenience (and because of their importance) the phosphates, arsenates, and vanadates are listed separately in Table 12, 13, and 14 respectively.

The optical and morphologic-structure crystallographic properties of a number of phosphates and arsenates present a peculiar problem. Torbernite, zeunerite, and artificial uranospinite are optically uniaxial. Autunite, uranocircite, and natural uranospinite are biaxial with rhombic symmetry. Trogerite appears to be monoclinic according to its optical properties but tetragonal according to its

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TABLE 10

URANIUM CARBONATE MINERALS

Mineral	Composition	Per Cent Uranium	Optical and Crystallographic Properties	Occurrence	Doelter (1929)
Rutherfordin	UO_2CO_3. (established for only one sample.)	~ 75	Rhombic(?) yellow crystals.	Morogoro, East Africa.	I, 547
Uranothallite Liebigite	$2 CaO \cdot UO_3 \cdot 3CO_2 \cdot 10 H_2O$	~ 30	Apple green rhombic crystals, a:b:c= 0.954:1:0.783. Strongly birefringent $n_\alpha = 1.50$, $n_\beta = 1.503$, $n_\gamma = 1.537$.	Joachimsthal; Johanngeorgenstadt, Saxony; Adrianople, Turkey.	I, 545 I, 546
Schroekingerite	A carbonate of Ca and U of unknown structure. Optical properties differ from those of uranothallite.	No analyses	Presumably monoclinic, green. Optically negative. $n_\alpha = 1.658$, $n_\beta = 1.687$ $n_\gamma = 1.690$ Pleochroic.	Joachimsthal, Bohemia. Bedford, N.Y. Wyoming.	I, 546
Randite	Probably identical with liebigite			Philadelphia, Pa.	I, 547
Voglite	May be $Cu(UO_2)(CO_3)_2 \cdot 10H_2O$	~ 30	Apple green to dark green, probably rhombic. Optically positive. Pleochroic.	Joachimsthal, Bohemia; Ferghana, Turkestan.	I, 546

morphology and structure crystallography. It has been conjectured that all these minerals are tetragonal, despite the anomalies which result from such an assumption (Goldschmidt, 1899). This view is reinforced by the fact that uniaxial specimens of trögerite and uranospinite have occasionally been found in nature. The anomalous optical properties of trögerite have been explained by Goldschmidt as having resulted from distortion of the crystal lattice of this mineral by zeunerite and distortion of the crystal edges and faces by small flakes produced by displacement of the cleavage lamellae. The problem would benefit by a renewed investigation.

Few chemical studies have been made on the minerals of this class. Solubilities have been determined for most of them, and some studies on the dehydration of the hydrated minerals have been made. A study of the alteration of autunite and zeunerite has also been made (Starik, 1941). The relationship encountered in torbernite deserve special mention (Rinne, 1901).

$$\text{Torbernite} \xrightleftharpoons{60-65^\circ} \text{Metatorbernite I} \xrightleftharpoons{100^\circ} \text{Metatorbernite II}$$

$Cu(UO_2)_2(PO_4)_2 \cdot 12H_2O$	$Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$	$Cu(UO_2)_2(PO_4)_2 \cdot 4H_2O$
Tetragonal, uniaxial, Optically negative.	Tetragonal, Optically positive.	Rhombic, biaxial, Optically negative.

This transformation is, as might be expected, also a function of pressure (Hallimond, 1913). The minerals which contain calcium in place of copper (autunites) behave in a similar fashion.

Carbonaceous Uranium Minerals. A number of occurrences of uranium-rich carbonaceous materials are known. Kolm is a peat-like coal which occurs as disc-shaped lenses in an alum shale (Wickman, 1942; Wells and Stevens, 1931) in Cambrian slates of the Västergotland plains in Sweden. On combustion it leaves a residue of about 27 per cent ash which has a uranium content up to 2.87 per cent (average 1.87 per cent U_3O_8) and has been used as a commercial source of radium. Numerous asphalts are also known which contain small amounts of uranium. Thucholite is a substance of unknown chemical structure which contains C, H, O, H_2O, Th, U, Ce, Y, Er, V, P, Ca, Si, and many other common elements. It is found in Canada.

Despite the very wide distribution of the large number of minerals described in this section, only carnotite has been of considerable economic importance in the past. This mineral is discussed further in section 3.3.

2.6 <u>Fluorescence of Uranium Minerals.</u> (Meixner, 1939, 1940a, b; Haberlandt, 1935). It has been known for a long time that many uranium minerals fluoresce. With rare exceptions strong luminescence is observed only with secondary uranium minerals. Few uranium minerals of pegmatitic origin show luminescence. The strongly luminescent uranium minerals are phosphates, sulfates, and arsenates, which show an intense and characteristic yellow-green color under ultra-violet light. These minerals include autunite, uranospinite, uranocircite, and uranopillite. The uranium carbonates, schroeckingerite and uranothallite, exhibit an intense green fluorescence. Weakly luminous with a yellowish color are carnotite, dewindite, soddyite, becquerlite, and some specimens of zipeite, uranotile, gummite, and torbernite, although the last named minerals are usually not luminescent. The uranium silicates and the uranium micas containing Cu, Pb, Bi, Mn and Fe are non-luminescent; this is true of zeunerite, fritzcheite, bassetite, trögerite, phosphouranylite, tjujamunite, walpurgite, cuprosklowdowskite, ianthinite, kasolite, curite, fourmanierite, johanite (gilpinite), uranosphaerite, betafite, hatchettolite, and ellsworthite. No definite relationship between fluorescence and chemical structure can be established at present.* It has been observed that spraying non-luminous uranium compounds with acids, such as H_2SO_4, HNO_3, HCL, CH_3COOH, or H_3PO_4, causes them to luminesce under ultra-violet light. Of these acids, phosphoric acid has only a weak effect, while acetic acid produces the most intense fluorescence (Melkov and Sverdlov, 1941).

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*A survey of fluorescent uranium minerals given recently by DeMent (1945) differs in some details from the results of Meixner quoted above.

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TABLE 11

URANIUM SULFATE MINERALS

Mineral	Composition	Per Cent Uranium	Optical and Crystallographic Properties	Occurrence	Doelter (1929)
Gilpinite Johannite	$CuO \cdot 2UO_3 \cdot 2SO_3 \cdot 7H_2O$, or $(Cu,Fe,Na_2)O \cdot UO_3 \cdot SO_3 \cdot 4H_2O$, or $CuO \cdot 3UO_3 \cdot 3SO_3 \cdot 4H_2O$	~ 40-50	Triclinic, a:b:c= 1.218:1:0.6736, $\alpha = 69°24'$ $\beta = 124°56'$ $\gamma = 132°56'$ Strongly pleochroic, $n_\alpha = 1.630$, $n_\beta = 1.689$, $n_\gamma = 1.616$. Pale greenish yellow to canary yellow.	Gilpin Co., Col. Johanngeorgenstadt, Saxony; Joachimsthal, Bohemia; Cornwall, England; Middletown, Conn.	IV^2, 649
Uraconite	Hydrous sulfate of uranium and copper	~ 60-70	Amorphous, orange or yellow	Joachimsthal, Cornwall, England.	IV^2, 651
Uranopillite	$CaO \cdot 8UO_3 \cdot 2SO_3 \cdot 25H_2O$	64	May be monoclinic. Lemon yellow. $n_\alpha = 1.621$, $n_\beta = 1.623$, $n_\gamma = 1.631$	Joachimsthal, Bohemia; Johanngeorgenstadt, Saxony.	IV^2, 651

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TABLE 11 (continued)

Mineral	Composition	Per Cent Uranium	Optical and Crystallographic Properties	Occurrence	Doelter (1929)
Voglianite	Probably a variety of uranopillite. There are known both a calcium variety and a copper variety of voglianite.	67	Apple green.	Joachimsthal, Bohemia.	IV^2, 652
Uranochalcite	Hydrous sulfate of uranium, copper and calcium. Related to uranopillite.	~ 30	Grass green. Optically positive. $n_\alpha = 1.655$, $n_\gamma = 1.662$. Pleochroic.	Joachimsthal, Bohemia.	IV^2, 654
Zippeite	$2UO_3 \cdot SO_3 \cdot 3H_2O$. Some samples contain Cu. See voglianite	~ 50-60	May be monoclinic. $n_\alpha = 1.630$, $n_\beta = 1.689$, $n_\gamma = 1.739$. Pleochroic.	Joachimsthal, Bohemia; Fruita, Utah.	IV^2, 655

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TABLE 12

URANIUM PHOSPHATE MINERALS

Mineral	Composition	Per Cent Uranium	Optical and Crystallographic Properties	Occurrence	Doelter (1929)
Phosphor-uranylite	$(UO_2)_3(PO_4)_2 \cdot 6H_2O$	60-64	Deep lemon yellow, Probably rhombic. Optically negative. $n_\alpha = 1.691$, $n_\beta = 1.720$, $n_\gamma = 1.720$. Pleochroic	Mitchell Co., N.C.	III[1], 573
Autunite	$Ca(UO_2)_2(PO_4)_2 \cdot 12H_2O$	~ 50	Small, green to yellow crystals. Rhombic, a:b:c= 0.9376:1:2.8530, may actually be tetragonal. Optically negative, weak double refraction. $n_\alpha = 1.557$, $n_\beta = 1.575$, $n_\gamma = 1.553$	Autun, France; Madagascar; Falkenstein, Saxony; Conn.; Mass.; Pa.; N.C.; S.C.; Utah; China; Cornwall, England.	III[1], 573
Bassetite	The usual formula given is $Ca(UO_2)_2(PO_4)_2 \cdot 8H_2O$; Meixner claims (probable correctly) that it really is $Fe(UO_2)_2(PO_4)_2 \cdot nH_2O$.	~ 50	Yellow, monoclinic crystals: a:b:c= 0.3473:1.0:0.3456. $\beta = 89^\circ\ 17'$ optically biaxial, $2E = 110^\circ$. $n_\beta = 1.574$ $n_\gamma = 1.580$. Pleochroic.	Cornwall, England.	IV[2], 959

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TABLE 12 (continued)

Mineral	Composition	Per Cent Uranium	Optical and Crystallographic Properties	Occurrence	Doelter (1929)
Uranocircite	$Ba(UO_2)_2(PO_4)_2 \cdot 8H_2O$	~ 50	Rhombic. Yellow-green, resembling autunite. Doubly refracting, optically negative. $n_\alpha = 1.61$, $n_\beta = 1.623$, $n_\gamma = 1.623$. Pleochroic	Schneeberg, Saxony.	III ^{1}, 575
Saleite	$Mg(UO_2)_2(PO_4)_2 \cdot 8H_2O$	~ 60	Yellow. Rhombic with pseudo-tetragonal symmetry. Optically negative. $n_\alpha = 1.559$, $n_\beta = 1.570$, $n_\gamma = 1.574$	Chinkolobwe, Katanga.	
Fritzcheite	$Mn(UO_2)_2(PO_4)_2 \cdot 8H_2O$ Also contains significant amounts of V.		Reddish-brown quadratic tables. Resembles autunite. Apparently tetragonal-prismatic.	Erzegebirge, Saxony; Autun, France; Neudeck, Czechoslovakia.	III ^{1}, 575
Torbernite (Chalcolith)	$Cu(UO_2)_2(PO_4)_2 \cdot 12H_2O$	~ 50	Tetragonal, a:c=1:2.97. Green. Weakly double refracting. Optically uniaxial. Negative. $n_\omega = 1.6323$, $n_\epsilon = 1.5745$. Pleochroic.	Found frequently with autunite. Johanngeorgenstadt, Saxony; Schneeberg, Saxony; Cornwall; Vielsalm, Belgium; Joachimsthal, Zinnwald, Bohemia; Portugal.	III ^{1}, 576

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TABLE 12 (continued)

Mineral	Composition	Per Cent Uranium	Optical and Crystallographic Properties	Occurrence	Doelter (1929)
Meta-Torbernite I	$Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$ See Text	30-50	Light-green to apple-green. Tetragonal, a:c=1:2.28. Optically positively uniaxial. Pleochroic. For Na light, n_ω=1.623, n_ϵ =1.625.	Gunnislake and Tincroft, Cornwall; Katanga, Belgian Congo; Temple Mountain, Utah; Spain.	IV^2, 960
Uranospathite	Probably autunite with different hydration.		Rhombic, pseudo-tetragonal, yellow to green. Biaxial, n_γ =1.521, n_β =1.510, Pleochroic	Redruth, Cornwall.	IV^2, 959
Parsonite	$2PbO \cdot UO_3 \cdot P_2O_5 \cdot H_2O$	~ 25	Monoclinic or triclinic. Light brown. Weak double refraction. n_α =1.85 n_γ =1.862	Kasolo, Katanga.	IV^2, 962
Dewindite (Stasite)	$3PbO \cdot 5UO_3 \cdot 2P_2O_5 \cdot 12H_2O$	~ 50	Canary yellow. Rhombic, doubly refracting optically positive n_α =1.762, n_β =1.763.	Kasolo, Chinkolobwe, Katanga.	IV^2, 964
Dumontite	$2PbO \cdot 3UO_3 \cdot P_2O_5 \cdot 5H_2O$	45	Ocher yellow in large crystals. Prismatic. b:c=1:1.327 Strong pleochroism. Doubly refracting, optically positive. n_α =1.88, n_β =1.89	Closely associated with torbernite at Chinkolobwe, Katanga	IV^2, 963

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TABLE 13

URANIUM ARSENATE MINERALS

Mineral	Composition	Per Cent Uranium	Optical and Crystallographic Properties	Occurrence	Doelter (1929)
Trogerite	$(UO_2)_3(AsO_4)_2 \cdot 12H_2O$	56.2	Golden yellow tetragonal, a:c=1:2.16, or monoclinic a:b:c=0.463:1:0.463. (see text) Optically negative, biaxial. n_{α} =1.585, n_{β} =1.630, n_{γ} =1.630. Other samples show one axis, n_{ω}=1.624, n_{ε} =1.580.	Schneeberg, Saxony. Bald Mt., Black Hills, S.D.	III^1, 730
Uranospinite	$Ca(UO_2)_2(AsO_4)_2 \cdot 8H_2O$ Isomorphic with autunite.	50	Rhombic or tetragonal. Yellow to apple green. Biaxial negative. Optical anomalies. (see text)	Schneeberg, Saxony. Utah.	III^1, 730
Zeunerite	$Cu(UO_2)_2(AsO_4)_2 \cdot 8H_2O$	50-53	Grass-green, tabular tetragonal crystals. Uniaxial negative. n_{ω}=1.643-1.635 n_{ε} =1.623-1.615 Pleochroic.	Schneeberg and Erzgebirge, Saxony. Cap Garronne, France. Cornwall, England.	III^1, 731
Walpurgite	$Bi_{10}(UO_2)_3(OH)_{24}(AsO_4)_4$	16.5	Orange, honey and straw-yellow. Triclinic, pinacoidal, or monoclinic. Biaxial, negative. Very high refractivity. n_{α}=1.90, n_{β} =2.00 n_{γ} =2.05 a:b:c.=0.6862:1	Schneeberg, Saxony. Portugal.	III^1, 729

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TABLE 14

URANIUM VANADATE MINERALS

Mineral	Composition	Per Cent Uranium	Optical and Crystallographic Properties	Occurrence	Doelter (1929)
Ferghanite	$UO_3 \cdot V_2O_5 \cdot 6H_2O$ (Perhaps identical with tjujamunite)	65	Apparently rhombic, a:b=0.75:1. Sulfur-yellow. Uniaxial. Weak double refraction and low refractive index. Practically no pleochroism.	Ferghana, Turkestan.	III^1, 849
Tjujamunite	$CaO \cdot 2UO_3 \cdot V_2O_5 \cdot 4H_2O$	50-60	Rhombic, a:b: =0.77:1. Canary-yellow to green. Biaxial. Optically negative. Very high index of refraction and double refraction. $\eta_\alpha=1.67$, $\eta_\beta=1.87$, $\eta_\gamma=1.895$. Pleochroic	Ferghana, Turkestan; Paradox Valley, Colo.; Hery Mts., Utah.	III^1, 848
Rauvite	$CaO \cdot 2UO_3 \cdot 6V_2O_5 \cdot 20H_2O$	17	Reddish purple. Anisotropic. Index of refraction ~1.88	Green River, Utah.	IV^2, 968
Carnotite	$K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$	~ 50	Rhombic, a:b=0.81:1. Yellow, birefringent, optically negative. $\eta_\alpha=2.06$, $\eta_\beta=2.06$, $\eta_\gamma=2.06$-2.06. Pleochroic.	Colorado; Utah; S. Australia. As a powdery impregnation in sandstone. Pa.; Katanga.	III^1, 844
Uvanite	$2UO_3 \cdot 3V_2O_5 \cdot 15H_2O$	33	Brownish-yellow, rhombic, biaxial. $\eta_\alpha=1.817$, $\eta_\beta=1.879$, $\eta_\gamma=2.057$. Pleochroic.	Temple Mt., Utah.	IV^2, 967

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These observations are of practical importance in prospecting. In addition to fluorescence techniques, methods depending on the detection of gamma rays also are of increasing importance in prospecting for uranium deposits. For examples see Dreblow (1942).

3. Economic Mineral Deposits of Uranium

Before 1942 no mining operations were conducted solely for the sake of obtaining uranium. Uranium ores were mined primarily for their radium content. Appreciable quantities of uranium were obtained incidentally in vanadium production from carnotites. No large market existed for uranium compounds; the economy of mining any particular ore was determined exclusively by the market value of its radium or vanadium content. With the discovery of nuclear fission and its technical applications, uranium became a material of tremendous importance. The economic criteria formerly applied now became irrelevant, and occurrences of uranium which were not exploited in the past acquired a new importance. It is not possible to describe here the present mining operations or to give the quantity of ore produced, the estimated reserves, or the results of the very intensive prospecting which has been carried out since 1940. When and if such information becomes available, it should not be difficult to integrate it with the older data presented here.

Although uranium is not an excessively rare component of the earth's crust, relatively few uranium deposits were worked in the past. The two richest known deposits are those at Great Bear Lake in Canada and at Katanga in the Belgian Congo. There also are deposits of commercial importance in Czechoslovakia and in the United States. Several minor deposits have been worked at one time or another.

3.1 Great Bear Lake Pitchblende Deposits, Northwest Territories, Canada.

(Kidd, 1932, 1936; Krusch, 1937a). Great Bear Lake is exactly on the Arctic Circle, east of the Mackenzie River, 1380 miles by boat or 800 miles by air from the rail head at Waterways, Alberta. The deposits were discovered in 1930 at Echo Bay on the east side of the lake.

TABLE 15

AN ALPHABETICAL REFERENCE LIST OF URANIUM MINERALS

Mineral	Table	Mineral	Table
Ampangabeite	7	Fourmarierite	8
Autunite	12	Fritzcheite	12
Bassetite	12	Gilpinite	11
Becquerelite	8	Gummite	8
Betafite	7	Hatchettolite	7
Bloomstrandinite	7	Ianthinite	8
Bloomstrandite	7	Ishikawaite	7
Brannerite	7	Johannite	11
Bröggerite	5,6	Kasolite	9
Carnotite	14	Lambertite	9
Chalcolith	12	Liebigite	10
Chinkolobwite	9	Metatorbernite	12
Clarkeite	8	Microlite	7
Cleveite	5,6	Nivenite	5,6
Curite	8	Parsonite	12
Delorenzite	7	Phosphoruranylite	12
Dewindite	12	Polycrase	7
Dumontite	12	Priorite	7
Ellsworthite	7	Pyrochlore	7
Euxenite	7	Randite	10
Ferghanite	14	Rauvite	14
Fergusonite	7	Rutherfordin	10

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TABLE 15 (continued)

Mineral	Table	Mineral	Table
Rutherfordite	7	Trogerite	13
Saleite	12	Uranoconite	11
Samarskite	7	Uraninite	5,6
Samiresite	7	Uranochalcite	11
Schoepite	8	Uranocircite	12
Schroeckingerite	10	Uranolipidite	9
Sklodowskite	9	Uranophane	9
Soddyite	9	Uranopillite	11
Stasite	12	Uranospathite	12
Thorianite	5	Uranospharite	9
Tjujamunite	14	Uranospinite	13
Toddite	7	Uranothallite	10
Torbernite	12		

The uranium occurs as pitchblende in a highly mineralized area. The ore is found in replacement lodes and stockworks along fracture and shear zones that traverse pre-Cambrian sedimentary rocks and altered volcanic rocks cut by granodiorite. Several zones are known ranging from 30 to 800 feet wide. The process of mineralization was apparently very complex; some 40 minerals have been recognized. The principal minerals of the area are pitchblende, native silver, pyrite and chalcopyrite. Compounds of iron, cobalt, nickel, copper, lead, zinc, silver, molybdenum, bismuth, and manganese are also found. Kidd and Haycock (1935) consider this deposit to have been formed from hydrothermal solutions released by a congealing granite magma. The mineralization was in several stages; the pitchblende appears to have been deposited in the earliest phase of the hydrothermal process, followed by Co-Ni, the Pb-Zn-Cu, and finally Cu-Ag. The pitchblende may represent colloidal deposition in cavities. A similar sequence is postulated by Furnival (1939) for the Contact Lake deposits in the Great Bear Lake area. The pitchblende content of the ore shipped from the Eldorado mines at Great Bear Lake varies from 30 to 62 per cent U_3O_8 (Parmelee, 1938).

The only deposit other than the Great Bear Lake which has been worked extensively in Canada is at Wilberforce Station, Cardiff Township in Haliburton County, Ontario. The mineral is a uraninite which occurs in pegmatites and has an average uranium content of only about 0.1 per cent. (Ellsworth, 1932a). Numerous small pegmatite deposits are described by Ellsworth, none of which seem to have been exploited.

3.2 <u>Belgian Congo Deposits</u> (Hess, 1934). Until the development of the Canadian Great Bear Lake deposits, the pitchblende deposits at Chinkolobwe, Katanga in the Belgian Congo were the world's leading source of uranium and radium. The deposits were discovered in 1915. Systematic mining began in 1921. The deposit is in isolated silicified breccia 15 miles south of Kambove on the divide between the drainage basins of the Mura and Panda Rivers. The rocks form a ridge 40 to 45 feet high and 250 feet long. The uranium is in some case very close to the surface; solid masses of pitchblende have been found under only a few centimeters of top soil.

Since the entire region is heavily mineralized, a magmatic source for the solutions from which the deposits formed cannot be doubted. The post rock containing the ore deposits resembles that observed in numerous copper deposits in Katanga. It consists of altered carbonate rocks of the "Sérle des Mines" which is surrounded by comparatively undisturbed orgillaceous and talcose schists (Kundelungu formation). In addition to uranium, there are found at Chinkolobwe copper, cobalt, nickel, vanadium, iron, and precious metals. None of these elements is found in the Kundelunga formation itself. The "Sérle des Mines" in which the uranium is found is about 200 meters (656 feet) thick and consists mainly of dolomitic limestone. The uranium minerals are free of visible gangue materials. The pitchblende veins are capricious and can rarely be followed more than a dozen meters. A vein a few centimeters wide may suddenly swell to a meter and yield masses of compact pitchblende weighing several tons. To minimize losses, the entire mass of rock is removed during mining operations. The veins tend to parallel the main faults in the dolomite although they are not in them. The occurrences are so irregular that it is difficult to make estimates of the reserves.

The disseminations are found a short distance outward from the veins. The pitchblende in them is altered completely into other uranium minerals. Other disseminations made up principally of torbernite have no apparent relation to the veins. More than half of the uranium in the oxidized zone is in the form of torbernite, but numerous other oxidation products of pitchblende (Buttgenback, 1935) also have been observed here. Kosolite and sklodowskite occur as disseminated minerals, with the sklodowskite lining cavities in the rock similarly to the torbernite. Uraninite is also present (Stanfield, 1934). Small quantities of copper, cobalt, and nickel sulfides, which are present in considerable quantities in other parts of the "Sérle des Mines," are found in the uranium veins.

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Molybdenum (as MoS_2 and wulfenite) has also been observed.

The mineralization sequence is complex. According to Thoreau and de Terdonck (in Hess, 1934) the ores were formed by siliceous solutions entering carbonate rocks and producing a series of silicate minerals,

TABLE 16

PER CENT COMPOSITION OF TWO SAMPLES OF AFRICAN ORE CONCENTRATES*

Component	I	II
U_3O_8	69.02%	8.13%
V_2O_5	0.03	0.22
SO_3	1.27	0.37
MoO_3	0.74	0.30
PbO	6.09	0.91
SiO_2	10.53	51.40

*Dried at 110°C.

pitchblende was deposited next, and this was followed by a succession of sulfide minerals. Later processes altered the ores and yielded many secondary minerals. The deposition of pitchblende is thus considered to be a higher temperature phase of the copper mineralization. This mineralization sequence appears to be common in this region. Pitchblende or its alteration products have been found in seven deposits from Ruashi on the southeast to the extreme northwest of the copper zone, passing through Lurshia and Kambove (Vandendriessche, 1935).

According to published statements, the average ore shipped from the Belgian Congo mines has a U_3O_8 content of 40 per cent. Ore with lower values is left at the mine. Partial composition of some samples is given in Table 16. Krusch (1937b) estimated that the total radium production of the Belgian Congo totaled

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323 grams from 1922 to 1934, from which it can be estimated that about 950 tons of uranium were removed from the mine during this period. According to the "Minerals Yearbook for 1943" 700 tons of U_3O_8 were produced in 1943. No really accurate picture of the mining operations is available.

3.3 Colorado and Utah Deposits (Hess, 1933; Krusch, 1937c). The carnotite deposits in Colorado and Utah are the only deposits in the United States from which uranium has hitheroto been obtained commercially. There are uraninite occurrences in North Carolina, Connecticut, New Hampshire (Schaub, 1937), the Black Hills of South Dakota, at Barringer Hill in Texas, and various other places; but the limited size of these deposits seems to have precluded commercial development in the past.

The carnotite deposits cover an area 130 miles long and 50 miles wide in southwestern Colorado and southeastern Utah, and are to be found from Coal Creek near Meeker, Colo. to Carizo Mountain on the line between New Mexico and Arizona, and from Huerfano County, Colorado westward to Silver Reef in the southeastern corner of Utah. On the Colorado Plateau (west of the Rocky Mountains, east of the San Rafael Swell, and south of the Unita Mountains) are located patches of sandstone that carry very large quantities of uranium and vanadium minerals widely distributed. The ore occurs in seams and pockets frequently as an incrustation or impregnation in sandstone. The vanadium is much in excess of the uranium. The greatest deposits are reputed to be in the area between Paradox Valley and the San Miguel River. The sandstone containing the ores is about 100 feet thick in places. It is estimated that in this particular region before erosion the ore-bearing belt was at least 11.3 miles in length and about 4 miles wide.

The uranium minerals found in this general region are principally carnotite, but other complex vanadium-uranium minerals (uranite, rauvite, zeunerite) also are found. These are of course not primary minerals. The deposits appear to be of sedimentary origin (Fischer, 1937). The ore is invariably associated with fossil logs, plant remains, and saurian bones, or with asphalt. According to Hess, the process of formation of the Colorado Plateau deposits may be reconstructed as follows. It can be assumed that the uranium and vanadium in this region originally existed in veins which also contained pyrites. Oxidation resulted in the formation of sulfuric acid and ferric sulfate which then dissolved the uranium and vanadium as sulfates. The present deposits of carnotite occur in cross-bedded sandstones of Morrison age. The nature of the sandstones indicates an origin in shallow waters with shifting islands, spits, and shores. The sulfate solutions of uranium and vanadium entered these shallow waters, where abundant algae vegetation was macerated by wind and waves. Logs were swept into the shallows by rivers and stranded there. Around them were packed sand and macerated vegetation. The organic matter is thought to have concentrated the uranium and vanadium from the very dilute solutions either by reduction or by ion displacement. In time, after organic remains became petrified, replacement of organic material by calcite and then by uranium-vanadium minerals may also have occurred. The importance of the vegetable matter in the formation of carnotites is indicated by the exceedingly high concentration of uranium and vanadium in some petrified logs formed near the San Miguel River. For example, one petrified log 100 feet long and 4 feet in diameter contained roughly 105 tons of carnotite. Fischer (1937) suggests the possibility that micro-organisms may also have played a role in the concentration of the uranium and vanadium from dilute solutions.

The ores mined in this region have averaged 1.25 to 1.5 per cent U_3O_8 and about 3.5 per cent V_2O_5. The composition of typical carnotite ore is given in Table 17. Undoubtedly, considerable quantities of ore which was formerly considered to be too low grade to justify mining exist in this region. It was estimated in "Minerals Resources of the U. S." for 1930 that there were at least 3000 tons of recoverable uranium present in the whole region.

The carnotite deposits are unique geologically. The largest known vanadium deposits in the world (at Minasragra, Peru) contain no uranium despite the presence of organic matter such as asphalt. The Ferghana deposit of carnotite and tjujamunite in Turkestan, about which little has been published, appears to be similar to the American carnotite deposits.

TABLE 17

PER CENT COMPOSITION OF CARNOTITE ORE

Component	Range
V_2O_5	2.25-10.5%
U_3O_8	0.25-3.0
SiO_2	70-80
$Fe_2O_3 + Al_2O_3$	5-12
$CaCO_3$and + $CaSO_4$	Trace to 3
$BaCO_3 + BaSO_4$	Trace to 2
$CuCO_3 + CuS$	Trace to 2
Pb	~1
Na, K, Mg, Ra, etc.	Small amounts
H_2O	5-25

Prior to the development of the carnotite deposits small amounts of uranium were mined in Gilpin County, Colorado, where pitchblende is found associated with pyrite and zinc and lead sulfides (Bastin, 1915; Alsdorf, 1916). The deposits occur in the midst of the oldest gold fields of Colorado. They lost their commercial significance with the development of the carnotite deposits. Gilpin County supplied only 10-20 tons of ore with 60 per cent U_3O_8 content from 1871 to 1916. From 1921 to 1926 (the only period for which reliable statistics exist) the total production was 165 tons. The real extent of these deposits is unknown. It was estimated in 1915 that they were capable of supplying 10 g of radium or some 30 tons of uranium.

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The leading domestic producer of uranium ores today is the United States Vanadium Corporation of Uravan, Colo. A new plant was built in 1940 for the recovery of uranium from the tailings accumulated from the vanadium operations. The total capacity of the plant is 50 tons of tailings a day, but details of uranium recoveries have not been published (Minerals Yearbook, 1940).

3.4 <u>Uranium Deposits of Minor Significance</u>. In addition to the three major deposits discussed above, there are many localities, scattered all over the earth, where uranium has been obtained at one time or another. These are briefly enumerated below.

<u>Czechoslovakia and Germany</u>. (Moore and Kittril, 1913; Krusch, 1937d). The Erzgebirge is a mountainous area along the boundary between Saxony in Germany and Bohemia in Czechoslovakia. In this area pitchblende and many other uranium minerals have been found at Schneeberg, Annaberg, and Johanngeorgenstadt in Germany and particularly at Joachimsthal (Jachymov) in Bohemia. The deposits appear to be similar in nature and origin in all these places. The most important area is that at Joachimsthal; it furnished the uranium from which radium was first extracted by M. and Mme. Curie. The geology of this region has been much studied. At the present time the historical and scientific aspects of this region are more important than its economic role.

Silver and cobalt have been mined at Schneeberg in Saxony since the end of the fifteenth century. Here pitchblende is associated chiefly with native bismuth and bobalt and nickel minerals. The minerals are found in the mountains near the towns of Schneeberg, Annaberg, and Johanngeorgenstadt in a network of veins in altered slate cut by granite masses. The gangue minerals are calcite, ankerite, barite, fluorite, and quartz. The mineralization of this region is very complex (Kohl, 1941).

At Jachymov (Joachimsthal) (Schneiderhöhm, 1938, 1939) the ore deposits in a mica schist interbedded with lime schist and crystalline limestone with the whole intruded by large masses of late Palaeozoic granite and cut by numerous dikes of quartz porphyry and basalt. The mineral veins of hydrothermal origin cut the quartz porphyry dikes and are themselves cut by the basalt. These minerals veins are usually six inches to two feet thick. The character of the mineralization varies widely. Silver, nickel, bismuth, and arsenic minerals are present together with copper, lead, zinc, cobalt, and iron. Redeposition occurred in three stages: first cobalt and nickel, then uranium, and lastly silver.

The present economic significance of these deposits is not great. The average uranium content of the ore from Jachymov is about 1 per cent, which is concentrated to 42 per cent U_3O_8. Based on the radium production figures, the mines have an annual capacity of about 20 tons of uranium per year (Krusch, 1937e).

Other small uranium deposits in Germany are described by Kohl (1933).

Portugal. (Moore and Kittril, 1913a; Krusch, 1937f). The uranium-bearing zone lies in the area of massive granite that occupies nearly the entire northern part of Portugal between the desert of Gallice and Castello Branco and reaches into the provinces of Minho, Tras-os-Montes and Beira The richest parts of the district are between the towns of Guarda and Sabugal and in the region of Villar-Formosa. The veins near Guarda are especially rich in wolframite.

The uranium minerals occur in narrow pegmatite dikes 0.5 to 1 meter in width. In the Rosmanefra region tungsten and tin in addition to uranium are present in commercially valuable amounts. Autunite, $Ca(UO_2)_2(PO_4)_2 \cdot 12H_2O$, appears to be the oldest uranium mineral here, it is accompained by numerous alteration products (Lepierre, 1933). The autunite is present as small groups of square tablets of an intense yellow color, in small plates, as a yellow coating on the rock, or still oftener as bright yellow specks disseminated throughout the dull yellowish rock. In the clay parts of the veins the uranium mineral often is invisible and can be detected only by it radioactivity. There are also blotches

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on the surface of the granite which give it an intense yellow color, although the actual uranium content of the granite is very low. The uranium content of the veins varies within very wide limits. Ore containing 2 per cent U_3O_8 is considered excellent, and that carrying 1 per cent is good average ore (Dorpinhaus, 1914; see also Ebler and Bender, 1915).

In the period from 1913 to 1935 about 4000 tons of ore averaging 1 to 2 per cent U_3O_8 were exported. The ore reserve in the Maceira-Guarda region was estimated in 1926 to be 1600 metric tons with 0.5 to 0.7 per cent U_3O_8 content. ("Mineral Resources of the U. S., 1926).

England. (Dines, 1930; Ellsworth, 1932b). The mineral deposits in Cornwall and South Devon have been mined from antiquity for tin and copper. The main occurrences of uranium are at Wheal Trenwith, St. Ives, and the South Terras Mine, St. Stephen. This last deposit is the only known vein in Cornwall in which the chief minerals are the uranium compounds. This vein contained enough uranium to warrent mining. The South Terras vein lies in slate intruded by granite. The adjacent veins are mainly tin-and copper-bearing, and others carry such minerals as ores of cobalt, nickel, lead, uranium, and iron, and occasionally some arsenic and copper pyrites. It is likely that the veins high in uranium, cobalt, and nickel are not contemporaneous with those carrying iron.

The uranium lode at South Terras is a typical fissure vein with quartz gangue, which varies between 0.5 and 3.5 feet in thickness. The uranium production has never been large. The average uranium content of the ore mined is about 1 per cent. Probably not more than 4000 tons of ore averaging 1 per cent U_3O_8, have been mined here since 1873 (Krusch, 1937g).

Union of Soviet Socialist Republics. (Krusch, 1937h). Numerous small deposits of uranium have been reported in Russia. Uraninite has been found in Northern Karelia, near Zhitomer, at Ekaterinoslav (Dnepropetrovsk) in the Ukraine, and in a number of other localities (For references see Gmelin, 1936b).

These are in all probability small deposits which have never been exploited. The most important known deposit of uranium in Russia is in the province of Ferghana, in Russian Turkestan (the region now included in the Kirgiz Soviet Republic). The principal mineral in this deposit is tjujamunite, which is closely related to (if not identical with) carnotite. The ore formation is reputed to resemble the Utah and Colorado deposits. About 1000 tons of ore (averaging 8.3 per cent V, 1 per cent U_3O_8, and 3.7 per cent Cu) were mined from 1904 to 1914; and it was estimated in 1925 that approximately 5000 tons or ore (about 60 tons of U) still remained in the bed (Chirvorisky, 1923).

Although intensive prospecting has been carried out, little has been reported in the literature concerning the results of this search. A deposit of uranium-vanadium ore has been discovered at Taboskov 69 km north of Andizhan in Kirghizia (about 100 miles northeast of Ferghana). The vein is about one meter thick and 250 meters long and it averages about 3 per cent U_3O_8.* Large deposits of uranium are also reputed to have been uncovered in Transcaucasia. The ore resembles carnotite and averages 3 per cent U_3O_8. The Caucasian deposit is said to be larger than those at Tjujamujan and Taboskov.** The opinion has been expressed (Tyurin, 1944) that no uranium will be found in the Karataw vanadium deposits.

The Radium Institute of the Academy of Sciences of the U.S.S.R. has been very active, and Russia is reputed to possess a considerable radium industry about which very few details are available in this country (Monsavoff, 1943.

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* "Economic Review of the Soviet Union," IX, 276 (1934).

** U. S. Bur. Foreign Domestic Commerce, "Russian Economy," p. 13, 9-15-34, New York (1935).

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Bulgaria. There are two known deposits of uranium in Bulgaria. At Goten (13 miles northeast of Sofia) 25,000 tons of uranium ore with 2 per cent U has been discovered. The ores consist of torbernite and metatorbernite I and II, which must have originated through hydrothermal action (Konjarov, 1938). Extensive deposits of autunite have been reported near the village of Streltsch (Minerals Yearbook, 1935)

Norway and Sweden. The pegmatite deposits in Norway north of Christiansund and Evji have been known and studied for a long time, but are of no economic importance. In Sweden the state-owned oil-shale plant at Kvantorp in the Province of Narke utilizes Kolm-carrying slates which yield a residue containing uranium and other metals (Minerals Yearbook, 1943; Krusch, 1937i).

Madagascar (Krusch 1937j). Madagascar is one of the few places where pegmatitic uranium minerals have been mined in the past. The majority of these occur in the older rock complex in the middle of the island. The uranium minerals found there are euxenite-polycrase, betafite, ampangabeite, fergusonite, samarskite, and bloomstrandite. Those economic interest occur mainly in potassium and only ocassionally in sodium-rich pegmatites. Autunite and uranocircite are found in an ancient lake bed (Lake Antsirabe) which presumably received the drainage from weathering pegmatites which contained betafite and other complex uranium-columbium-tantalum minerals. The total yield has been very small in the past, with an annual production of from one to twenty tons with about 27 per cent U_3O_8 content (Mineral Resources of the U. S., 1926; Krusch, 1937j).

Africa (Other than the Belgian Congo) (Krusch, 1937b). Pitchblende has been found at Ulugura, Morogoro District, East Africa and in the Loldaiga region (Nangaki District), British East Africa. Small deposits have also been reported near Messina, North Transvaal and in the Gordonia District, Cape Province. The extent of these deposits is unknown.

Australia.* Krusch, 1937k). Two uranium deposits have been reported from

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Australia. One is at Radium Hill (Mt. Painter) near Olary in South Australia, and the other is in the Pilabara gold field in Western Australia. At Radium Hill (20 miles southeast of Olary and 275 miles northeast of Adelaide) are found torbernite, autunite, uranophane, gummite, and fergusonite. The carnotite appears to have originated from uranium-titanium-tantalum-columbium minerals in nearby pegmatites. The ores are low grade (1 to 2 per cent U), and the total output has been very small (Crook and Blake, 1910; Radcliffe, 1914).

Recently pilabarite, a complex lead-thorium uranate containing small amounts of cerium and yttrium (Simpson, 1910) has been mined at Pilabara in West Australia. The total output is unknown.

Mexico (Krieger, 1932; Krusch, 1937l). The deposits, of unknown extent, are said to be mainly 120 miles northeast of Guadalupe in the State of Chihuahua. Gold is found with the uranium. The vein varies between a few centimeters and 5 meters in width.

Brazil. Recently, uranium has been found at Proina, Minas Geraes. Ore containing 13 to 18 per cent U_3O_8 has been obtained from pegmatites exploited for mica, tourmaline, and beryl. The deposits at Uba, Minas Geraes contain 75 per cent samarskite, 15 per cent monazite, and 10 per cent columbite (de Orange, 1945). Euxenite was found at Pomba, Minas Geraes as long ago as 1911 but has never been mined (Krusch, 1937m). A survey of Brazilian uranium occurrences are in the State of Minas Geraes (Hess and Henderson, 1925). The tenor of the deposits may be judged from the statement that 37 tons of euxenite yielded one g of radium or 3 tons of uranium.

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* " Mineral Resources of the U. S.," 1925, p. 617; 1926, pp. 267-8; 1927, pp. 441-2; 1928, p. 136; 1929, pp. 108-9; 1931, p. 188.

"Minerals Yearbook," 1932-33, pp. 188, 333; 1934, p. 506; 1935, p. 558.

3.5 Statistics. At this time there is little point in attempting to discuss the statistics of uranium production and price. A very rough idea of the economic history of uranium can be gained from the successive volumes of the Minerals Yearbook. By way of illustration, the latest data from the Minerals Yearbook is given in Table 18.

TABLE 18

URANIUM ORE AND COMPOUNDS IMPORTED FOR CONSUMPTION IN THE UNITED STATES, 1939-43.

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Year	Uranium Ores		Uranium Oxide and Salts	
	Weight	Value	Weight	Value
1939	5 lb	$ 10	1,439,324 lb	$ 1,197,786
1940	2,400,198	2,110,927	240,199	388,355
1941	--	--	387,505	501,370
1942	541,307	806,919	377,398	851,098
1943	-	-	211,348	431,410

No good data appear to be available on the world production in recent years.

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CHAPTER IV

EXTRACTION OF URANIUM FROM ORES AND PREPARATION OF URANIUM METAL

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CHAPTER IV

EXTRACTION OF URANIUM FROM ORES AND PREPARATION OF URANIUM METAL

1. Extraction of Uranium From Ore

Although uranium ores until very recently were processed mainly for their radium content, this situation has now been altered; and radium is likely to become a by-product of uranium production. The older literature was concerned almost exclusively with the efficient isolation of radium, and little attention was devoted to the best methods of uranium recovery.

Only two uranium ores have been processed extensively, pitchblende and carnotite. A variety of methods has been employed, which depend on the nature of the ore and the character of the other elements present in it. The general procedure for all ores is about as follows: (1) Leaching of the ore with sulfuric, nitric, or hydrochloric acid to solubilize the uranium; (Occasionally, alkaline extraction or fusion have been used to open up the ore.) (2) Converting the uranium to a soluble complex carbonate, a treatment which removes Fe, Al, and Mn; (3) Precipitation of PbS and CuS from the uranyl solutions; (4) Recovery of the uranium as $Na_2U_2O_7$ or $(NH_4)_2U_2O_7$. In the case of carnotite, special steps must be taken to eliminate vanadium and phosphate from the uranium. The details can best be followed by considering a number of specific processes.

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1.1 Recovery of Uranium from Canadian Pitchblende.

(MP Chicago 1; Pochon, 1937; Safford and Kuebel, 1943; Kuebel, 1944.) The recovery process is complicated by the presence in the ore of considerable quantities of gold and silver. Carbonates and sulfates also present must be destroyed before acid treatment; otherwise considerable frothing occurs. In addition, considerable amounts of arsenic and copper must be removed.

The ore mined at Radium City on Great Bear Lake is concentrated in the ratio 50:1 by mechanical separation and flotation. The mined rock contains about 1 per cent U_3O_8. The concentrate contains about 50 per cent U_3O_8 and from 1 to 7 per cent silver, depending on the section of the mine. This concentrate is shipped to the Port Hope, Ontario refinery. The process carried out there is outlined in Fig. 1. (Compare with Mactaggert, 1943).

The concentrate is first pulverized in a ball mill and sent through a magnetic separator to remove magnetite. A series of flotation cells removes the lighter components of the ore. The product from the flotation cells is dried in a furnace at 600° C, which decomposes the sulfides and carbonates and volatilizes part of the arsenic and antimony. Sodium chloride is then added, and the temperature is increased to 800°C, which converts silver to AgCl. The cooled roasted material is then leached with sulfuric acid which removes the uranium, manganese, copper, and iron. At the leaching stage, it is customary to add barium chloride to provide a carrier for the radium present and insure that it remains in the undissolved portion of the ore. The pH of the acid extract is

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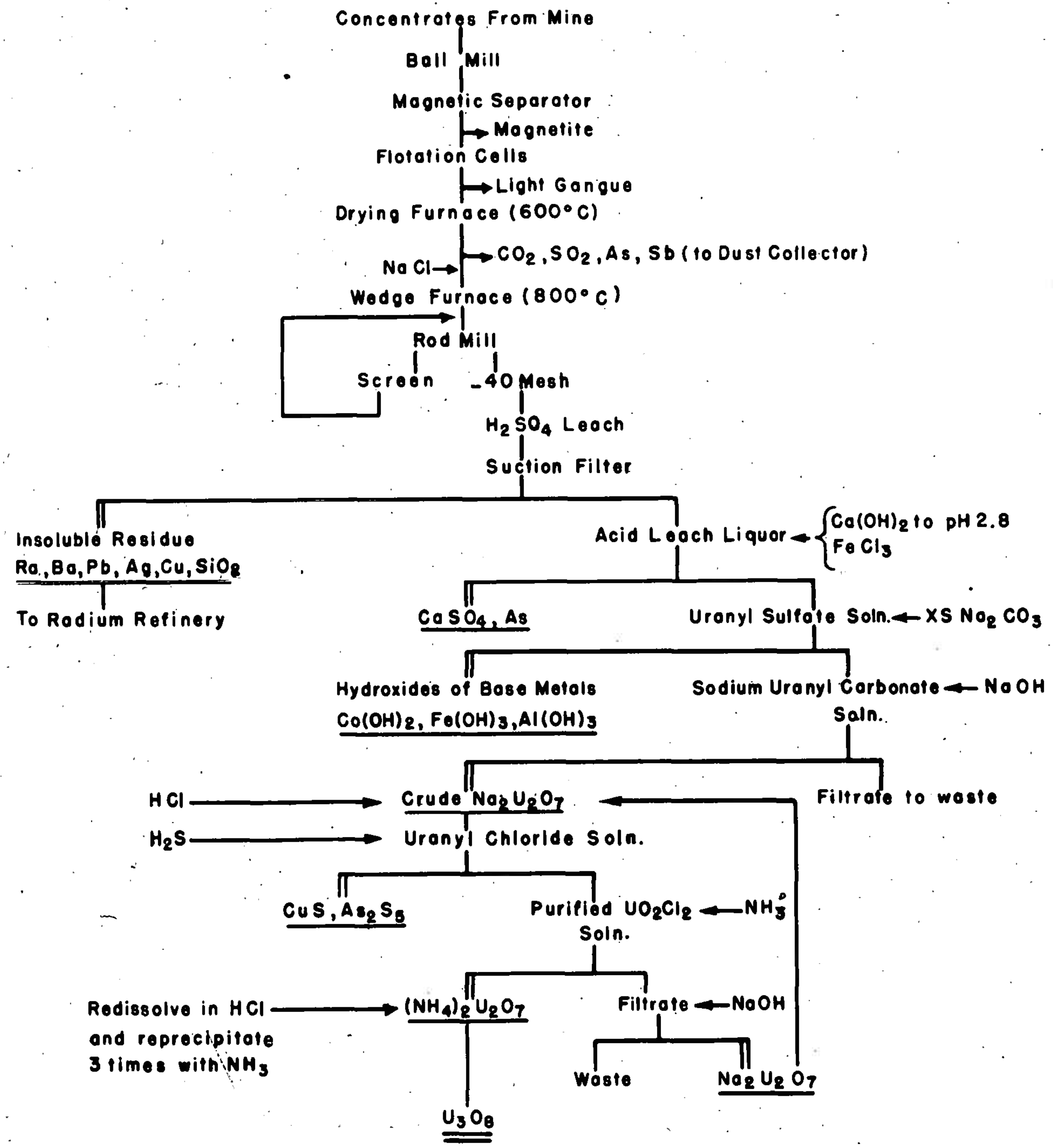
FIG. I.

Flow Sheet For Production of U_3O_8 at Port Hope (Ontario) Refinery From Canadian Pitchblende



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adjusted to 2.8 by the addition of calcium hydroxide, and ferric chloride is added to remove arsenic as insoluble ferric arsenate. After filtration, a sufficient excess of sodium carbonate is added to solubilize the uranium and to precipitate ferric, aluminum, and manganese hydroxides, etc. After decantation, sodium hydroxide is added to the uranium tricarbonate liquor to precipitate $Na_2U_2O_7$. The sodium diuranate is purified by dissolving it in hydrochloric acid and saturating the solution with H_2S, which precipitates the sulfides of Cu and As. After the excess H_2S is removed by boiling, ammonium hydroxide is added and the uranium is recovered as $(NH_4)_2U_2O_7$. This is converted to U_3O_8 by ignition at 1000°C. It was at one time the practice to leach the U_3O_8 three times with hot hydrochloric acid to remove acid soluble impurities which had not been removed, but this has been abandoned because of the high uranium losses. The oxide so produced has a U_3O_8 content of 99.1-99.6 per cent.

The sodium chloride treatment described above is suitable when native silver is present in the ore. Alternatively, the pulverized ore after magnetic concentration may be subjected to a cyanide treatment, which removes not only silver but also any gold which may be present. This procedure is preferred when gold is present in appreciable amounts.

The sulfuric acid leach is carried out in stoneware apparatus. As has been pointed out above, it is customary to add barium chloride to provide a carrier for the radium. For 375 lb of roasted ore there are used 350 lb H_2SO_4 (d=1.8), 300 lb water, and 20 lb sodium nitrate. The sodium nitrate

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is added to insure complete oxidation of the uranium to the hexavalent state.

1.2 Recovery of Uranium from African Pitchblende.(1) The chemical problems associated with uranium recovery from African pitchblende are on the whole simpler than those encountered in the recovery from Canadian ores. Since gold and silver are absent, the roasting and cyanide treatments are omitted. However, some minor modifications are usually introduced in processing African ore, particularly in the extraction step; for example, manganese dioxide may be used as the oxidizing agent instead of sodium nitrate. The processes used for the various types of pitchblende are identical after the leaching step. A typical flow sheet for African ore is given in Fig. 2.

Since molybdenum is present in African pitchblende, it is necessary to make sure that it is removed completely, especially if uranium is to be converted ultimately to uranium hexafluoride. This purification may be accomplished by adding 1 lb of ferric sulfate per 100 lb of ore during either the acid or the alkali digestion. If the pH is <8, the molybdenum is removed. This operation can be carried out equally well at either 50° or 90°C (Report A-1023, Jan. 15, 1944).

1.3 Extraction of Uranium from Joachimsthal Pitchblende. Numerous processes have been devised by successive generations of chemists for the recovery of uranium and radium from Joachimsthal pitchblende. The minor significance at present of these deposits makes it unnecessary to give a detailed

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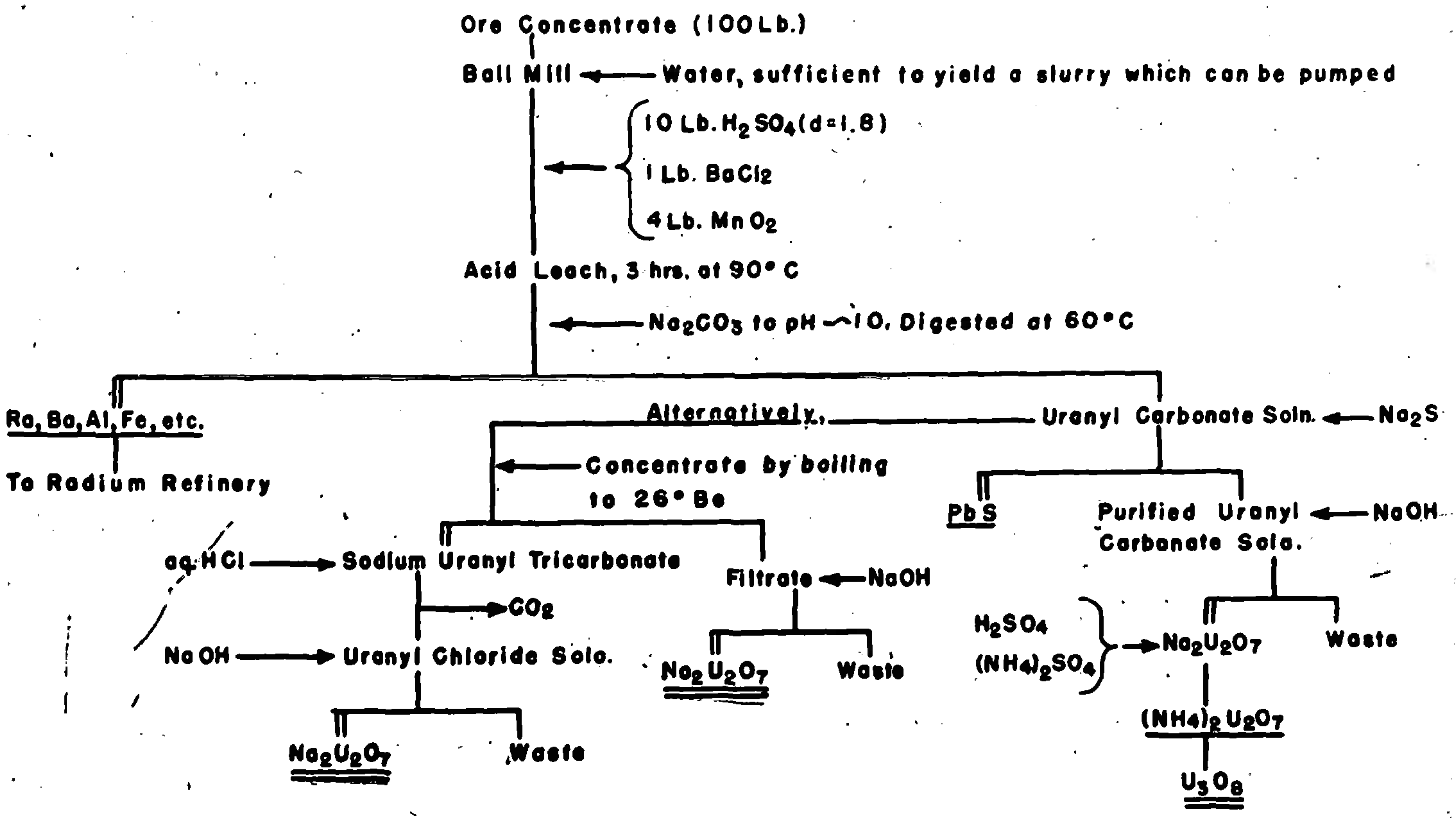
(1) See reports A-1021, Jan. 15, 1944 and A-1026, Feb. 15, 1944.

FIG. 2

Flow Sheet For Production of U_3O_8 From African Pitchblende



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description of the very complex processes which have been used because of the presence of about thirty metals in the ore. The ore is usually concentrated by hand-picking and flotation. The concentrated ore is ground and roasted with a mixture of soda ash and sodium sulfate at 800°C for ten hours. Sulfur is eliminated as SO_2, and U, Sb, W, Mo, and V are converted to the sodium salts. The roasted ore is then reground and leached first with sulfuric acid and then with nitric acid. The bulk of the uranium is thus converted to water-soluble uranyl sulfate. Purification of the uranium is then dependent on the nature of the other elements present in any particular case (Ulrich, 1923; Henrich, 1918). Extraction of the ore directly with sulfuric and nitric acids has also been employed (Marckwald, 1908, 1911).

1.4 Extraction of Uranium from Carnotite.(2) Extraction of uranium from carnotite ores presents a considerably more difficult problem than extraction from pitchblende, because of the necessity of processing relatively large amounts of crude ore. The quantitative removal of vanadium and phosphate from the uranium has also proved troublesome.

Although little attention was devoted in the past to producing uranium-rich concentrates from low grade carnotite, considerable efforts have been made in this direction recently. The carnotite occurs in small aggregates of clear friable particles as a fine-grained component of the clayey matrix (limonite) which cements the individual grains of quartz together, and also as a thin tenacious coating on the quartz grains. By grinding to 200 mesh (roughly the particle size

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(2) See Doerner (1930) for a bibliography of patents relating to radium production.

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of the individual quartz grains) much of the carnotite can be recovered (DeVaney, 1938). The recovery is proportional to the amount of fines produced; 65 to 78 per cent recoveries have been achieved, with a concentration factor of two to four (Shelton and Engel, 1942; Nye and Demorest, 1939). Wet grinding appears superior to dry grinding. It has been suggested that the remnants of carnotite adhering to the sandstone particles be freed by agitating the ground ore with a jet of air in such a way that the individual particles undergo attrition; the fines would then be collected in a cyclone separator (Dunn, 1939, 1940). Preliminary studies have been made on various ore dressing procedures, and a tentative flow sheet (Fig. 3) for a concentration procedure based on deflocculation and flotation has been proposed (Davis, 1938; Engel and Shelton, 1942; McCoy, 1916).

A preliminary roasting of carnotite ores has been advocated by Doerner. Many advantages are claimed. Frequently the carnotite contains very appreciable amounts of carbonaceous materials (asphalts, etc.) which make grinding very difficult and interfere with subsequent acid treatment. Roasting destroys the organic matter and simultaneously converts iron to the insoluble oxide, which resists solution in acid. It is claimed that exceptionally high recoveries of the mineral values are obtained by utilizing this roasting procedure (Doerner, 1928).

Various methods are available for the extraction of uranium, vanadium, and radium from carnotite. The most widely employed procedure involves the treatment of the ore with dilute or concentrated sulfuric acid at either normal (Fleck, 1907) or

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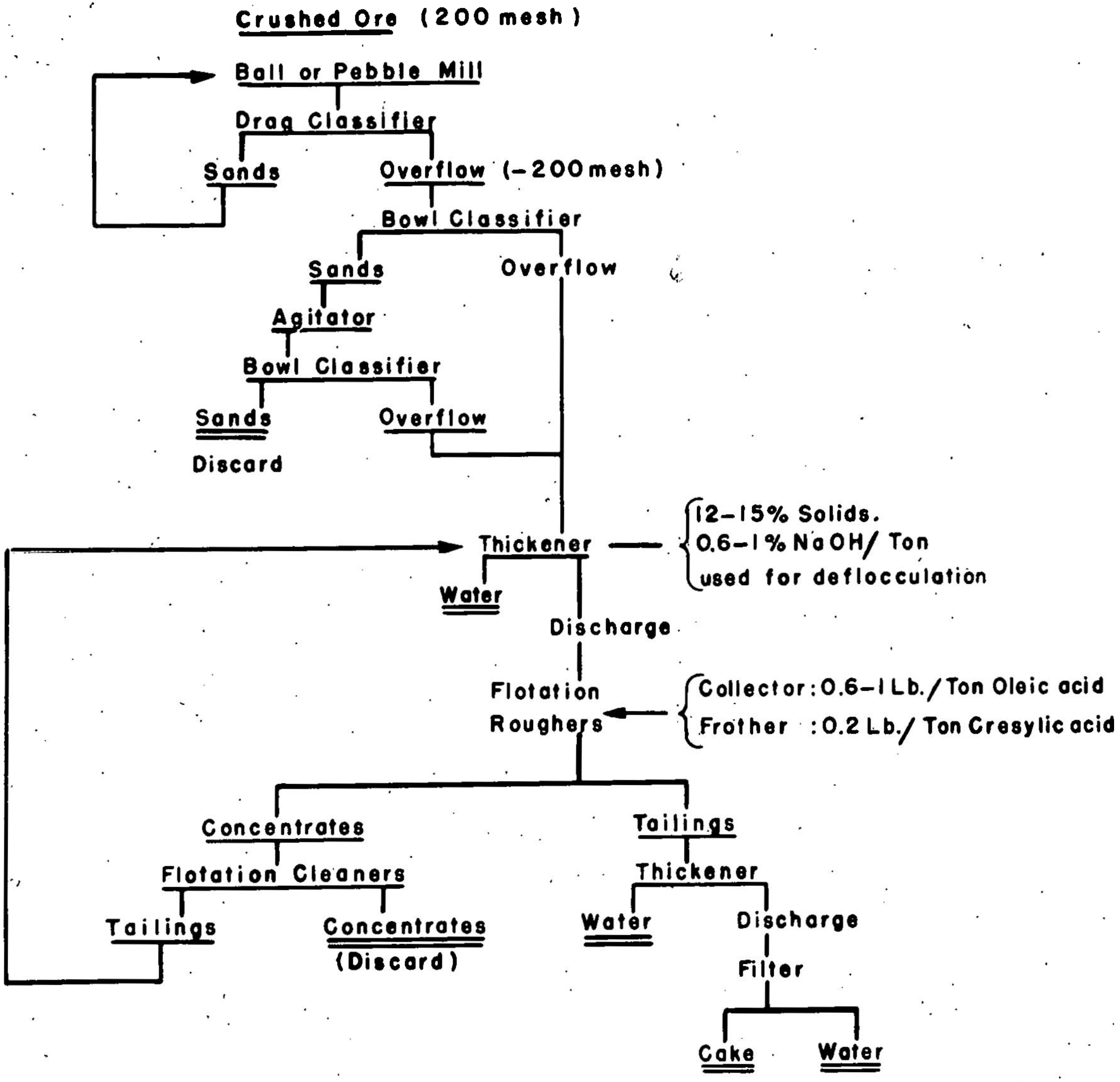
FIG. 3

Suggested Flowsheet For Concentration of Carnotite Ores



Final Product
Bulk Reduction = $\frac{1}{5}$
Concentration Factor of U_3O_8 X 3.5

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elevated temperatures (100°-300°C) (Danforth, 1915; McCoy, 1914; Schlundt, 1916, a, b; Bredt, 1914). When the operation is carried out at normal temperatures, the pulverized ore is moistened with 5 to 10 per cent by weight of 60° Baumé sulfuric acid and allowed to age for 20 to 90 days. At elevated temperatures extraction is much more rapid. After the acid treatment, the extraction is completed by leaching with dilute sulfuric acid. Uranium and vanadium are obtained as an aqueous solution of the sulfates.

The U. S. Bureau of Mines at one time advocated leaching with hydrochloric or nitric acid (Parsons, 1915) instead of the cheaper sulfuric acid. Most ores have been found to require a preliminary treatment with sodium carbonate or sodium hydroxide before hydrochloric acid extraction can be performed satisfactorily. Although numerous methods specifying hydrochloric acid have been patented, they do not appear to have received much use (Moore, 1916; Bell, 1922). It has also been proposed to use a mixture of hydrochloric and oxalic acids (Bell, 1921). In general, hydrochloric acid treatment is unsuitable where radium recovery is desired.

Nitric acid treatment (Moore, 1916; Plum, 1915; Viol, 1916; Parsons, 1916) is not effective for ores containing carbonaceous matter. The recovery of vanadium from such ores is very poor, and considerable amounts of uranium and vanadium are lost by precipitation during the subsequent filtrations, which are very slow and are difficult to perform. Nitric acid solution is considered an unsatisfactory method, especially for dust concentrates (Doerner, 1928, 1930 a). A much improved nitric acid procedure has been described by Doerner (Fig. 4).

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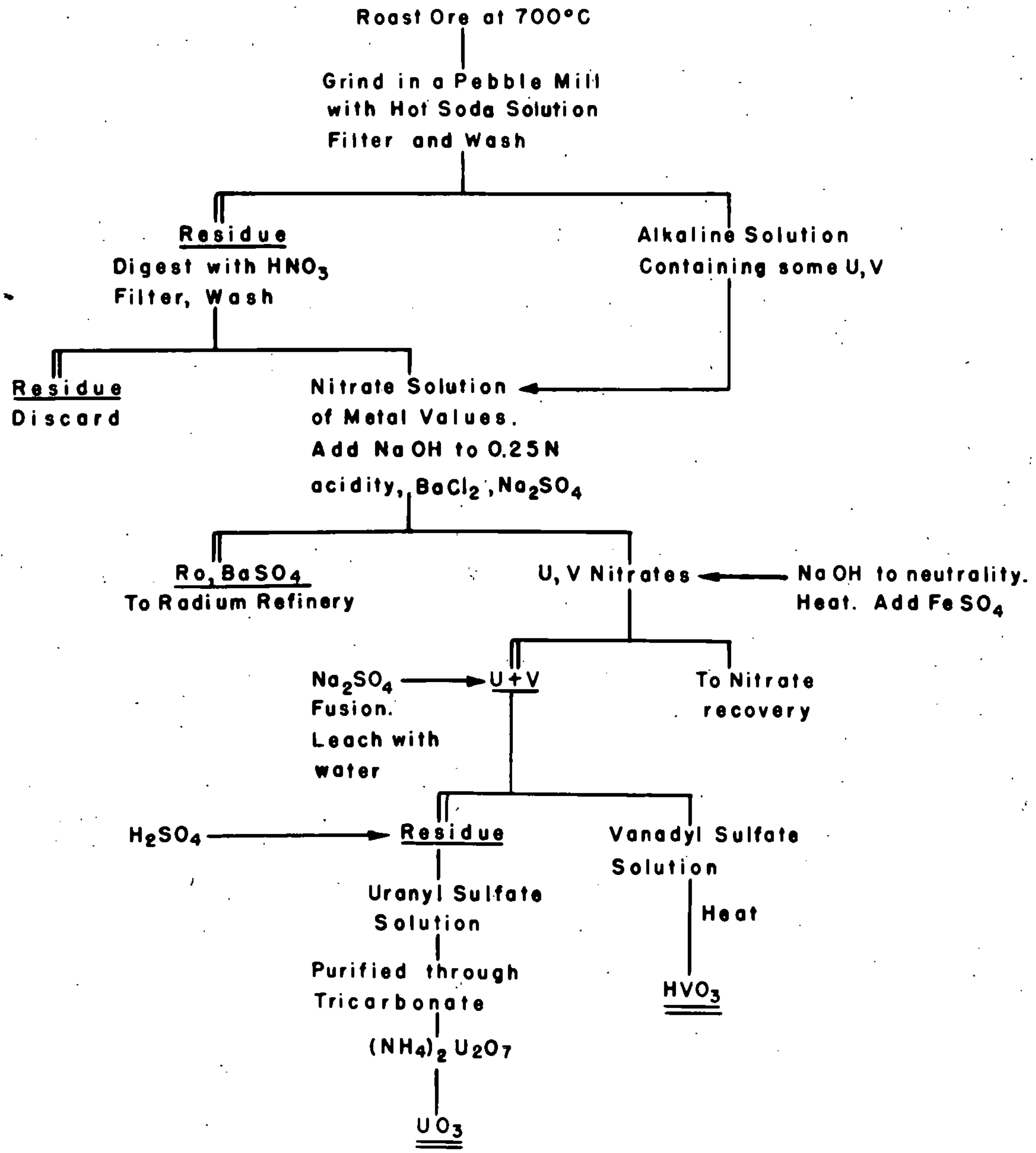
FIG. 4

Flow Sheet For Bureau Of Mines Nitric Acid Process For Carnotite Ore (Modified by Doerner)



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Small amounts of hydrofluoric acid in other acids aid the extraction of all the mineral values from the ore.

By and large, sulfuric acid remains the leaching agent of choice.

Leaching can also be effected by treatment with solutions of <u>alkali carbonates</u> (Haynes, 1905; Bleecker, 1913; Thews, 1923). The finely pulverized ore is heated with sodium or potassium carbonate solution at 90°C, whereupon as much as 80 per cent of the uranium and 60-65 per cent of the vanadium may go into solution. The concentration of the carbonate solution is varied with the amounts of uranium and vanadium present in the ore and their ratio to each other. Alkali leaching has also been performed under pressure (Bleecker, 1919).

When a mixture of carbonates and alkali hydroxides is used, vanadium is extracted as the soluble vanadate, whereas the uranium remains in the residue as insoluble uranate. After removal of the bulk of the vanadium, the uranium can be leached out with acid (Bleecker, 1913a; Moore, 1913). Treatment of the ore with sodium hydroxide solution at 200°-300°C has also been proposed (Fischer, 1912; Schlesinger, 1918; Ebler, 1915). It is doubtful that a clean cut separation of the uranium and vanadium can be effected in this way; however, the method may be useful when the vanadium is present in much greater quantity than the uranium. A modification of the alkaline leaching process has been proposed wherein a per-compound (such as hydrogen peroxide) is added to the NaOH-Na_2CO_3 solution. Under these conditions the uranium is dissolved (Gibbs, 1935).

In addition to the extraction processes discussed above which all operate in aqueous solution at moderate temperatures, a number of high-temperature fusion methods have been proposed to open up the ore. Thus, the finely powdered ore (or concentrate) may be fused with a mixture of NaCl and NaOH. The sodium vanadate is leached with water, and the uranium is removed from the residue with sulfuric acid (Bleecker, 1909; Vogt, 1915). Fusion with a three fold excess of sodium acid sulfate ($NaHSO_4$) has also been recommended (Radcliffe, 1911, 1914), as has fusion with solid sodium carbonate (Parsons, 1915a). Recently the use of ammonium sulfate at 380°-430°C has been proposed. This is an attractive method in that the ore is roasted and decomposed in a single operation. At these temperatures, ammonium sulfate is equivalent to SO_3, which may also be used directly (McCormack, 1939). The uranium and vanadium go into solution when the reaction product is treated with water. Little comparative data are available on the efficiencies of these procedures. They appear to have been little used. They may be valuable for rich concentrates but are obviously difficult to apply when large amounts of low grade material are to be treated. Large amounts of silica are likely to be solubilized by alkali fusion and may cause difficulties in subsequent operations.

As was mentioned above, the separation of uranium from vanadium and phosphate offers some difficulty. It has been shown that vanadium and phosphate may be removed as insoluble ferrous vanadate and insoluble ferric phosphate by the combined addition of ferrous and ferric sulfates to a sodium uranyl

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carbonate solution.(3) The pH of the carbonate liquor is adjusted to 8.5-8.6, and equal amounts of ferric and ferrous sulfates are added. The addition of 8 lb of ferrous sulfate and 12 lb of ferric sulfate per 100 lb of carnotite concentrates decreases the V_2O_5 content from 5 per cent of the U_3O_8 content to less than 0.03%, and the P_2O_5 content from 1 per cent to less than 0.1%.

Separation of uranium and vanadium by heating the mixture of uranyl and vanadyl sulfates obtained by evaporation of a sulfuric acid leach of carnotite has been proposed. At 500°-650°C the vanadyl sulfate decomposes and forms insoluble iron vanadate by reaction with the iron present. The uranyl sulfate redissolves on leaching (Potter, 1939). Separation of uranium and vanadium can also be effected by adjusting the acidity of the solution of uranyl and vanadyl sulfates (from the sulfuric acid leach) to pH 1.0 to 2.0 and oxidizing the vanadium with sodium chlorate or manganese dioxide. The bulk of the vanadium precipitates under these conditions as vanadic acid, HVO_3 (Stamberg, 1939; Fleck, 1940).

Torbernite (copper uranyl phosphate) has been processed in a fashion similar to carnotite.(4) The ore contained U_3O_8 (17.7%), SiO_2 (51.14%), Fe_2O_3 (1.92%), Al_2O_3 (6.45%), MgO (5.16%), P_2O_5 (4.62%), CuO (2.75%), NiO (1.17%), MoO_3 (0.31%), CoO (0.23%), V_2O_5 (0.42%). The pulverized ore is treated with 50 lb of concentrated sulfuric acid per 100 lb of ore, and the leach is diluted to 15 to 30 per cent. The mixture is digested for three hours at 90°C, and a 99 per cent uranium extraction

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(3) See reports A-1065, Dec., 1944 and A-1072, Jan. 1, 1945.

(4) See report A-2902, May, 1945.

is obtained. The acid slurry is then diluted and treated with sodium carbonate (130 lb) and sodium bicarbonate (13 lb) at 90°C for one hour. The insoluble residue is filtered; copper and phosphate are removed from the filtrate as insoluble phosphates by addition of 40-50 lb of ferric sulfate. The U_3O_8 produced contains more than 99 per cent U_3O_8, less than 0.26 per cent phosphate, and 0.01 per cent vanadate.

Similar procedures may be used for autunite (Glaser, 1912).

1.5 Special Extraction Procedures for Low Concentration Ores (Ulzer, 1908; Ulrich, 1923a; Loomis, 1916; Ebler, 1913). A number of ingenious procedures have been suggested for low-grade uranium minerals. While these procedures have been of little significance in the past, they are discussed briefly here since they may be useful in the development of new methods in the future.

(a) Chlorination. This method has been used on betafite from Madagascar. The finely pulverized mineral is mixed with wood charcoal and treated with chlorine at red heat. The volatile chlorides UCl_5, $CbCl_5$, and $TaCl_5$ are formed and distilled from the reactor (Curie, 1925). An analagous method has been applied to American pitchblende containing pyrite. Treatment with chlorine at elevated temperatures results in distilling uranium and iron chlorides from the reaction mixture (Cable, 1918). The chlorinating agent is presumably SCl_2. (See chap. , sec.). Along similar lines, it has been shown that phosgene will react with autunite (Barlot, 1913):

$$Ca(UO_2)_2(PO_4)_2 + 10\ COCl_2 \xrightarrow{800^\circ C} 2UCl_4 + 2POCl_3$$

$$+ 10\ CO_2 + CaCl_2 + Cl_2$$

Other chlorinating reagents, such as thionyl chloride and carbon tetrachloride, should also be of interest in connection with the problem of devising efficient methods for treating low-grade ores.

(b) Extraction with Sulfur Dioxide. On treatment of pulverized carnotite with a saturated aqueous solution of sulfur dioxide at normal temperatures and pressures, uranium and vanadium are reported to go into solution (Burfeind, 1914; Loomis, 1916). The use of liquid SO_2 for this purpose has also been reported (Hedström, 1922).

(c) Solvent Extraction. Very recently, a number of patents have been issued to A. W. Hixson covering a process for extracting uranium (and other metals) from ores by a solvent extraction method. In brief, the ore is leached to provide an aqueous solution of the mineral values, and these are then separated and recovered by counter-current extraction with a solvent immiscible with water. Recycling may be employed for increased efficiency. This is a very promising approach and will no doubt be the subject of intensive investigation in the future (Hixson, 1941).

A similar procedure has been in use for some time for purifying crude U_3O_8. For certain purposes it is necessary to remove all traces of rare earths from the uranium. This has been accomplished by a solvent extraction process which depends on the solubility of uranyl nitrate in ethyl ether, in which the rare earths are insoluble (Peligot, 1842). A very pure uranium oxide can be thus obtained. The process used by the Mallinckrodt Chemical Works is indicated in Fig. 5. The wash

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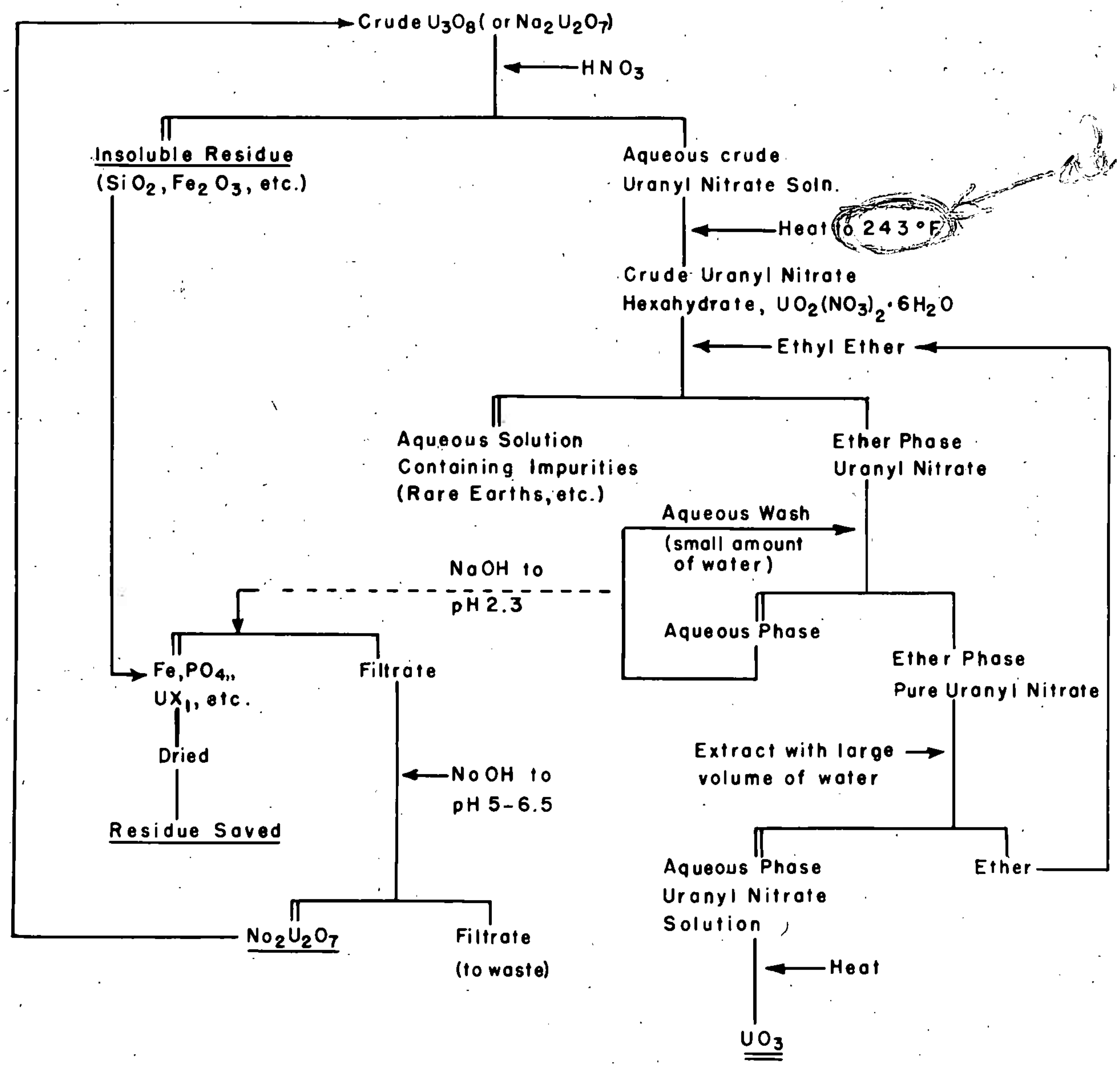
FIG. 5

Flow Sheet For Purification of U_3O_8 by Solvent Extraction (Mallinckrodt Process)



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waters used to treat the crude ether solution of uranyl nitrate are recycled until impurities accumulate to such an extent that special chemical treatment is required (indicated by dotted line in Fig. 5). The washing of the ether phase is normally continued until the ether solution is free of UX_1, as determined by a Geiger counter. Experience has shown that all other water soluble impurities are removed when all of the UX_1 is gone, which provides a convenient method for following the course of the operation. (See chap.   for further discussion of solvent extraction processes as applied to uranium compounds.)

2. Metal Preparation

Although metallic uranium was first prepared more than a hundred years ago, it is only within the past few years that it has become possible to produce the pure metal on a large scale. Prior to the development of the procedures described in this chapter, uranium metal had been prepared principally for scientific study and only a small scale. The processes were inefficient, and the metal produced was impure. The lack of purity is evidenced by the fact that the melting point of the metal so produced was in error by many hundreds of degrees. The modern metallurgy of uranium is treated in detail in other volumes of this series. In this chapter it is proposed to present only a brief survey of uranium metal preparation.

2.1 Historical Survey of Uranium Metal Preparation. In 1789 Klaproth, the discoverer of the element uranium, reduced uranium trioxide with carbon at high temperatures. The product had a metallic appearance and was assumed by him to be the free metal. This assumption persisted until 1840 when Peligot demonstrated that the product obtained by Klaproth's procedure was a lower oxide (UO_2). Klaproth succeeded in preparing the metal for the first time by the reduction of uranium tetrachloride with potassium metal.

Following Peligot's discovery, other workers prepared uranium metal on a laboratory scale. The methods used fall into four classes: (a) reduction of uranium oxides with carbon; (b) reduction of uranium oxides with aluminum, calcium, and magnesium; (c) reduction of uranium halides with alkali metals or alkaline earth metals; (d) electrolytic reduction of uranium halides. With few exceptions these methods yielded metal in the form of powder. In all cases the metal produced was impure to such an extent that it was not possible to determine accurately such physical constants as the melting point or electrical conductivity of the metal.

(a) In order to reduce uranium oxide to the metal with carbon it is necessary to use a very high temperature. H. Moissan was able to carry out this reduction in the electric arc furnace (Moissan, 1883, 1894, 1896, 1901, 1904). A mixture of U_3O_8 and carbon obtained from sugar is strongly compressed into a carbon crucible. Reduction takes place in a few minutes in an arc (450 amperes, 60 volts). The product obtained contains considerable carbon. (Moissan stated later that essentially carbon-free metal could be obtained, but since uranium reacts rapidly with carbon at elevated temperatures to form uranium carbide, this statement cannot be correct.)

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If smaller amounts of carbon (40g C/500g U_3O_8)are used, the metal formed contains oxide. Using a carbon crucible makes formation of uranium carbide on long continued heating at elevated temperatures inevitable. Recently, Moissan's work was repeated, using UO_2 and U_3O_8 with sugar charcoal, acetylene black, graphite, and other forms of carbon. In all cases, uranium carbide was formed in appreciable amounts. Variation of the oxide-carbon ratio over a wide range did not eliminate carbide formation (MP Ames 1). Moissan also emphasized the importance of eliminating nitrogen as well as oxygen from the reaction system. J. Aloy (1901) repeated this work and reported that milder conditions than those used by Moissan could be used to effect reduction.

(b) Thermodynamic calculations show that uranium dioxide is reducible by calcium, magnesium, or aluminum at sufficiently elevated temperatures. Reactions of this kind were usually carried out in an evacuated steel apparatus. Jander (1924) reduced UO_2 with calcium at 950°-1250°C in a tightly sealed iron crucible. Finely powdered metal of a fair degree of purity was reportedly obtained. Essentially the same procedure was employed by Botolfsen (1929); U_3O_8 and calcium were heated in a steel tube which was inserted into an evacuated quartz tube. As in the earlier work of Wedekind (1911, 1914), who used a similar procedure, the metal obtained was in the form of very fine powder. While these workers claimed that metal produced by reduction of uranium oxide with calcium was of a high degree of purity, others were unable to confirm this. Thus, when James and co-workers (1926) reduced U_3O_8 with the theoretical quantity of calcium at 1000°C for 45 minutes in an evacuated steel bomb, the product was a brown powder; some globules of metallic uranium were present, but the metal contained considerable amounts of iron and oxygen. These observations have been confirmed by more recent work (MP Ames 2).

Reduction with calcium metal has been modified by carrying out the reaction in the presence of alkali halides or alkaline earth halides. These procedures are described in a number of patents assigned principally to the Westinghouse Lamp Company (Marden, 1923; Rich, 1927; see also Cachemaille, 1924). The addition of calcium chloride or magnesium chloride is reported to facilitate the reaction by acting as a flux and to produce the metal in a coarser form. Magnesium metal may also be used to reduce uranium oxide, but owing to its high vapor pressure, it tends to distill from the reaction mass and must therefore be used under pressure (Marden, 1926). Once initiated, the reaction is violent and difficult to control. The use of a calcium-magnesium alloy of the approximate composition Ca_3Mg_4 was reported to be advantageous (Rich, 1927).

Uranium oxide can also be reduced with calcium hydride:

$$UO_2 + 2\ CaH_2 \longrightarrow U + 2CaO + 2H_2$$

(Alexander, 1937; MP Chicago 2 and 3)(5). A mixture of uranium oxide and calcium hydride is placed in a steel cylinder which is then placed in a gas-heated retort. At 960°C, reaction occurs. The charge is allowed to cool under vacuum to eliminate hydrogen. The removed charge is crushed and ground, and the

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(5) See also reports CA-243 and A-1304.

lime is removed by leaching with dilute acetic acid. The wet uranium powder is washed with water, dried, pressed into compacts, and sintered.

Numerous workers have investigated the reduction of uranium oxide with aluminum metal (Moissan, 1896 a; Stevenhagen, 1899, 1902; Aloy, 1901; Giolitti, 1908; Marden, 1927). At 600°C, U_3O_8 is reduced by aluminum powder to a lower oxide, but apparently a much higher temperature is required to obtain reduction to uranium metal. Stevenhagen attempted to achieve this by employing liquid air as oxidant. He claimed to have obtained a molten regulus of uranium metal; but in view of the tendency of uranium metal to react with oxygen and nitrogen, it is not surprising that his results have not been confirmed. Although aluminum can be separated from uranium-aluminum alloys by vacuum fusion, the tendency of uranium to form such alloys during aluminothermic reduction of oxide is a complicating feature.

(c) The first successful preparation of uranium metal was achieved by Peligot (1842) by the reduction of uranium tetrachloride with metallic potassium. Since then, the reduction of uranium halides with alkali metals or alkaline earth metals has been frequently employed. The metal obtained by Peligot was contaminated by platinum, since the reduction was carried out in a platinum crucible. Replacement of potassium by sodium did not improve the procedure greatly (Peligot, 1869). In Peligot's method, potassium chloride is added as a flux, and the platinum crucible is protected from the air by a layer of charcoal. C. Zimmerman (1883) modified

Peligot's procedure by the use of an iron bomb (Wilson, 1878). A layer of fused sodium chloride was employed in an effort to preserve the bomb from attack; uranium tetrachloride, sodium chloride, and metallic sodium were charged into the bomb, and the reactants were heated to white heat after screwing the bomb cover into place. Zimmermann claimed that the metal so produced was pure and massive. H. Moissan (1896 b) repeated Zimmermann's work and reported that the uranium metal obtained in this way contained up to 2 per cent iron. Moissan preferred to use the double salt Na_2UCl_6 rather than UCl_4 because of its less hygroscopic nature. He also carried out the reduction with metallic sodium in an iron cylinder closed with a screw stopper; but the metal obtained was a finely divided powder of rather doubtful purity. A number of other workers employed the same bomb technique without obtaining substantially better results. W. G. Mixter (1912) followed Moissan's procedure very closely using Na_2UCl_6, and obtained 97-99 per cent pure uranium powder.

A. Roderburg (1913) conducted an extensive investigation into the methods for preparing pure uranium, with particular reference to the reduction of uranium halides by alkali metals. In an effort to improve the purity of the product, bombs of various alloy steels were investigated, but in all cases the uranium metal produced contained substantial amounts of iron. Roderburg also attempted the reduction of uranium tetrafluoride with sodium and potassium but obtained only partial reaction. Fischer (1913) and Rideal (1914) also investigated various methods for the preparation of uranium metal. Of a considerable number of possibilities explored, they preferred the reduction of uranium tetrachloride with magnesium or sodium in the presence of calcium chloride. The metal obtained in this way, however, was of an uncertain degree of purity evidenced by variations in the electrical conductivity. In an effort to minimize contamination by oxygen and nitrogen, Lely and Hamburger (1914) performed the reduction of uranium tetrachloride with sodium in an evacuated metal bomb. The product was in the form of a fine powder and still contained significant amounts of oxygen. A description of such a vacuum reduction is given in considerable detail by Moore (1923). The reduction of uranium halides by calcium, magnesium, calcium-magnesium alloys, and aluminum has been investigated by Marden and made the subject of a series of patents assigned to the Westinghouse Lamp Co. (1922). In these procedures UF_4, KUF_5, or other non-volatile halides or double salts of uranium are reduced by one of the previously mentioned metallic reducing agents, usually in the presence of a flux such as calcium chloride. After leaching and washing the reaction mass, the production is a fine powder.

James and co-workers (1926) appear to have been successful in preparing massive uranium metal with a fair degree of purity. These workers employed the reaction

$$UCl_4 + 2Ca \longrightarrow 2CaCl_2 + U$$

which was carried out in an evacuated steel bomb. By using redistilled calcium, a product quite free of iron could be obtained in the form of massive metal. The success of these workers can be attributed, at least in part, to the fact that experiments were carried out on a fairly large scale, which served to minimize contamination and the heat loss from the system. This work is probably the best that is recorded in the older literature.

(d) The last of the methods employed by earlier workers in this field was electrolytic reduction of uranium halides in fused salt baths. A good historical survey of this method is given by Driggs and Liliendahl (1930). Apart from the pioneering study of H. Moissan (1904 a), the most significant work in the electrochemical preparation of uranium metal has been carried out at the Westinghouse Electric Company (Driggs, 1928, 1930; Marden, 1934)(6). In the Westinghouse process the electrolytic bath consisted of the double salt potassium uranium fluoride, KUF_5, or of uranium tetrafluoride, UF_4, dissolved in a molten mixture of 80 per cent calcium chloride and 20 per cent sodium chloride. The bath was contained in a graphite crucible which served as the anode; the cathode was made of molybdenum. The bath was operated at 900°C at a current density of about 150 amp/dm^2. The uranium deposit dm^2 was granular and pyrophoric and required an elaborate sequence of washing and drying operations in order to eliminate occluded salts.

Numerous workers have attempted to deposit metallic uranium from an aqueous solution, but there is no evidence to indicate the feasibility of such a procedure. In all cases, complex hydrated oxides were obtained on the cathode. This failure of metallic uranium to deposit from an aqueous solution is not surprising, since manganese is the most electropositive metal which has yet been plated from aqueous solution,

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(6) See also report A-605, Mar. 25, 1943.

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and uranium is almost certainly above manganese in the electro-chemical series. There is some indication that dilute uranium amalgams may form when aqueous solutions are electrolysed at high current densities with a mercury cathode (Ferré, 1901). Repeated attempts have also been made to electrodeposit uranium from solutions in nonaqueous solvents (Pierlé, 1919; Audrieth, 1931; MP Berkeley 1). Saturated solutions of uranium tetrabromide in benzene, ethylbromide, diethylether, dioxane, acetone, acetone saturated with sulfur dioxide, nitrobenzene, formamide, and formamide containing hydrogen bromide have been subjected to electrolysis. Only in the formamide solution was there any evidence for the deposition of metallic uranium and it is not certain that the deposit was uranium metal. It may be concluded that at present electrolysis of either aqueous or non-aqueous solutions of uranium salts does not appear to be a practical method of making uranium. However, relatively little work has been done in this field, and future research may change these conclusions.

A number of reactions for preparing uranium metal have been known for a considerable length of time. It was possible to reduce the oxides with calcium, magnesium, or aluminum. These procedures, although feasible, were difficult to carry out in practice. Low yields of impure products were usually obtained. The reduction of uranium oxide with calcium hydride was exceptional in that metal could be produced satisfactorily on a large scale, but it required very careful control. Reduction of uranium <u>halides</u>, particularly the tetrachloride, by

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alkali metals or alkaline earth metals was known to proceed more satisfactorily. The chief difficulties in this case were the very hygroscopic nature of the tetrachloride and attack by the reaction mixture on the steel reaction vessels. Only finely divided uranium metal was produced. The product required leaching and washing, which were rendered difficult by the chemical reactivity of the finely divided uranium and its extreme tendency to oxidize. To convert the finely divided uranium powder into massive metal, it was necessary to resort to powder metallurgy with all the difficulties attendant upon handling a pyrophoric substance in this way. Similar difficulties were encountered with metal obtained by electrolytic reduction.

2.2 Contemporary Methods for the Preparation of Uranium Metal (MP Ames 3). The difficulties inherent in handling finely divided pyrophoric metal obtained by the methods described in Section 2.1 made it desirable to devise procedures for producing uranium metal in massive form. The thermal aspects of the problem appeared to be of prime importance. To obtain massive uranium, the reaction system must attain a temperature sufficiently high to melt both the uranium and the slag. This requires a sufficiently exothermic reaction. If a reaction which might otherwise be suitable is not in itself sufficiently exothermic, it may be aided by pre-heating the reaction mixture without allowing the reaction to set in or by combining the reduction of the uranium compound with another simultaneous exothermic reaction ("booster reaction"). Finally, since the reaction must be carried out in the absence of air, the boiling point of the slag must lie above the maximum temperature attained in order to avoid the production of excessive pressures in the closed reaction vessel. A number of reactions come into consideration. Their pertinent thermochemical data are given in Table 1.

TABLE 1

POSSIBLE REACTIONS FOR THE PREPARATION OF URANIUM METAL

No.	Reaction	ΔH/mole U at 298°C	M.p. of Slag (°C)	B.p. of Slag at 760 mm(°C)
1.	$UO_2 + 2Ca \rightarrow U + 2CaO$	-47	2572	2850
2.	$UO_2 + 2Mg \rightarrow U + 2MgO$	-35	2500-2800	...
3.	$UO_2 + 4/3Al \rightarrow U + 2/3Al_2O_3$	-11.4	2050	2250
4.	$U_3O_8 + 8Ca \rightarrow 3U + 8CaO$	-123.1	2572	2850
5.	$U_3O_8 + 8Mg \rightarrow 3U + 8MgO$	-108.1	2500-2800	...
6.	$U_3O_8 + 16/3Al \rightarrow 3U + 8/3Al_2O_3$	-76.4	2050	2250
7.	$UF_4 + 4Na \rightarrow U + 4NaF$	-98	980-97 (1040)	1700
8.	$UF_4 + 2Ca \rightarrow U + 2CaF_2$	-134	1330	2500
9.	$UF_4 + 2Mg \rightarrow U + 2MgF_2$	-82	1225	2260
10.	$UF_4 + 4/3Al \rightarrow U + 4/3AlF_3$	6	1040	...
11.	$UCl_4 + 4Na \rightarrow U + 4NaCl$	-141	801	1413 (1490)
12.	$UCl_4 + 2Ca \rightarrow U + 2CaCl_2$	-131	772	1925
13.	$UCl_4 + 2Mg \rightarrow U + 2MgCl_2$	-55	708	1420
14.	$UCl_4 + 4/3Al \rightarrow U + 4/3AlCl_3$	28	190 (2.5 atm)	182.7; subl. 177.8
15.	$UBr_4 + 4Na \rightarrow U + 4NaBr$	-144	755	1390
16.	$UBr_4 + 2Ca \rightarrow U + 2CaBr_2$	-124	765	1200 (?) (806-812)
17.	$UBr_4 + 2Mg \rightarrow U + 2MgBr_2$	-44	695	1125
18.	$UBr_4 + 4/3Al \rightarrow U + 4/3AlBr_3$	31	97.5	263.3
19.	$UCl_3 + 3Li \rightarrow U + 3LiCl$	...	613	1353

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An examination of Table 1 shows why the uranium oxides are reducible by Ca, Mg, and Al (Li, Be, Ba, and a few rare metals not included in the table also can reduce them). The melting points of the oxide slag produced in reactions 1-6 are high enough to prevent agglomeration of the uranium metal produced. The greater heats of reaction observed with U_3O_8 compared to UO_2 do not contribute very much towards the attainment of higher temperatures, since U_3O_8 is very resistant to reduction to the metal; the reduction usually stops when UO_2 is produced. Consequently, it has not been found feasible to utilize the reduction of uranium oxides for the production of massive metal.

The reduction of uranium halides with alkali metals or alkaline earth metals presents a much more favorable picture. The slags, for the most part, melt at relatively low temperatures. A number of reactions appear exothermic enough to attain sufficiently high temperatures. The heats of reaction indicate that UF_4, UCl_4, and UBr_4 could be reduced by either Na, Ca, or Mg, but that reduction by aluminum would not tend to occur spontaneously. Sodium is the most powerful reductant for chlorides and bromides, while calcium is superior for the fluorides. Magnesium is much less powerful than calcium in all cases.

A consideration of the various factors involved led to the suggestion that reactions 7, 8, and 9 should be most suitable for large scale use. While reduction of uranium tetrachloride instead of tetrafluoride has the advantage of producing lower melting slags, the difficulties in handling

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the hygroscopic tetrachloride more than offset this advantage. In actual practice it is found that the presence of traces of moisture or oxygen compounds exercises a very detrimental effect on the reduction of the uranium halides. Uranium tetrafluoride, on the other hand, can be prepared free from oxygen compounds and in a nonhygroscopic form which lends itself readily to metal production. The reaction

$$UF_4 + 2Ca \longrightarrow U + 2CaF_2$$

was the first to find large scale use (reviewed in MP Ames 4). Most of the uranium metal produced by British workers was prepared by this method. Since it has been superseded by the magnesium reduction method, it will not be discussed in detail here. The general procedure and equipment resemble closely that described below for magnesium reductions.

The use of calcium presents difficulties. Supplies are limited, and crude calcium metal is so contaminated as to make its use inadvisable. Pure calcium can only be prepared by vacuum sublimation, which is a tedious and expensive process. Sodium and magnesium by virtue of their availability, purity, and low price suggest themselves as alternatives. The difficulties of handling finely divided sodium metal in quantity precludes its use. Magnesium, on the other hand, is available in unlimited quantities and in a very high degree of purity.

The reaction of UF_4 with calcium can be initiated by an electrically heated fuse wire buried in the charge near the top of the bomb. The reaction then propagates through the entire reaction mass. When the same technique is used with magnesium, only pyrophoric uranium metal powder results.

Table 1 shows that considerable heat must be added to the heat of reaction 9 to equal that produced by reaction 8. Two procedures were evolved to supply the necessary heat. The first consists in carrying out a simultaneous "booster reaction", a method well known in thermite reactions. Chlorates, persulfates, peroxides, iodine, bromine, sulfur, and binary metal halides reducible by magnesium can serve as boosters for the preparation of massive uranium from UF_4 and magnesium. The use of these substances complicates the problem of obtaining a sufficiently pure product, and the possibility of generating dangerous pressures is present in some cases. The alternative method of supplying heat, preheating the reaction mixture, therefore has certain advantages. The reaction mixture $Hg + UF_4$ can be heated to 650°C without initiating the reaction. When the reaction starts, the liberated heat added to the heat already present in the system is sufficient to produce a fluid reaction mixture and give massive uranium.

2.3 Preparation of Uranium Metal by Thermal Decomposition of Uranium Halides (UCRL 1,2,3; MP Chicago 4,5). A number of metals have been prepared by thermal decomposition of the metal halide vapors on a hot filament. The method has been applied particularly to the preparation of zirconium, titanium, tungsten, and thorium (Van Arkel, 1939). Very pure metal can be obtained in this way.

In applying this method to the preparation of pure uranium metal, a number of difficulties arose. Compared to metals which had been successfully prepared by the hot wire technique, uranium has a low melting point (1125°C). The process was carried out in such a way that molten uranium was allowed to drip off the wire (MP Chicago 6), but this was not considered a satisfactory procedure (MP Chicago 7). A more satisfactory solution is to use such low decomposition temperatures that the uranium remains solid.

The most satisfactory halide for this process is uranium tetraiodide (MP Ames 5). The other halides of uranium either require too high a filament temperature to have much practical significance or are not volatile enough. The equilibrium (See chap. , sec.)

$$\text{(a)} \quad UI_4 \rightleftharpoons UI_3 + 1/2\ I_2$$

has an important bearing on the problem. A certain partial pressure of iodine is required to prevent uranium tetraiodide from dissociating in the vapor phase. (Uranium triodide is substantially non-volatile.) The reaction which occurs on the filament is:

$$\text{(b)} \quad UI_4 \rightleftharpoons U + 2I_2 \,.$$

Whereas a high partial pressure of iodine favors the reaction by increasing the amount of uranium tetraiodide in the vapor phase (according to equation (a)), it tends to reverse the metal deposition step by preventing dissociation of the UI_4 on the filament (according to equation (b)). The optimum iodine pressure is a function of the temperature of the filament and can be derived from the equilibrium constants for the reactions involved.

This procedure for the preparation of metallic uranium has been successfully carried out at a filament temperature below the melting point of uranium. The reduction is carried

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out in a glass bulb immersed in an air reflector furnace. Solid UI_3 is introduced and the system is evacuated. The region where the UI_3 rests is surrounded by a copper cooling coil which is used to maintain the UI_3 at any desired temperature relative to the reflector oven. Iodine is connected with the bulb through a long vertical tube which allows the iodine to be maintained at any desired temperature, thus regulating its partial pressure in the system. A suitable set of operating conditions is: filament 1030°-1100°C, bulb temperature 520°-560°C, UI_3 temperature 500°-540°C, IP_2 7×10^{-3} mm Hg. Under these conditions, solid uranium metal is deposited on the filament.

A theoretical analysis of the thermal dissociation of uranium tetraiodide has been made (UCRL 4). In earlier treatments, it was assumed that all iodine leaving the filament was in the form of iodine molecules, I_2; in actuality, complete dissociation to iodine atoms occurs at the filament temperature. Taking this into account and assuming that all atoms leaving the filament are in thermal equilibrium with the filament while all molecules striking the filament are in thermal equilibrium with the bulb, Prescott showed that for a bulb temperature of 800°K

$$\text{Log } P_{I_2} = 7.860 - 1.234 \frac{10^2}{T_2} \quad ;$$

where P_{I_2} is the partial pressure of iodine which has to be maintained in order to obtain metal deposition when the filament temperature is T_2.

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2.4 Small Scale Preparation of Uranium Metal (For discussion of methods applicable to quantities from 1 μg to 200 g, see MP Chicago 8; MP Ames 6, 7). When the methods described in Section 2.2 are applied on a small scale, finely divided metal is usually produced. This is due principally to the fact that heat losses from a small system are proportionally greater than from a large system. Because of the desirability of preparing metal on a 10 g to 100 g scale, considerable efforts have been devoted to the development of such a procedure. The Brown University Group has achieved a certain measure of success (Brown 1). The most effective method consists in heating uranium trichloride with lithium metal at 1100°C in a helium atmosphere:

$$UCl_3 + 3Li \longrightarrow U + 3LiCl \ .$$

The addition of NaCl to the charge improves the yield of massive metal. The best crucible material appears to be beryllia fused at 1900°C. Calcium metal is nearly as good a reductant as lithium, but sodium and potassium are inferior. Excellent yields of massive metal can be obtained.

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Chapter 5

PHYSICAL PROPERTIES OF URANIUM METAL

1. **Structure and Mechanical Properties of Solid Uranium**
    - 1.1 Crystal Structure of Uranium Metal
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CHAPTER V

PHYSICAL PROPERTIES OF URANIUM

1. Structure and Mechanical Properties of Solid Uranium

Uranium is a very dense metal 80 per cent heavier than lead. The freshly polished metal surface is silver-bright but tarnishes in air within a few hours. The low temperature form of uranium (α-uranium) is ductile and somewhat malleable; its elasticity is so low, that it has been described as "semi-plastic". The medium temperature form (β-uranium) is brittle, while the high temperature form (γ-uranium) is plastic. The metal can be hot forged, hot drawn, extruded, or cold worked.

1.1 Crystal Structure of Uranium Metal. The early interpretations of the x-ray diagram of uranium metal by which it was first assigned a space-centered cubic crystal structure (Mc Lennan, 1930), and later a triclinic lattice, (Wilson, 1933), have proved erroneous. Jacob and Warren (1937) established the crystal lattice of α-uranium to be orthorhombic (space group V_h^{17}). This structure can best be interpreted as possessing distorted hexagonal closest packing. The unit cell contains four atoms. The following values of the lattice parameters were found by various observers:

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TABLE 1

CRYSTAL LATTICE PARAMETERS OF α-URANIUM AT ROOM TEMPERATURE

Parameters (Å)			Density	References
a_o	b_o	c_o	(g/cc)	
2.852	5.865	4.945	18.97	(Jacob, 1937)
2.852	5.859	4.944	19.00	(Battelle 1)
2.8482	5.8565	4.9476-0.01%	19.050	(M.I.T. 1)

For the most precise determination at M.I.T. two samples of uranium of highest purity were used. They were quenched from 750°-800°C for grain refinement, and the structure was determined by means of a symmetrical focusing back reflection camera.

The exact structure of the β-phase uranium is unknown. It cannot be "frozen" in pure uranium, but, according to observation of the Ames group (MP Ames 1), this can be achieved in uranium-chromium alloys. Study of these alloys indicate that the β-phase may be cubic with a giant unit cell (a_o = 12.88 Å) containing 58 atoms. At Battelle (2) similar quenching experiments were carried out with uranium-molybdenum alloys. At first it was thought that a cubic face-centered phase obtained by furnace-cooling a 5 per cent molybdenum alloy held for 90 min. at 650°C was the β-phase, but its lattice constant (4.93 Å) indicates that it probably is the oxide, UO (See Table, Chapter X). Later a 0.6 per cent molybdenum quenched from 690°C was found to

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contain a new, probably orthorhombic phase, which was tentatively identified as the β -phase. Attempts to obtain the x-ray diagram of pure β-uranium by means of a high temperature camera have failed because of the weakness of the lines (Battelle 3). Usually only lines of a face-centered cubic phase, probably the oxide, UO, are observed in high temperature photographs (MP Ames 2).

The structure of the γ-phase of uranium was determined by the high temperature camera at 785°C (Battelle 3) and 680°C (MP Ames 3). It was found to be a body-centered cubic crystal. Like the β -phase, this phase cannot be "frozen" in pure uranium, but was successfully frozen in uranium-molybdenum alloys (MP Ames 4). A lattice constant of $a_o = 3.48$ Å was calculated for γ -uranium at room temperature by linear extrapolation of the data obtained for alloys with 10 per cent and 5 per cent molybdenum ($a_o = 3.39$ and 3.43 Å respectively). An identical value was observed at 785°C Battelle (4); reduction to room temperature gave $a_o = 3.43$ Å.

1.2 <u>Atomic Dimensions</u>. Most metallic elements, with the exception of such non-typical metals as bismuth or antimony, have crystal structures which only slightly deviate from the closest cubic or hexagonal packing of solid spheres. Uranium is an exception. Its atoms behave as if they were non-spherical. The cause probably lies in a rather strong atomic binding between an uranium atom in the lattice and its four nearest neighbors. Consequently, the atomic radius of uranium cannot be defined unambiguously, at least as far as the α -phase is concerned. Each uranium atom in this phase has two nearest neighbors at a distance of 2.75 Å (at room temperature), two second-nearest neighbors at a distance of 2.85 Å, four neighbors at a distance of 3.25 Å, and four neighbors at a distance of 3.34 Å.

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Thus the uranium atoms can roughly be described as ellipsoids with a small half-axis of 1.4 Å and a large half-axis of 1.65 Å.

The atomic radius of uranium in the cubic γ-phase, calculated from the extrapolated lattice constant at room temperature, is 1.485 Å.

1.3 **Density.** Density values calculated from lattice structure are given in Table 1. The most reliable value is 19.050 g/cc. If the γ-phase existed at room temperature, its density would be 18.7 g/cc. The experimentally determined density of uranium often is somewhat lower than the value calculated from the x-ray structure of the α-phase. This is probably due to the presence of impurities, especially carbon. At M.I.T.(2) the density of Metal Hydrides (Beverly Plant) metal was found to be a linear funcion of its carbon content.
The density values obtained fitted the equation:

$$(1) \qquad \rho = 19.05 - 2.14\,[C]$$

where $[C]$ is the carbon content in weight per cent. The highest measured value was 19.02 g/cc (0.01 per cent C) and the lowest, 18.58 g/cc (0.23 per cent). Extrapolation to $[C] = 0$ gave 19.05 g/cc for the density of pure uranium which agrees well with the value calculated from x-ray data. Measurements made elsewhere (Driggs, 1930; MP Ames 5; MP Chicago 1,2; British 1; Nat. Bur. Standards 1) gave values between 18.7 and 19.08 g/cc with the lower figures corresponding to carbon content of 0.05 to 0.06 per cent (Los Alamos 1). The average density of 22 α-rolled slugs of commercial metal was 18.882 g/cc (MP Chicago 1, 2). The density of uranium prepared by sintering metal powder may be as low as 15 g/cc without pressing and 17 g/cc after pressing (MP Chicago 3).

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The density of uranium powder was given by Marden (Columbia 1) as 9.4 g/cc after pressing at 20 tons/sq. in., 12.3 g/cc after pressing at 79 tons/sq. in., and 15.0 g/cc after pressing at 140 tons/sq. in.

1.4 <u>Thermal Expansion.</u> The coefficient of thermal expansion of uranium in the anisotropic α-state is strongly dependent on crystallographic direction. Table 2 and Figure 1 illustrate this dependence as found by high temperature x-ray studies at Battelle (5).

TABLE 2

COEFFICIENT OF THERMAL EXPANSION OF α-URANIUM IN THE THREE MAIN CRYSTALLOGRAPHIC DIRECTIONS

Direction parallel to the axis		Average expansion coefficient in 10^{-6} cm/(cm °C)	
		25-300°C	25-650°C
a	[100]	23 ±3	28±1
b	[010]	3.5 ±2	-1.4±1
c	[001]	17 ± 2	22±1

The volume expansion coefficient, calculated from the dilatometrically determined linear coefficients, is 44 x 10^{-6} cc/(cc °C), for the range 25-300°C. The x-ray data in Table 2 give a volume coefficient of 37 x 10^{-6} in satisfactory agreement with the dilatometric results.

In rolling or extrusion of uranium metal, individual crystals tend to orient themselves, the preferred orientation being such that the b-axis is parallel to the direction of strain. Consequently,

[redacted]

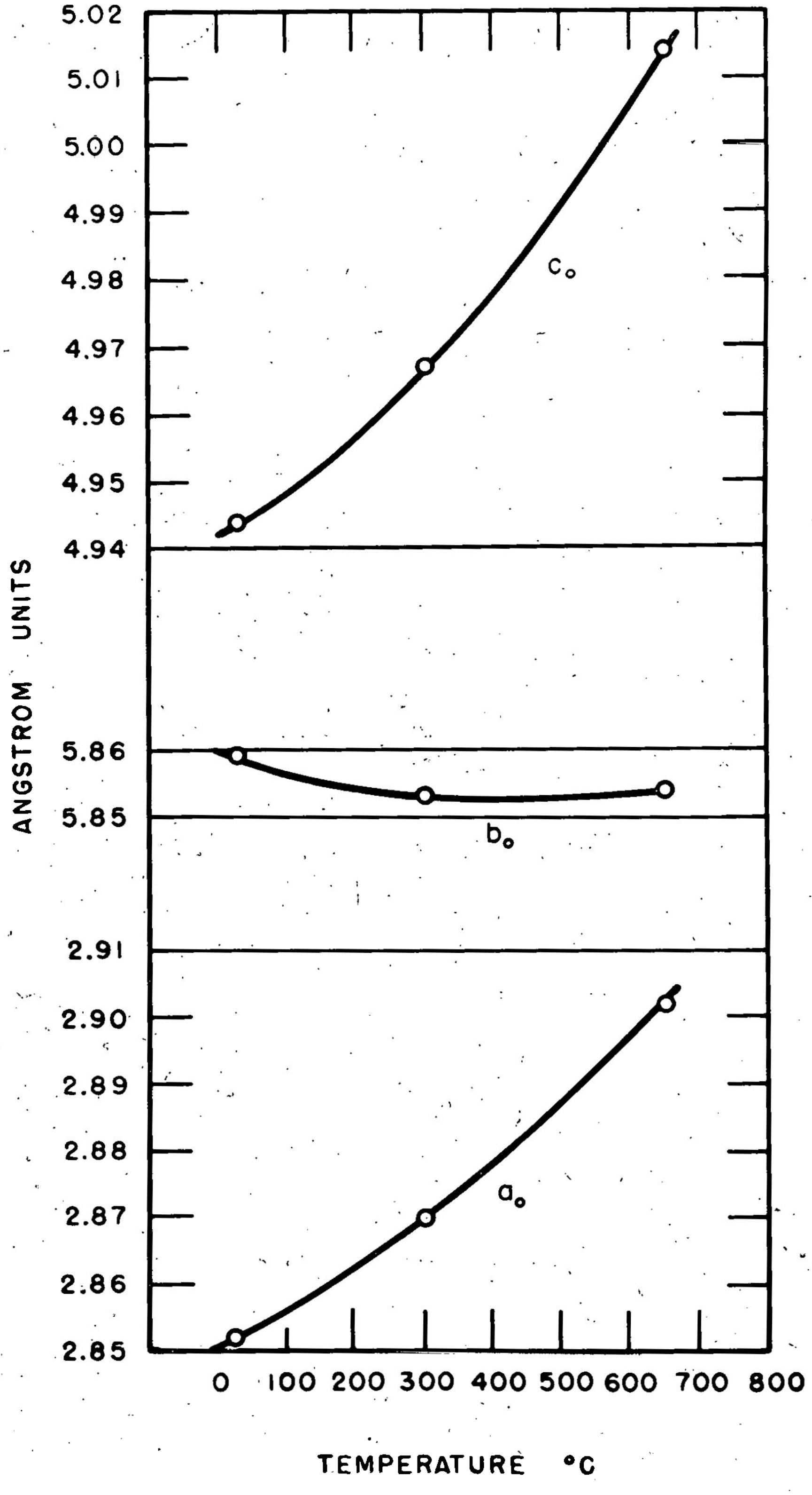

FIG. I. CONSTANTS OF α URANIUM AS FUNCTION OF TEMPERATURE.

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"longitudinal" specimens of uranium metal, rolled or extruded in the α-state, have a much smaller expansion coefficient than "transverse" specimens. For example, the expansion coefficient is from 3×10^{-6} to 6×10^{-6} cm/(cm °C) for transverse samples (Battelle 6,7).

The same difference also appears, although less pronouncedly, in specimens of γ-rolled or γ-extruded metal. In this case the orientation must arise in the recrystallization of the metal with cooling. Longitudinal γ-extruded specimens have expansion coefficients of the order of 15×10^{-6} cm/(cm °C), while transverse specimens may have expansion coefficients up to 20×10^{-6} or 23×10^{-6} cm/(cm °C) (Battelle 7).

The expansion coefficient in different directions can be equalized to a certain extent by thermal cycling (heating to the isotropic β temperature region and cooling). One or two thermal cycles of this type usuallybring the linear expansion coefficient of longitudinal and transverse specimens of γ-extruded uranium to a common value of about 20×10^{-6} cm/(cm °C). Since the recrystallization occurs while the specimen is hot, the expansion coefficient is different on the heating and cooling branches of the thermal cycle (See Fig. 2); consequently, a net dimensional change remains after cycling. The specimen contracts by about 0.5 per cent in the direction of extrusion and dilates by about 0.25 per cent in the two directions perpendicular to that of extrusion. This change leaves the density practically unchanged. Similar although less detailed observations were also made in Britain.(2).

If thermal cycling is repeated several times, new and not yet clearly understood recrystallization phenomena occur with the result that the apparent length of longitudinal samples begins to increase again (Fig. 3). In the β-region, the linear expansion coefficient

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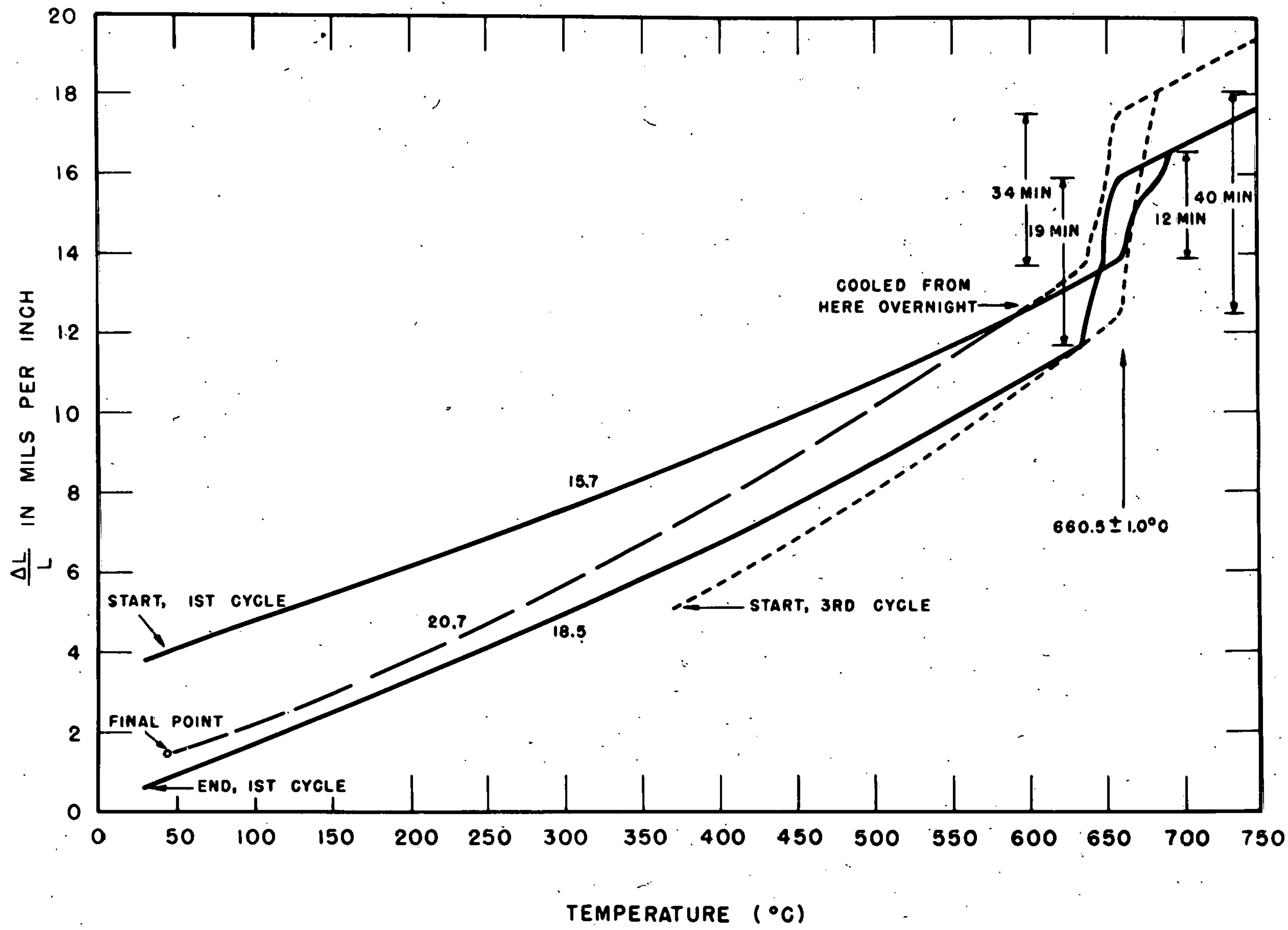

FIG. 2. DILATOMETRIC CURVE OF A LONGITUDINAL SPECIMEN OF γ-EXTRUDED URANIUM.

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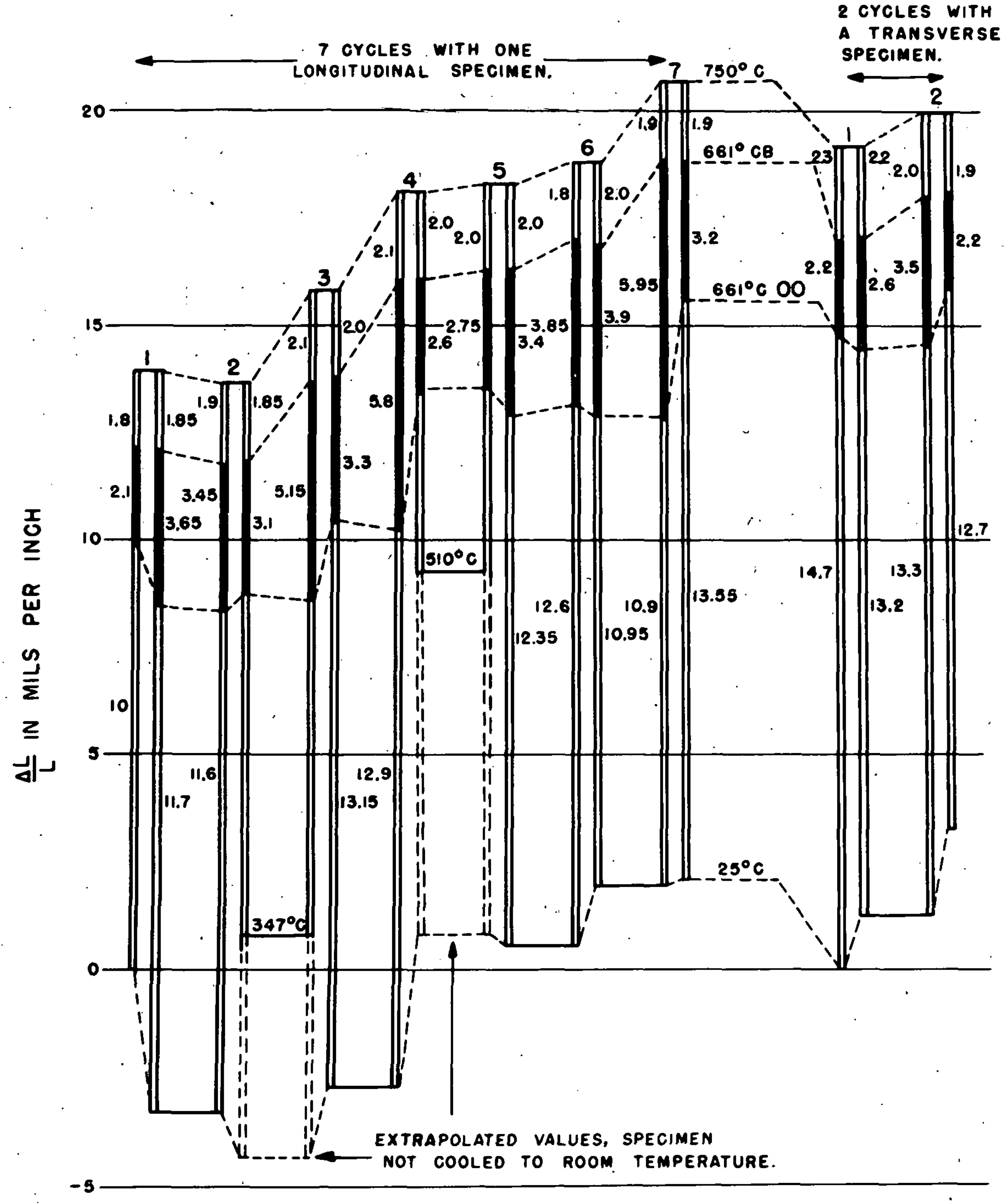

FIG. 3. CHANGES IN LENGTH CAUSED BY REPEATED CYCLING OF LONGITUDINAL AND TRANSVERSE SPECIMENS OF γ-EXTRUDED URANIUM.

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of uranium is about 22 x 10^{-6} cm/(cm °C) independent of direction (Battelle 6,7). Figure 2 is a typical dilatometric curve of a longitudinal sample of γ-extruded uranium in the α - and β -regions. The dimensional changes of uranium by thermal cycling are a source of trouble in some of its uses. This was the reason for the extensive dilatometric studies carried out at Battelle (8), the salient of which results were described above (See also Vol. 12A). Dimensional changes accompanying the α - β and β - γ transition (also shown in Fig. 2) will be discussed in Section 3.2.

2. Mechanical Constants of Uranium.

These constants are discussed in more detail in Volume 12 of this series. Here we shall give only the most important results. Annealing in the β-region (>660°C) approximately equalizes the mechanical properties of γ-extruded and cold worked metal. It was therefore suggested that the β-annealed state should be used as the "standard" state in the determination of mechanical constants of uranium metal (Battelle 7), but this suggestion has not been generally followed.

2.1 Hardness. Uranium cast at 1200°C usually has a surface hardness of about 100 on Rockwell B scale, but hardness declines to $85R_B$ at 0.05 in. depth (MP Chicago 4). The maximum hardness, 70-71 on Rockwell A scale corresponding to 115 on the Rockwell B scale, can be obtained by heating uranium at 900°C for 5 hours or more and then quenching in cold water (MP Los Alamos 2). This hardening effect may be due to the dissolution of carbide in the metal. British observers (British 3) found that the average hardness of cast refined Widnes Metal was 110 to 120 on the Brinell scale.

Uranium may also be work-hardened, as by swaging or rolling from $90R_B$ to $115R_B$ ($57R_A$ to $71R_A$) (Battelle 9,10). Most of the work-

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hardening is associated with the first 20 per cent reduction in thickness. Work-hardened metal begins to soften at [illegible]°C; [illegible] annealing is achieved at 650-700°C (Battelle 9; M.I.T. 5,4; Nat. Bur. Standards 2).

TABLE 3

ANNEALING OF WORK-HARDENED URANIUM (M.I.T. 4)

Temperature * °C	Rockwell C Hardness
310	36.5
490	24
600	22
720	9
770	0

*Samples annealed one hour at these temperatures.

Microhardness measurements of uranium by the methods of Knoop and Eberbach were carried out at Nat. Bur. Standards (3,4,5,6) and M.I.T. (5). Table 4 gives some typical results (Nat. Bur. Standards 3,6).

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TABLE 4

HARDNESS OF α-ROLLED URANIUM

Scale	Transverse Specimen	Longitudinal Specimen
Rockwell B	97	98
" G	80.5	83
Vickers Diamond (10-15 kg load)	220	240
" " (30-45 kg load)	--	250
Brinell (calculated from R_B)	240	260
" (calculated from R_G)	250	280
Knoop (200 g load)	260	320
" (500 g load)	250	300
" (1000 g load)	240	320
Eberbach (263 g load)	270	300
" (645.6 g load)	260	290

The decrease in uranium hardness with temperature was measured at Battelle (11,12) and in Britain (4). It changes but little up to 200°C, then declines rapidly from 252 Brinell at 20°C to 13 Brinell at 650°C, but increases again 30 to 40 Brinell in the β-state (660-700°C). The hardness drops below the range of measurability on the Brinell scale in the plastic β-state ($>$ 770°C).

2.2 <u>Elastic and Inelastic Deformation</u>. Uranium in the α-state was called above "semi-plastic", in fact, its stress-strains curves often show curvature even at loads of less than 10×10^3 psi (Nat. Bur. Standards 7). On the other hand, some stress-strain curves have been obtained which were apparently linear up to 50×10^3

psi (MP Chicago 5), but the elastic modulus calculated from the slope of these linear sections was so low ($\sim 5 \times 10^6$ psi) that the linearity was probably only an apparent one caused by insufficient precision of measurements at low stresses. More reliable may be the several stress-strain determinations (MP Chicago 6,7; MP Los Alamos 1,2,3; Battelle 5, 15; British 2,5; M.I.T. 6) which showed linearity up to 10×10^3 to 15×10^3 psi, and whose initial slope indicated an elastic modulus of 15×10^6 to 25×10^6 psi. Because of anisotropy of the α-phase, the elastic modulus probably depends on crystallographic direction. The available measurements are insufficient to establish this influence clearly, but the slightly lower value of the elastic modulus (15×10^6 to 20×10^6 psi) obtained with presumably longitudinal specimens of rolled metal may have been a consequence of crystal orientation due to cold working (MP Chicago 8,9; M.I.T. 3). Likewise, the elasticity of uranium, as well as the hardness, decreases rapidly with temperature in the α-phase, but increases again in the β-phase (MP Chicago 5; Battelle 14). (See Fig. 4).

The shear modulus of uranium was measured by Snyder and Kamm (MP Chicago 8,10). They found values of 6.6×10^6 psi and 6.8×10^6 psi for cold-swaged and annealed wire respectively.

A rigidity modulus of 8.5×10^6 psi was observed by Wollan and Stephenson (MP Chicago 11) with a sample whose elasticity modulus was 19×10^6 psi.

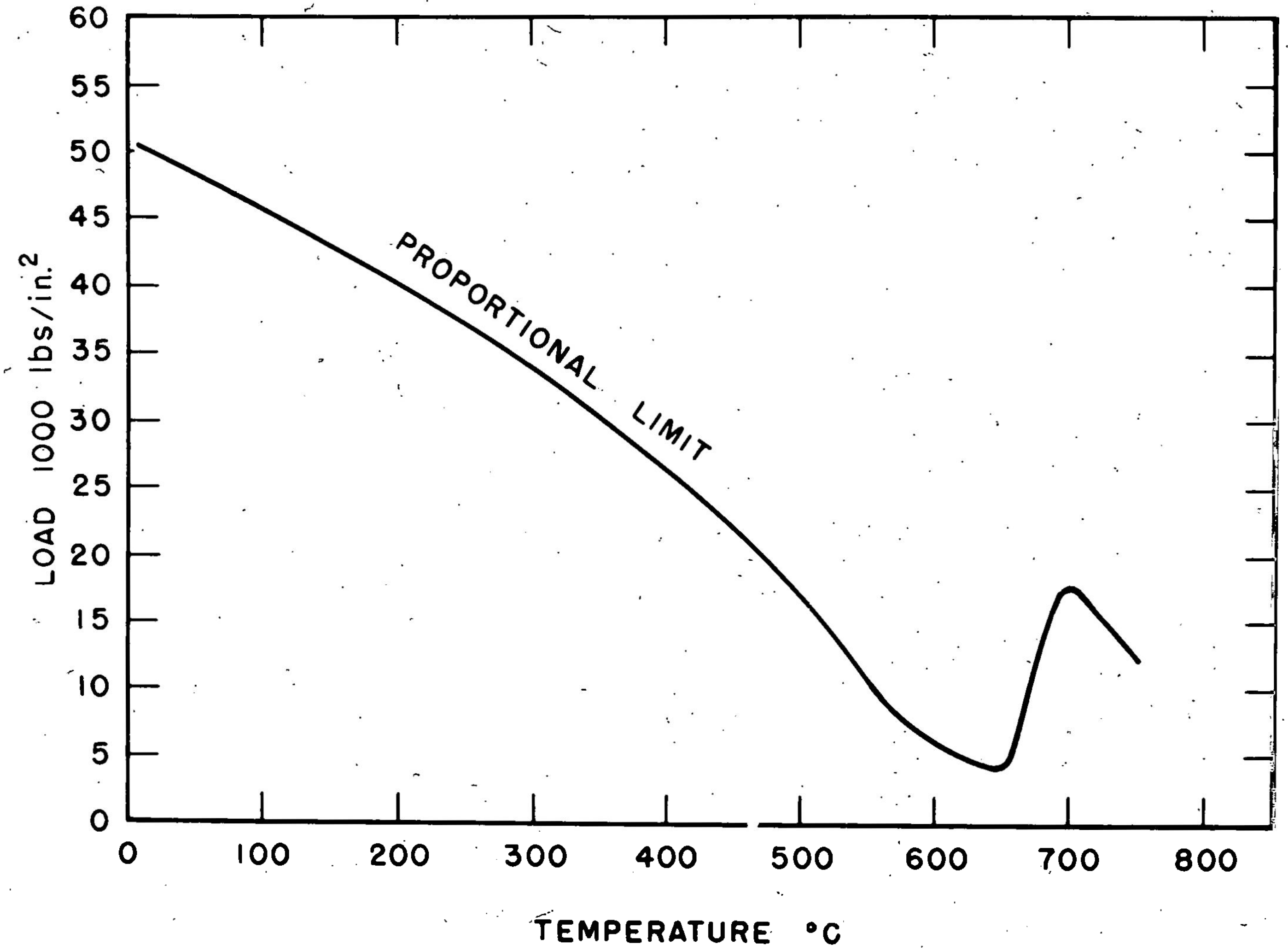

FIG. 4. ELASTIC CHANGE OF URANIUM WITH TEMPERATURE

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The measurements of Snyder and Kamm indicated a bulk modulus of $9x10^{-6}$ psi for cold-worked metal and $15x10^{6}$ psi for annealed wire. These values correspond to volume compressibilities of $12x10^{-8}$ and $6.4x10^{-8}$/psi respectively. Bridgman (1922) found that the average volume compressibility of probably not very pure uranium at 12,000 atm. (about $150x10^{3}$ psi) and 30°C is $9.7x10^{-7}$ cm^{2}/kg (about $7x10^{-8}$/psi).

Poissons's ratio (contraction normal to stress : elongation parallel to stress) is high in accordance with the semi-plastic nature of uranium. Battelle observers (6,13) found ratios of 0.32 to 0.43 for γ-extruded commercial metal, while Foote and co-workers (MP Chicago 8) found 0.42, 0.49 and 0.27 for α-rolled uranium annealed for over 12 hours at 565°, 750° and 800°C respectively. The above-mentioned measurements of Snyder and Kamm lead to a Poisson's ratio of 0.20 for the cold worked metal and 0.31 for the annealed wire. The elasticity and rigidity moduli found by Wollan and Stephenson correspond to an implausibly low value of Poisson's ratio, about 0.1.

The velocity of sound in uranium metal was calculated by Simmon (British 1) to be 1500 m/sec. It probably depends on crystallographic direction.

Being semi-plastic, α-uranium has no definite yield point. Its yield strength has been measured (MP Chicago 6,7; MP Los Alamos 1, 3; Battelle 7,13,14,15; British 2,3) as the strain under which the length of a specimen exceeds by a certain "offset" (usually 0.02, 0.1 or 0.2 per cent) the length which it would have if the deformation were elastic

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(i.e., if the stress-strain curve were linear). Because of the above-mentioned uncertainty of the initial slope of the stress-strain curve (that is, of the value of the elastic modulus) the determination of the yield strength by this method is very uncertain, and not much meaning can be ascribed to the variations in reported results. Most of the values given for the yield strength of uranium at room temperature are of the order of 25 x 10^3 to 35 x 10^3 psi for 0.2 per cent offset (MP Chicago 6, 7; MP Los Alamos 1), but some measurements gave results as high as 76 x 10^3 psi and some gave values as low as 8 x 10^3 to 13 x 10^3 psi (Battelle 13).

The highest yield strength was observed in α-worked metal (MP Chicago 7). Slow cooling after annealing decreases the yield strength and quenching, particularly from γ-phase temperatures, increases it. For example, the yield strength (0.2 per cent) of a set of α-rolled specimens was increased from 25x10^3 psi for furnace-cooled material to 32 x 10^3 psi for a specimen quenched from 570°C, and to 42x10^3 psi for a specimen quenched from 800°C (MP Chicago 6). In another example, the yield strength (0.1 per cent offset) rose from 17x10^3 psi for an "as -rolled" specimen, to 57x10^3 psi for a similar specimen quenched from 1000°C (Battelle 15). The yield strength of α-uranium decreases rapidly with increasing temperature, for example, from 43x10^3 psi at room temperature to 8.9x10^3 psi at 600°C (Battelle 14). Figure 5 shows that β-uranium has a definite yield point, 18x10^3 psi at 700°C and 13x10^3 psi at 750°C (MP Chicago 5).

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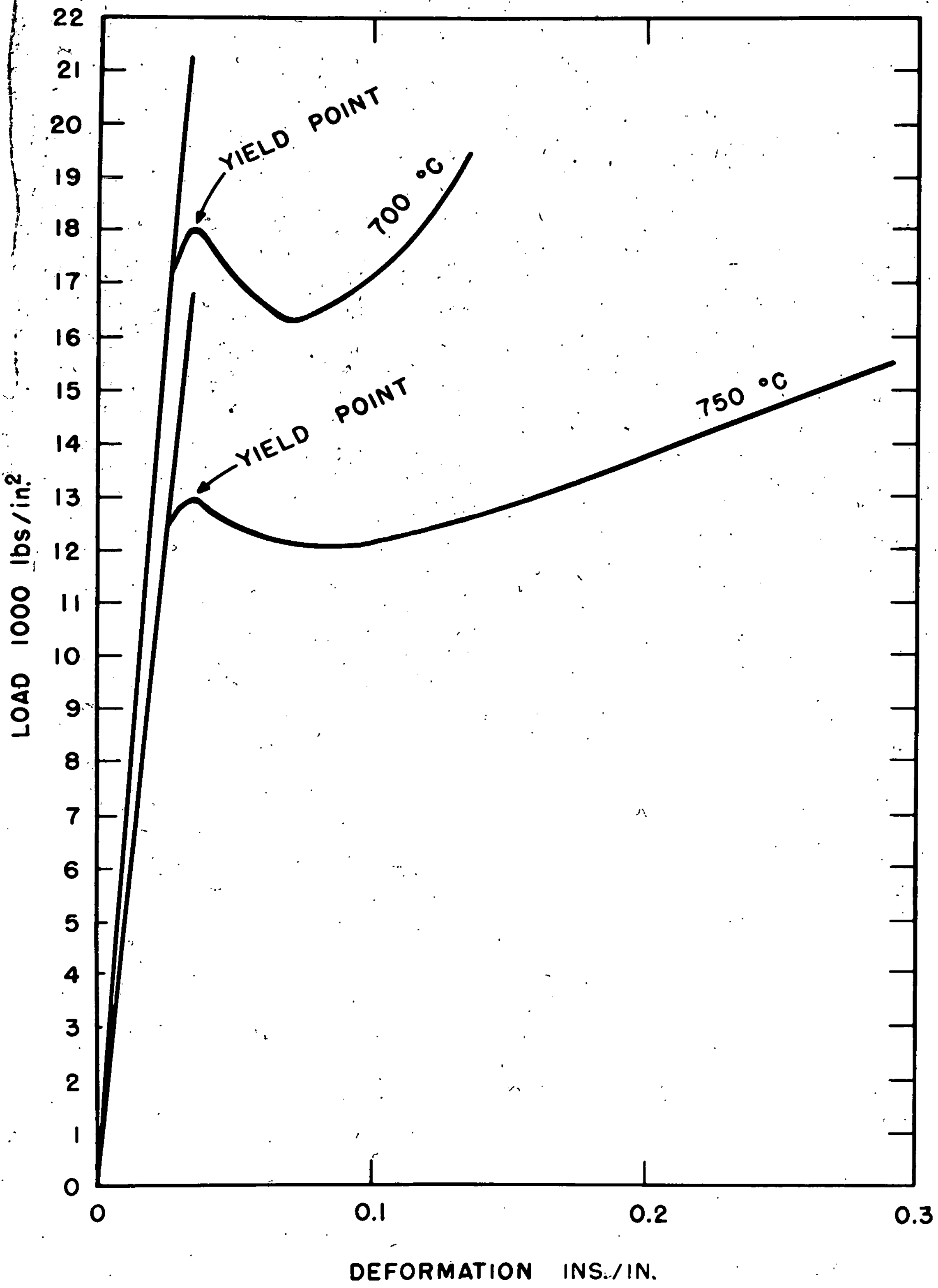

FIG. 5. COMPRESSION OF URANIUM AT 700 °C AND 750 °C.

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Similarly to the loading curves, the unloading curves of uranium also are non-linear (Battelle 6), and the residual deformation after unloading is therefore smaller than the offset measured under stress. The residual deformation remaining after the compression of uranium cylinders was measured in three laboratories (MP Chicago 5; MP Los Alamos 2; Nat. Bur. Standards 8). Such cylinders can be compressed to barrels with a decrease in height of 35 per cent without shattering. The pressure required for 10 per cent permanent compression decreases with temperature from 111×10^3 psi at 25°C to 7×10^3 psi at 650°C, but increases again in the β-phase to 17×10^3 psi at 700°C and 12.0×10^3 psi at 750°C (MP Chicago 5).

The offset under stress and the residual deformation after the release of stress both depend on the duration of loading indicating creep phenomena. Creep measurements on uranium were carried out at M.I.T. (7). Table 5 summarizes the results.

TABLE 5

CREEP OF URANIUM

Temperature (°C)	Load (10^3 psi)	Duration of Experiment (hrs.)	Average Elongation (% per 100 hrs.)
350	9	260	1.3
356	3.5	263	0.19
356	5.3	934	0.07 (last 300hrs)
355	3.52	~1000	0.037
355	5.27	"	0.089
353	8.80	"	0.22

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2.3. Strength. The ultimate tensile strength of uranium is similar to that of steel. It varies between 50,000 and 200,000 psi depending on cold working and thermal treatment of the specimen (MP Chicago 2,7; British 2; M.I.T. 3,4; Nat. Bur. Standards 3,7,8). Cold working (α-rolling or swaging) gives the highest tensile strength 170,000 to 200,000 psi (M.I.T. 3, 4; Nat. Bur. Standards 3,7). Annealing reduces it from 170,000 psi after swaging to 135,000 psi after annealing at 625°C and 65,000 psi after annealing at 830°C (Nat. Bur. Standards 3). Cast or γ-extruded specimens have almost as low tensile strength as γ-annealed and slowly cooled specimens, roughly 65,000 to 90,000 psi (MP Los Alamos 3; Battelle 11, 16; British 2,3,6). The tensile strength is somewhat improved by quenching particularly from the high temperature α - or γ-regions. Values of about 90,000 to 130,000 psi having been obtained for rolled, forged. or swaged specimens which were quenched from 600-1000°C (MP Chicago 2,7; M.I.T. 6; Nat. Bur. Standards 7).

Tensile strength decreases rapidly at elevated temperatures from 53×10^3 psi at room temperature to 27×10^3 psi at 150° and 12×10^3 psi at 600°C (Battelle 17).

Seitz (MP Chicago 12) commented on the low value of the ratio of tensile strength to elastic modulus for uranium, $2\times10^5/20\times10^6 = 0.01$, as compared to a theoretical value of approximately 0.3. He interpreted this as an indication of minute cracks in the metal which reduce considerably the area to which the stress is applied.

Elongation and area reduction in the tensile strength test are small in cold-worked metal, (British 2), 0-8 per cent (MP Chicago 7), and a little larger, 5-10 per cent and 3 to 15 per cent respectively, in γ-extruded material (MP Los Alamos 3; British 6). Much greater ductility (elongation and area reduction values up to 20 per cent) has been found for α-rolled specimens annealed and quenched from the high α-region (350-600°C). Quenching from the β or γ-region (700°-800°C) reduced the values to 10 per cent or less. Drop hammer tests showed very little ductility in the low β-region (660°-670°C), but this property increased from 4 to 44 per cent at 705°C (Battelle 18).

The Charpy impact strength of three uranium ingots was given as 13 to 16 ft lb (corresponding to 1.9 to 2.3 m kg (Nat. Bur. Standards 10) British observers gave a value of 5 ft lb for Widnes cast metal (British 2) and 8 ft lb for an extruded rod (British 6).

The fatigue strength of α-extruded bars of uranium was measured on a Krause 10,000 rpm cantilever beam machine at Battelle (19). The endurance limit is in the range of 25,000 psi. At 35,000 psi, the specimens failed after 1.2×10^5 to 2.5×10^5 cycles; preliminary treatment at 25,000 psi increased the endurance under higher stresses. The ratio of endurance limit to tensile strength is $\sim$0.2 which is a low value for metals.

<u>Rupture strength</u> of uranium discs was measured by supporting them in a holding ring and rupturing with a central

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column (0.5 in. in diameter). The average rupture strength was 3928 lb for γ-extruded metal (900 ppm C, 150 ppm Fe) and 4648 for α-extruded material (300 ppm C, 65 ppm Fe) (MP Chicago 13). Annealing for 15 hours at 600°-800°C decreased the rupture strength slightly, while annealing at temperatures greater than 900°C and quenching increased it considerably (MP Chicago 14).

3. Thermodynamic Properties of Uranium

3.1 Specific Heat, Energy and Entropy. The specific heats of uranium at low temperatures were measured by Long and co-workers (Columbia 2), those at high temperatures by Moore (Columbia 3) and more recently by Ginnings and Corruccini (Nat. Bur. Standards 16). The results are given in Tables 6 and 7 and Figures 5 and 6. The Dulong-Petit value is exceeded at a temperature as low as -73°C.

Long and co-workers gave only C_p values, Moore only values of $H_T - H_{298.16}$, and Ginnings and Corruccini $H_T - H_{273.16}$, C_p, $S_T - S_{273.16}$. The values of C_v, in Table 6 were calculated by Simon (British 1). In Table 7 one set of C_p, H_T and S values were calculated by Simon while the other set is from Ginnings and Corruccini. In the calculation of C_v and S, below 15°K, Simon used the Debye function with $\Theta = 162°K$. There is a discrepancy between Simon's values for H_T and for C_p in the region 300°-500°K, which is probably due to an attempt to acheive a smooth transition from the C_p values in Table 6 to those in Table 7.

Long and co-workers calculated for the entropy at 25°C

$$S_{298.16} = 12.03 \pm 0.03 \text{ e.u.}$$

while Ginnings and Corruccini gave the following equations for the entropy:

(10) β (941°-1047°K) $S_T - S_{273.16} = 23.362 \log_{10} T - 58.770$

(11) γ (1047°-1170°K) $S_T - S_{273.16} = 21.062 \log_{10} T - 50.745$

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TABLE 6
SPECIFIC HEAT OF URANIUM (15-300°K)

T (°K)	C_p (cal/mole °K)	C_v (cal/mole °K)	T (°K)	C_p (cal/mole °K)	C_v (cal/mole °K)	T (°K)	C_p (cal/mole °K)	C_v (cal/mole °K)
15.38	0.432		81.52	4.955		192.57	6.154	
16.61	0.496		87.05	5.072		198.47	6.203	
18.55	0.665		92.96	5.194		200		6.17
20		0.81	98.93	5.325		205.12	6.232	
21.01	0.914		100		5.33	211.07	6.274	
23.91	1.211		104.81	5.435		217.76	6.295	
27.55	1.639		111.00	5.532		224.89	6.335	
31.19	2.080		117.40	5.591		231.88	6.348	
35.32	2.530		123.48	5.639		238.73	6.381	
40.		2.94	128.23	5.697		245.59	6.417	
40.10	2.954		134.58	5.754		250		6.39
45.27	3.369		140.90	5.823		252.89	6.441	
50.49	3.731		147.06	5.874		259.36	6.476	
55.53	4.011		150		5.86	266.32	6.486	
60		4.20	153.35	5.924		273.02	6.524	
60.63	4.231		159.76	5.964		280.16	6.544	
65.78	4.446		166.65	6.008		287.50	6.548	
71.57	4.657		173.61	6.053		294.88	6.556	
75.99	4.807		180.04	6.091		297.71	6.574	
80		4.90	186.37	6.131		300		6.51

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TABLE 7

SPECIFIC HEAT, HEAT CONTENT AND ENTROPY OF URANIUM (300°-1375°K).

T °K	C_p^*	C_p^{**}	H_T^*	H_T^{**}	S^*	S^{**}
	(cal./°g. atom)		(cal./g. atom)		(e.u.)	
300	6.6	6.649	1440	1539.12	12.07	12.052
400	7.0	7.072	2160	2202.57	13.97	13.941
500	7.5	7.606	2940	2935.42	15.60	15.601
600	8.1	8.227	3730	3725.45	17.04	17.056
700	8.9	8.952	4580	4582.96	18.35	18.387
800	9.9	9.863	5535	5520.47	19.62	19.646
900	11.0	11.107		6566.80		20.882
935(α)	11.3		6975		21.29	
941(α)		11.737		7066.16		21.436
935(β)	10.2		7640		22.00	
941(β)		10.147		7740.37		22.152
1000	10.2	10.147		8336.97		22.760
1045(β)	10.2		8770		23.14	
1047(β)		10.147		8815.97		23.236
1045(γ)	9.2		9940		24.12	
1047(γ)		9.147		9947.04		24.316
1100	9.2	9.147	10440	10430.16	24.55	24.761
1200	9.2		11350		25.38	
1300	9.2		12260		26.12	
1375	9.2		13000		26.8	

*Values calculated by Simon.
**Values by Ginnings and Corruccini.

Moore gave the following equations as representing the experimental results for the three uranium phases:

(2) α (500°-935°K) $H_T - H_{298.16} = 0.076T + 5.817 \times 10^{-3}T^2 - 4.035 \times 10^5 T^{-1} + 814$ (± 0.9%)

(3) β (935°-1045°K) $H_T - H_{298.16} = 10.27T - 3402$ (± 0.2%)

(4) γ (1045°-1300°K) $H_T - H_{298.16} = 9.125T - 1035$ (± 0.2%)

Equation (2) does not accurately represent the results below 500°C. Ginnings and Corruccini gave the following equations as representing the experimental results for the β - and γ -uranium phases:

(3a) β (941°-1047°K) $H_T - H_{273.16} = -3170.52 + 10.147T$ (± 0.1%)

(4a) γ (1047°-1173°K) $H_T - H_{273.16} = -992.80 + 9.147T$ (± 0.1%)

The range from 273° to 941°K cannot be represented by a simple equation.

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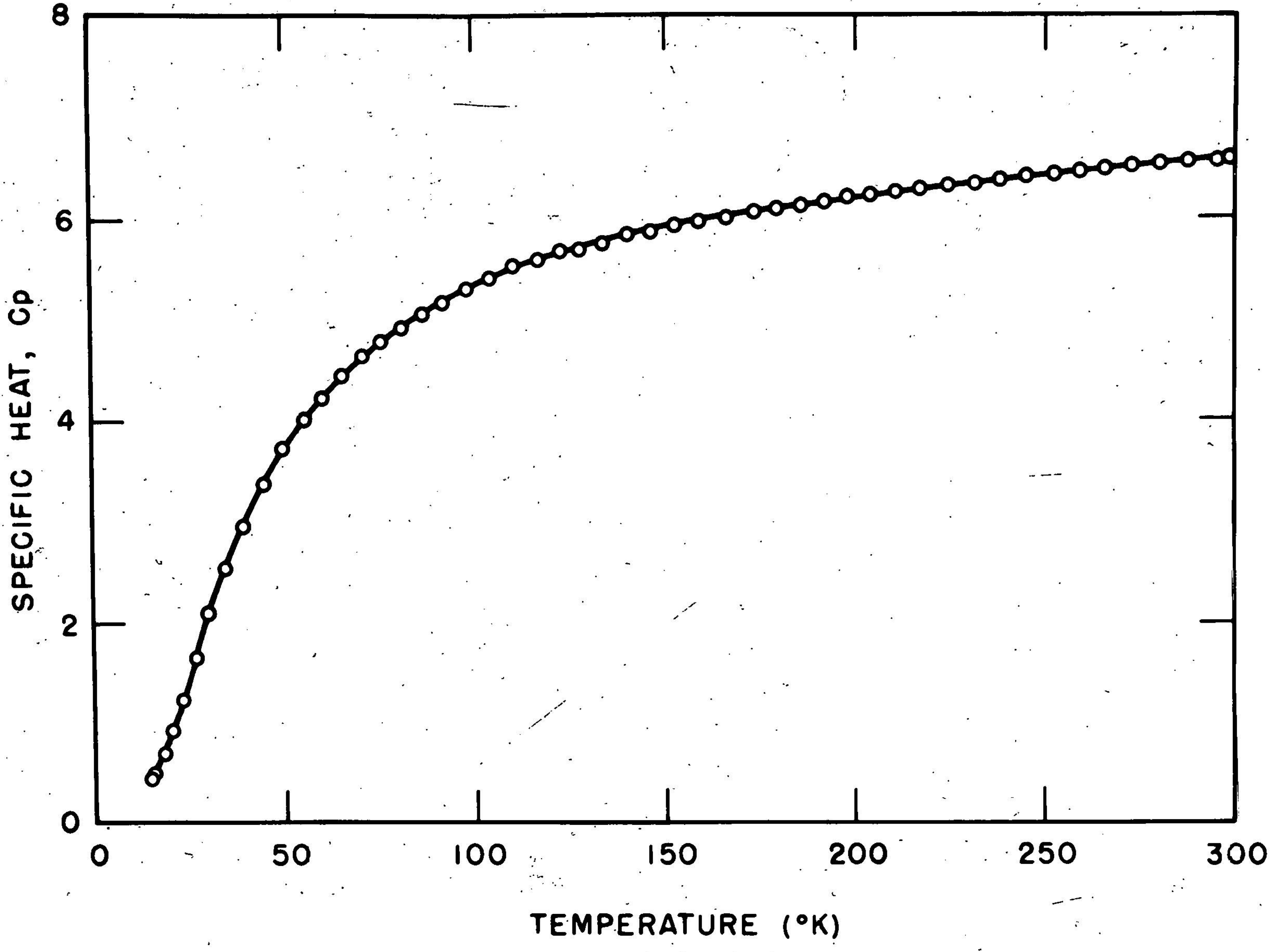

FIG. 6. SPECIFIC HEAT AT LOW TEMPERATURES

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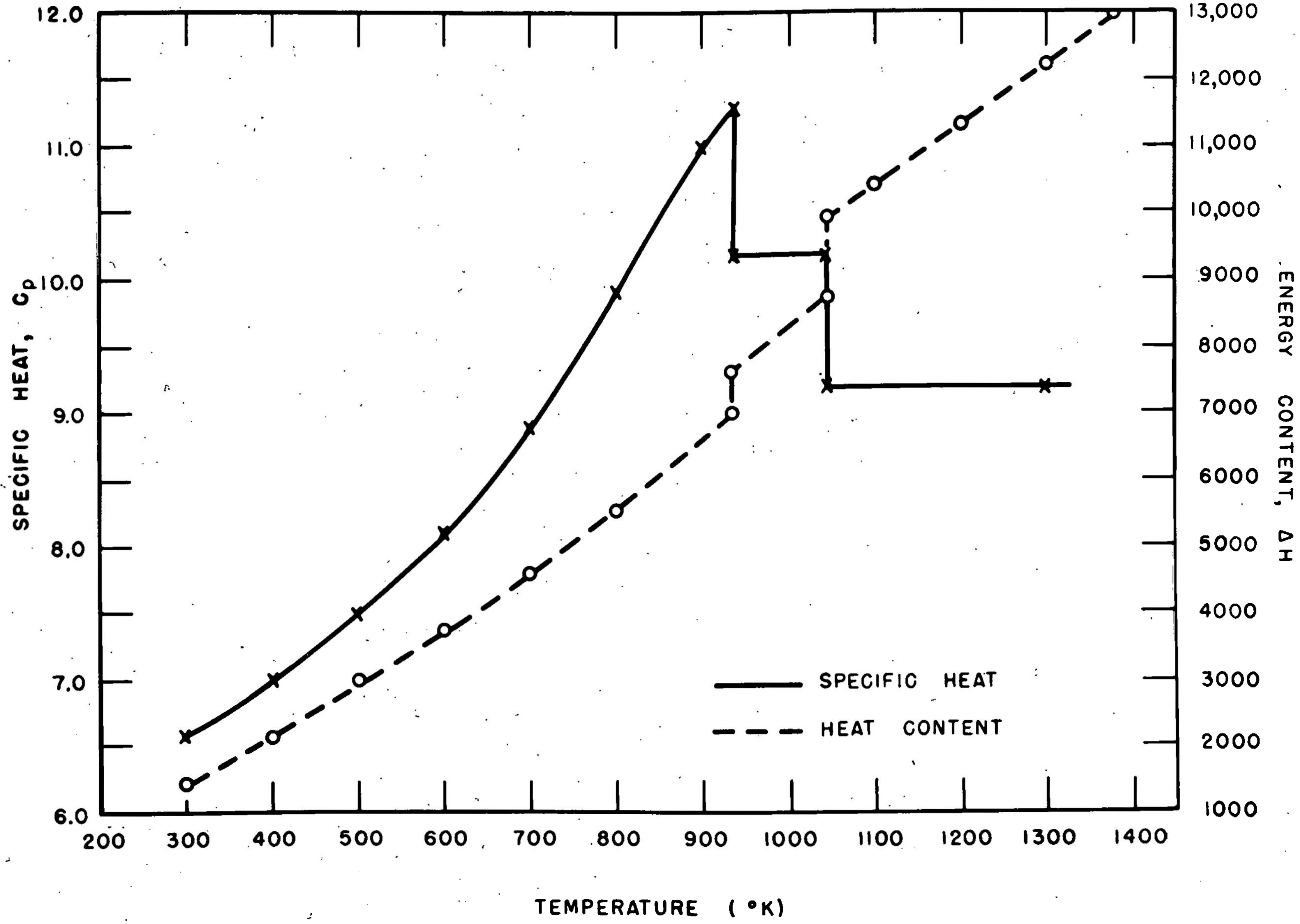

FIG. 7. SPECIFIC HEAT OF URANIUM AT ELEVATED TEMPERATURES.

3.2 Solid Transformations. The transition temperatures of the three uranium phases, α, β, and γ, have been determined by thermal analysis as well as from dilatometric curves (See Fig. 2) and electrical conductivity curves (See Fig. 8). The most reliable observed transition temperatures are given in Table 8.

Figure 8 illustrates the fact that with α-extruded metal, as well as with cast metal and biscuit metal, the allotropic transitions usually are delayed both on heating and on cooling. In γ-extruded material, on the other hand, the transitions begin without delay. However, even in this material the $\alpha - \beta$ transition is not strictly isothermal, but extends over a range of several degrees. This may be due to non-uniform internal pressure (Battelle 11). Since at the transition temperature the β-phase is less dense than the α-phase, increased pressure must raise the transition temperature.

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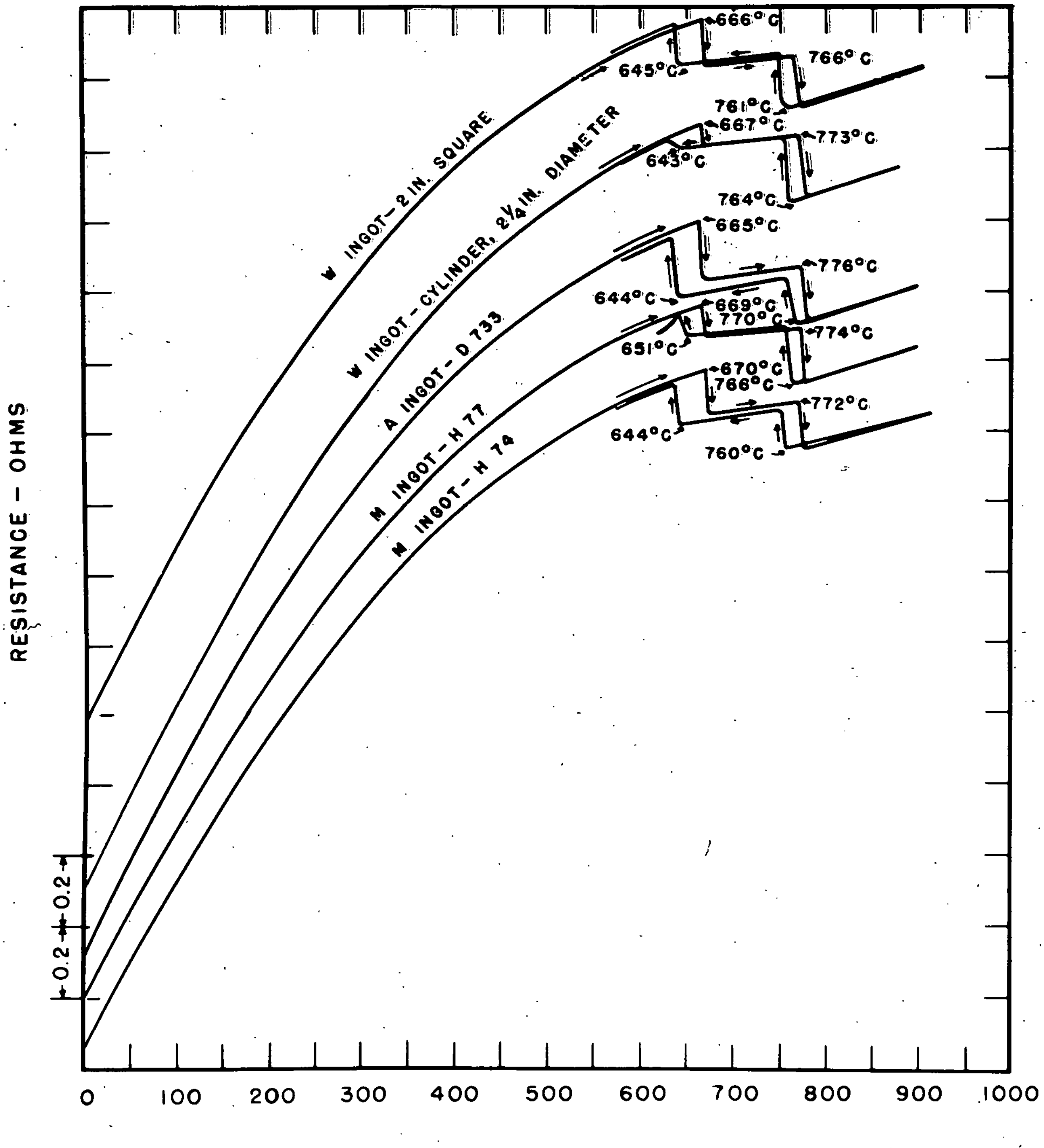

FIG. 8. ELECTRIC RESISTANCE OF URANIUM AS A FUNCTION OF TEMPERATURE.

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TABLE 8

TRANSITION TEMPERATURES OF URANIUM

Material	Transition Temperature (°C)				Method of Determination	References
	Heating		Cooling			
	α→β	β→γ	γ→β	β→α		
Forged 2/10 in. round bars of cast metal hydrides	673	775	770	...	Thermal arrests	(M.I.T. 6)
Not described	662±3	772±3	...	...	Heat content measurements	(Bureau of Mines 1)
U with 0.03% C U with 0.39% C U with 1.5% C	... ...	... ...	775 785 766	645 652 633	Thermal arrests	(MP Ames 6)
Not described	665	776	770	644	Resistivity	(Nat. Bur. Standards 9)
γ-extruded rod, longitudinal specimen	660.5 ±1.5	...	...	...	Thermal arrests	(Battelle 6)
M, A,W ingots	665-670	766-776	760-770	643-651	Electrical conductivity	(Nat. Bur. Standards 11)
Widnes metal	650	764-771	752	629	Thermal arrest	(British 2, 4)
Widnes billet	641	751	750	629	Thermal arrest	
extruded 99.9% U	669-671.5	779-785	765	642-643	Dilatometry	(British 7)
Extrapolated for pure U from results obtained with 98.6-99.9%	644±4	765±10	752±3	624±3	Thermal arrests	(British 3)

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The effect of carbon on the transformation temperatures shown in Table 8 is insignificant (Nat. Bur. Standards 11), but other additions affect these temperatures very much. For example, 2.5 per cent molybdenum decreases the lower limit of stability of the γ-phase by as much as 120°C and eliminates the β-region altogether. As mentioned in Section 1.1, the γ-phase can be preserved in these alloys at room temperature by rapid cooling. The emissivity of uranium changes suddenly at 1048-1050°C (Wisconsin 1); this may indicate a third allotropic transformation.

The dimensional change accompanying the $\alpha - \beta$ transformation depends on the previous history of the specimen, because the dimensions of the α-phase can be changed by thermal cycling, as described in Section 1.4. By repeated recycling of longitudinal specimens of γ-extruded metal (Battelle 6), the change in length associated with the $\alpha \rightleftharpoons \beta$ transformation (extrapolated graphically for isothermal transition at 661°C) varied between +0.2 and +0.6 per cent with heating and between +0.3 and +0.4 per cent with cooling. In transverse specimens the variation was from +0.2 to +0.35 per cent with heating and from +0.2 to +0.25 per cent with cooling (See Fig. 3).

The $\alpha \rightarrow \beta$ transformation absorbs 665 cal/g atom, and the $\beta \rightarrow \gamma$ transformation 1165 cal/g atom (See Table 7). The entropy of the first change is 0.71 e.u., that of the second one, 0.98 e.u. (Columbia 3).

3.3 Melting Point and Energy of Fusion of Uranium

Uranium was long considered as having a high melting point, a property which seemed consistent with its position in the periodic system at the bottom of the column occupied by metals with increasingly high melting point, chromium, molybdenum and tungsten. Driggs and Lilliendahl (1930) and Hole and Wright (1939) experimentally found melting points of 1690°C and 1700 1250°C respectively. However, these values were found to be much too high in 1941-1942 when work on the preparation of pure metal got under way. In England (British 8) a melting point of 1150°C was found for a sample prepared by reduction of UF_4 with calcium and magnesium. More recent determinations gave 1105° to 1116°C for 99.8 per cent pure and 99.9 per cent pure uranium (British 2,3). In America the first re-determinations gave a value of 1300°C (MP Chicago 15; Nat. Bur. Standards 12), and subsequent, more precise measurements at Nat. Bur. Standards (13) lead to still lower values, 1080°±20°C for 99.1 per cent pure uranium and 1125 ± 25°C for 99.7 per cent pure uranium. Values ranging from 1123°C (1.5 per cent carbon) to 1134°C (0.03 per cent carbon) were obtained at Ames (MP Ames 6). A value of 1125°C was extrapolated at M.I.T. (8) from the uranium-aluminum diagram of state.

Probably the most reliable determinations of the melting point were made in 1944 at Nat. Bur. Standards. They showed that uranium containing 0.03 to 0.05 per cent carbon first melted at 1125°C, but that if the metal was kept just above the melting point for up to 15 hours, its solidification point rose gradually to 1130°-1132°C. During this time the carbon content decreased to 1/100 of its original value (from 500 to 5 ppm), and the remaining carbon was largely segregated as carbide in the crust formed on the metal. It is thus reasonable to attribute the rise in melting

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point to "self-purification" of the metal. Consequently the most likely value for the melting point of pure uranium is:

$$t_F = 1132 \pm 1^{\circ}C$$
$$T_F = 1405 \pm 1^{\circ}K$$

The energy of fusion of uranium was estimated by Simon (British 1) as ΔH_F = 2.5 to 3.0 kcal/g atom. This gives ΔS 2 e.u. for the entropy of fusion.

3.4 Vapor Pressure and Energy of Evaporation

All presently available measurements of the vapor pressure of uranium are of preliminary nature and the observed values differ greatly. Early Chicago measurements (MP Chicago 16) made by the "rate of evaporation" method, gave values of 0.0013 mm at 1300°C, 0.0044 mm at 1620°C, 0.026 mm at 1900°C, and 2.4 mm at 2300°C. The log p versus 1/T curve shows clearly that the first two values are much too high. Figure 9 is vapor pressure curve based on "rate of effusion" measurements made at Nat. Bur. Standards and reported in a later Chicago report (MP Chicago 17). New effusion rate measurements at Chicago (MP Chicago 18) gave three points with tantalum crucibles and four with beryllia crucibles. Derge and Cefola considered the three measurements with tantalum crucibles to be more reliable than the others, but the slope of vapor pressure curve drawn in Figure 10 through one of these points and the average of the other two obviously is very uncertain.

Simon (British 1) undertook to construct the vapor pressure curve of uranium using only one experimental point (p = 0.05 mm at 2200°K) which he described as the "center of gravity" of the results of Creutz and of Anderson, and relying

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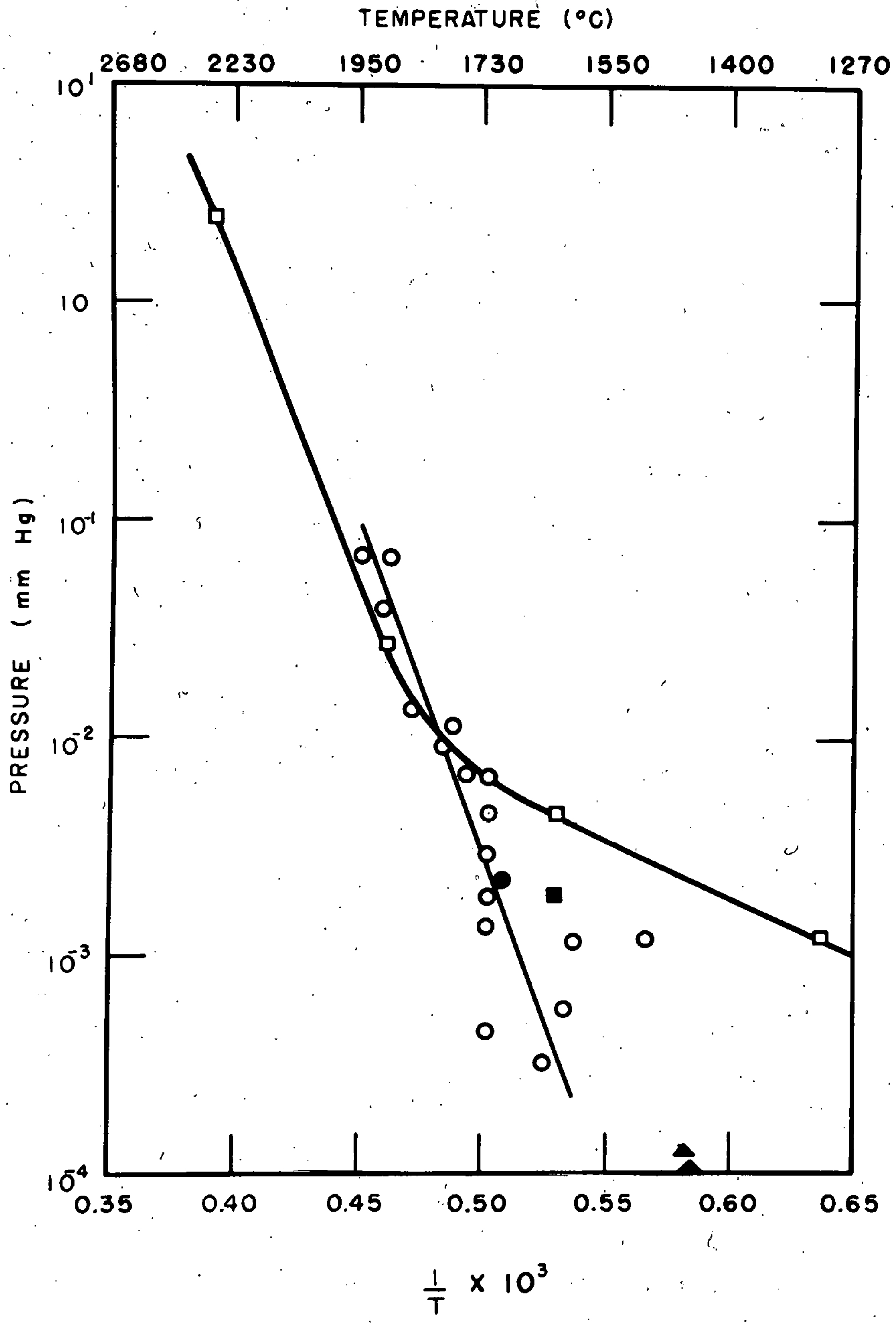

FIG. 9. VAPOR PRESSURE OF URANIUM AT 1300 – 2300 °C

SOURCES: ANDERSON, ○ CREUTZ, □ SIMON, ■

DERGE AND CEFOLA { ▲ Ta CRUCIBLES
● BeO CRUCIBLES

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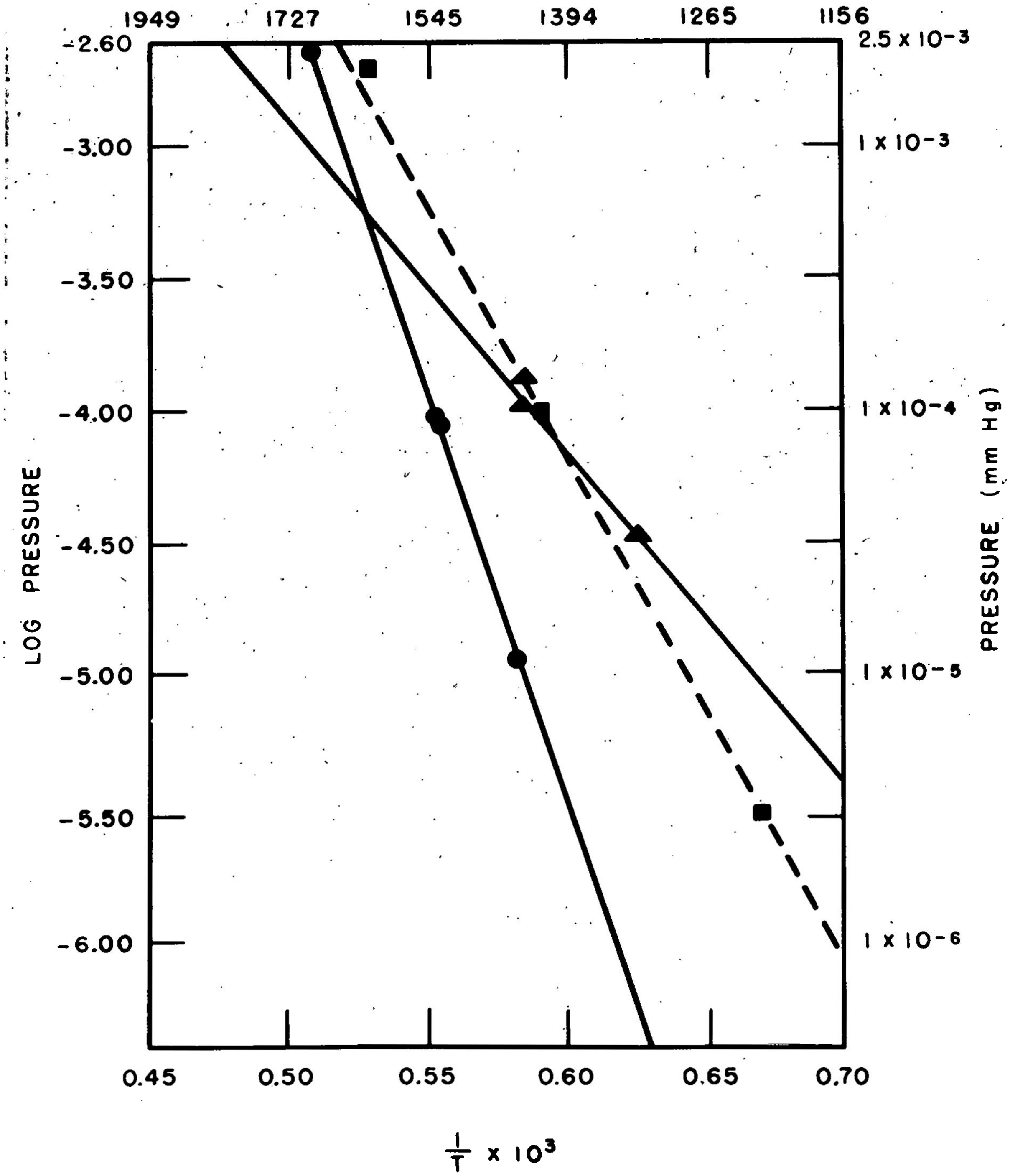

FIG. 10. VAPOR PRESSURE OF URANIUM

SOURCES: SIMON ■ - SEMI-THEORETICAL VALUES

DERGE AND CEFOLA { ▲ Ta CRUCIBLES
● BeO CRUCIBLES

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for the rest on theoretical considerations. He estimated the following entropy values:

$$(5)\quad S^{o}_{liq} = -36.3 + 20.7 \log T \text{ and}$$

$$(6)\quad S^{o}_{gas} = 4.57\,(2.5 \log T - \log p_{atm} + 3.66)$$

(A value log g = 0.6 was used for the symmetry factor in the last equation). With the help of these entropy values and the one above-mentioned empirical point on the vapor pressure curve, he arrived at the equation:

$$(7)\quad \log p(_{mm}H_{g}) = -(100\times10^{3}/4.57\,T) - 2.04 \log T + 14.5$$

which gives the following pressures:

TABLE 9

VAPOR PRESSURE OF URANIUM

Temperature (°C)	Pressure (mm Hg)
(4200)	(760)
2200	5×10^{-2}
1900	2×10^{-3}
1700	1×10^{-4}
1500	3×10^{-6}
1375	2×10^{-7}
1200*	1×10^{-9}
1100*	3×10^{-11}

*These values were calculated for solid γ -uranium.

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Figure 10 shows that Simon's curve lies approximately midway between the two curves of Derge and Cefola.

The energies of vaporization, calculated from the slopes of the log p versus 1/T curves, are as follows:

	λ (kcal/mole)		λ_0 (kcal/mole)
Simon	93		∼ 100
Derge and	58	(Ta-crucibles)	-
Cefola	137	(BeO-crucibles)	-

About the only thing which can be concluded from these figures is that uranium not only melts 2240°C lower than tungsten, but is also considerably more volatile than this metal. (The heat of vaporation of tungsten is about 175 kcal/g atom).

4. Electronic Properties of Uranium

4.1 Electrical Conductivity. Uranium is a rather poor conductor. Its electrical conductivity is about one-half that of iron. The conductivity values found by different observers vary between 2×10^4 mho. The highest conductivity at room temperature and the greatest increase in conductivity upon cooling to liquid air temperature are considered as indicative of superior purity.

Table 10 shows that the highest conductivity observed so far (4×10^4) was found at Nat. Bur. Standards with 1943 metal specimens, which have probably since been surpassed in purity. the largest value of the ratio, $K_{273^\circ K}/K_{90^\circ K}$, was found to be 2.6 by British observers with an American specimen having a specific conductivity of 3.5×10^4 at 0°C. This ratio is still considerably below the theoretical value ($K_{273^\circ K}/K_{90^\circ K} = 4$) calculated by Simon (British 1) for pure uranium from its Debye temperature.

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TABLE 10

ELECTRICAL CONDUCTIVITY OF URANIUM

K = conductivity, ρ = resistivity, α = temperature coeff. of ρ

Material	T°C	$K \times 10^4$ ohm cm.	$\rho \times 10^{-6}$ ohm cm.	$\alpha \times 10^{-3}$/°C	$\frac{K_{273°K}}{K_{90°K}}$	Reference
Cylinder (2.5"dia) from a W ingot, annealed, (10 min. at 600°C); Swaged wires (1-5 mm dia.) same material and treatment.	25	4.0	25.0	2.78	-	(Nat. Bur. Standards 11)
	25	3.6- 3.8	26.2- 27.5	2.70-2.82	-	
99.93% American rolled metal, after prolonged annealing (600°C) Same, no annealing.	0	3.47	28.8	-	2.6	(British 3,9)
	0	3.35	29.9	-	2.3	
99.86 to 99.90% British metal, after prolonged annealing (600°C) Same, no annealing.	0	3.11 3.38	29.6 32.2	-	2.5	(British 3,9)
		2.92 3.13	29.8 34.3	- -	1.9- 2.0	
ICI metal, rolled strip 99.8-99.9%	23	3.1 3.2	31-32			(British 2)
ICI metal, forged, turned.	23	3.0	34	2.0	2	
		3.1	32.1	2.1 (23-140°C)	-	Driggs (1930)
Rolled wire 1/3"		2.44	41			(MP Chicago 8,9)

Prolonged annealing in the high α -region at 600°C to release working stresses somewhat improved the room temperature conductivity and particularly the ratio, $K_{273^\circ K}/K_{90^\circ K}$, but not enough to approach the theoretical value. According to Nat. Bur. Standards (8) the conductivity is decreased by annealing in the β or α -region.

In another British report (10) reference is found to measurements of the conductivity of a uranium sample (containing 0.03% Ca, 0.02% Hg, 0.002% Sn, 0.14% Si, 0.19% Cu, 0.60% Fe, 0.04% Al and 0.30% C) from 13.9°K to 373°K. No figures are given, but it is states that the results can be represented within -0.5 per cent, by the equation:

$$(8) \quad R_T = R_A \quad (1-R_A) \frac{\rho_T}{\rho_{273.2}} \quad \frac{G(\theta/T)}{G(\theta/273.2)}$$

where R_T is the ratio, $\rho_T/\rho_{273.2}$, of the resistivites at T°K and at 273.2°K and G is the so-called Grüneisen function whose values can be taken from tables. A value of 175°K had to be assumed for θ , which is in satisfactory agreement with the characteristic temperature of 162°K derived from specific heat measurements (See Sec. 3.1). The quantity R_A can be represented by:

$$(9) \quad R_A = 0.194 + 0.000511\ T$$

A "residual resistivity" of $0.194\rho_{273.2}$ is much larger than could be expected from the presence of 0.1 per cent impurities listed above. Thus, the metal used must have contained either marked quantities of hydrogen or oxygen for which no analysis was available, or numerous physical disturbance centers.

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In renewed British investigations (British 6) the value of residual resistivity was re-determined for a 99.86 per cent pure uranium sample, which was annealed for 4 hours at 595°C, furnace cooled, and cold-rolled to 75 per ent reduction. Without annealing $\rho_0/\rho_{273.2}$ was 0.22_5. After 3/4 hour annealing at 800°C, cooling to 600°C in 2 and 1/4 hours, subsequent annealing for 8 hours at 595°C, and furnace cooling, this ratio was 0.15_5, while after simple annealing for 8 hours at 595°C and furnace cooling, it dropped as low as 0.135. The resistivity values given in Table 11 were obtained from the latest available British report (British 3).

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TABLE 11

EFFECT OF IMPURITIES AND HEAT TREATMENT ON THE RESISTIVITY

Analysis (Total Uranium and Major Impurities)				Heat Treatment
U	Fe	Si	C	
99.83	.086	.034	.001	As cold rolled S. C. 800°- 500°C and air cooled*
99.90	.033	.022		As cold rolled S. C. 800°- 500°C and air cooled Ann. 8 hrs. 600°C. and furnace cooled**
99.83	.038	.019		S. C. 800°-500°C and air cooled
99.87				As cold rolled S. C. 800-500°C and air cooled Ann. 8 hrs. 600°C and furnace cooled
99.86	.059	.052	.004	As cold rolled Ann. 8 hrs. 600°C and furnace cooled
99.79	.054	.053		As cold rolled Ann. 8 hrs. 600°C and furnace cooled
99.86	.052	.0005	.027	As cold rolled Ann. 8 hrs. 600°C and furnace cooled (Ann. 3/4 hr. 800°C, cooled to 600°C. (in 2½ hrs. held 8 hrs. 600°C. and (furnace cooled.
99.79	.057	.023	-	As cold rolled
99.74	.14	.018	.015	As extruded

*S.C. = slow cooled

** Ann. = annealed

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Resistivity (ohms x $10^{-6}/cm^3$)				Ratio	Residual Resistance Ratio	Conductivity at 20°C 10^{-4}/ohm cm.
20°C (293°K)	0°C (273°K)	-70°C (203°C)	-183°C (90°K)	$\frac{\sigma\ -183^\circ C}{\sigma\ \ 0^\circ C}$	$\frac{\sigma\ -273^\circ C}{\sigma\ \ 0^\circ C}$	
32.52	30.90	25.25	15.25	0.49		3.08
34.15	32.35	26.10	15.00	0.46		2.93
35.95	34.20	27.85	16.95	0.496		2.78
33.40	31.65	25.35	14.15	0.45		3.00
34.15	32.15	25.00	12.75	0.397		2.93
35.50	33.60	26.95	15.75	0.47		2.82
33.65	32.00	26.10	15.80	0.494		2.97
35.55	33.75	27.35	15.35	0.455		2.82
31.45	29.60	23.10	11.95	0.404		3.18
34.50	32.90	27.25	17.30	0.526		2.90
31.60	29.75	23.25	12.00	0.403		3.17
32.93	31.50	26.30	17.00	0.54		3.04
28.70	27.20	21.75	11.30	0.416		3.49
31.30	29.75	24.10	13.56	0.455	0.221	3.20
29.90	28.30	22.50	11.45	0.405	0.092	3.34
29.70	28.20	22.40	11.55	0.410	0.140	3.37
					0.244	
					0.194	

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In the anisotropic α-phase conductivity probably depends on crystallographic direction. Because of preferential orientation of crystals in drawn, rolled or extruded metal, the conductivities of "transverse" and "longitudinal" specimens of polycrystalline material which have undergone one of these treatments are likely to be different.

The change of resistivity at elevated temperature is illustrated in Figure 8, taken from Thompson's measurements at Nat. Bur. Standards (9). The sudden changes at 640-670°C and 760-780°C correspond to the α - β and the β - γ transition respectively. All curves show hysterisis, that is, overheating on the ascending branch and undercooling on the descending branch. The temperature coefficient of resistivity declines in the α-phase, from about 3×10^{-3} at room temperature to about 0.5×10^{-3} at 650°C, and drops to 0.14×10^{-3} in the β-phase (800-900°C) (Nat. Bur. Standards 9,11).

Under high pressure (up to 12,000 atm.) the resistance of uranium was found by Bridgman (1923) to decrease at an average rate of 4.36×10^{-4} per cent atm. However, the sample used by Bridgman for this determination was not very pure, as shown by its high resistivity at 0°C ($76 \times 10^{-6}\,\Omega$cm.)

4.2 <u>Thermal Conductivity</u>. With the exception of some early measurements on sintered Metal Hydrides metal (MP Chicago 3,8,11,20), which gave thermal conductivites of the order of 50 x 10^{-3} cal/(sec cm °C) or less, all other observations at Chicago (MP Chicago 11,21), Battelle (20) and England (British 2) lead to values of about 60-65x10^{-3} cal/(sec cm °C) for the thermal conductivity of uranium at room temperature and slightly above (30°-60°C). The average temperature coefficient of thermal conductivity is, according to Figure 11, about 1.5x10^{-3}/°C. in the range 100°-225°C and 0.4x10^{-3}/°C in the range 225°-450°C. The rather sharp break in the curve at 225°C has not been explained. Battelle measurements on the same kind of material (γ-extruded metal) gave a linear increase in conductivity between 125° and 300°C, with a temperature coefficient of about 1.3 x 10^{-3}/°C.

The thermal conductivity of α-uranium probably depends on crystallographic direction, and the conductivity of polycrystalline material with preferred orientation of crystals (rolled or extruded metal) may therefore differ in transverse and longitudinal specimens. However, Raeth and King's measurements (Chicago 21) of radial conductivity (conductivity transverse to extension stress) of γ-extruded uranium gave values not significantly different from those obtained with other specimens at 84-241°C [62 x 10^{-3} to 69 x 10^{-3} cal/(sec cm °C)].

Assuming that electrical conductivity of pure uranium at room temperature is 4x10^4 mho, one calculates, using a Wiedemann-Franz ratio of 5.8x10^{-9}, a thermal conductivity of 70x10^{-3} cal/(sec cm °C) which is slightly larger than the highest measured value (66x10^{-3}).

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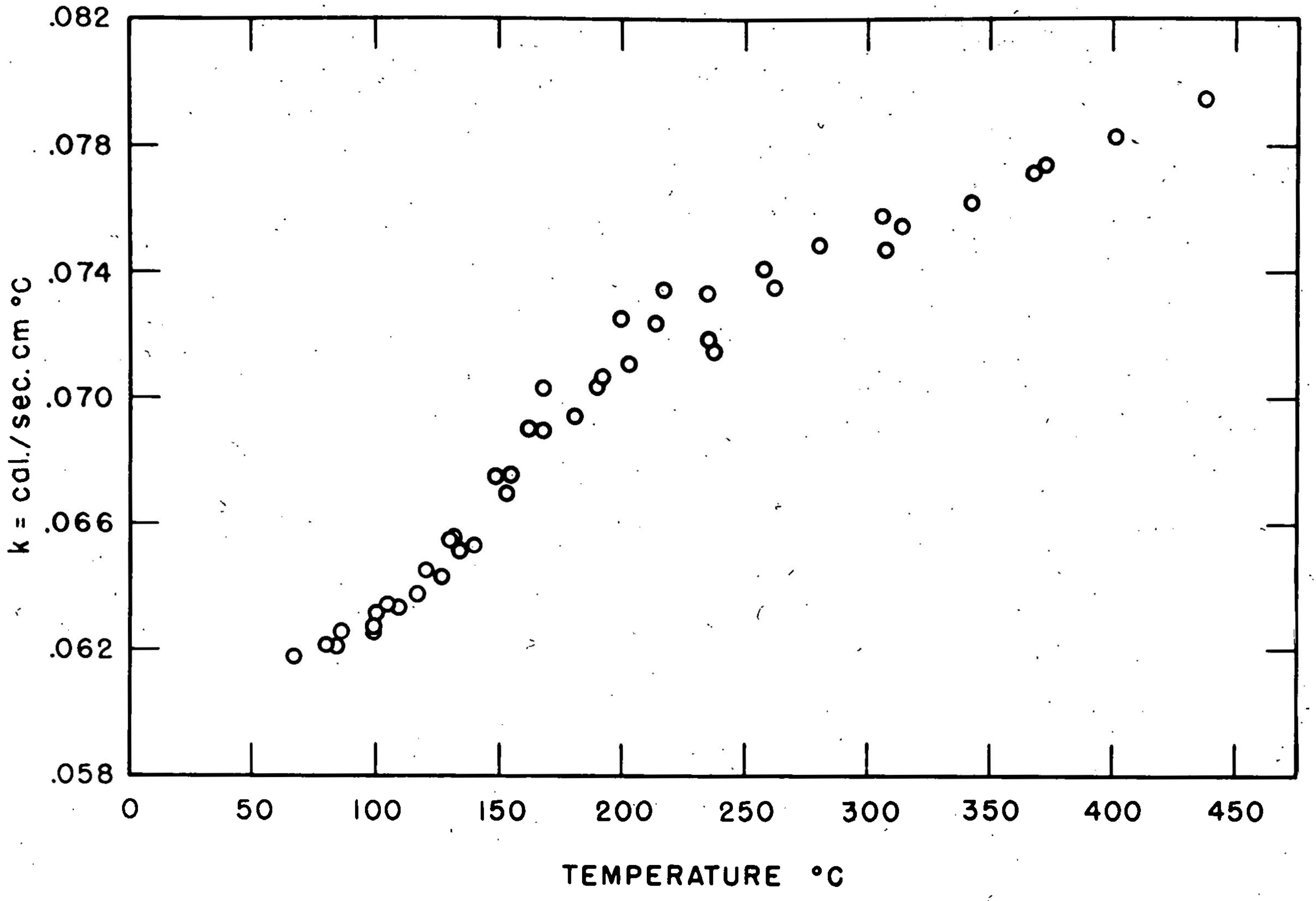

FIG. 11. THERMAL CONDUCTIVITY OF URANIUM

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4.3 Thermoelectric Potential. Table 12 gives the values found at Nat. Bur. Standards (10) for the thermoelectric potential of 99.9 per cent pure swaged uranium wire annealed 10 min. at 900°C.

TABLE 12

THERMOELECTRIC POTENTIAL OF
URANIUM AGAINST PLATINUM

Temperature (°C)	mv	Temperature (°C)	mv
0	0.00	500	10.54
100	1.19	600	13.90
200	2.87	700	17.51
300	5.03	800	21.35
400	7.59	900	25.50

The EMF versus temperature curve shows no discontinuities in the transformation points.

4.4 Electron Emission. The available determinations of the work function of uranium were all made before 1940 with metal of questionable purity. Dushman (1923) had calculated from the emission of a tungsten wire containing uranium an upper limit of 3.28 volt for the thermionic work function of uranium. Hole and Wright (1939) measured the thermionic emission of a Mackay strip and a Westinghouse rod of uranium at 680° to 1030°C and found values of the thermionic work function between 3.60 and 3.15 volts, generally decreasing with progressive outgassing. They

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estimated 3.27 ±0.05 volts as the most probable value.

From the threshold of the photoelectric effect, Rentschuler, Henry and Smith (1932) found 3.63 volts as the value of the photoelectric work function of uranium, and pointed out that the difference between this value and the value of 3.28 volts found by Dushman for the thermionic work function is outside the limits of experimental error.

4.5 Magnetic Susceptibility. Uranium is weakly paramagnetic. The available measurements (Honda, 1910; Tohoku, 1912; Owen, 1912) are rather old and the metal used probably contained considerable impurities, particularly iron. This may be the reason why the specific susceptibility ($\chi = 2.6 \times 10^{-6}$ at 18°C, according to Owen) was found to decrease somewhat with temperature.

4.6 Optical Emissivity. Hole and Wright (1939) found an average emissivity of 0.51 at 670 mμ. By comparison of the apparent temperature of a uranium surface with its true temperature determined from the emission of a hole in the metal which served as a black body, Wahlin (Wisconsin 1) calculated emissivity values of 0.453 at 97°-1050°C and 0.415 at 1052°-1097°C. The sudden change at 1050°-1052°C seems to indicate an allotrophic transformation. Since both emissivity coefficents are low, it is unlikely that one of them belongs to an oxide.

6. Radiation Effects

Seitz (Carnegie 1) discussed the effect of fission on mechanical properties of uranium. The possible effects are threefold:

(a) recoil displacement of uranium atom in the lattice, (b) localized heating along the fission product tracks, and (c) occlusion of fission products. These three factors could affect the mechanical as well as the thermal and electrical properties of the metal. One expected effect is an embrittlement of neutron-irradiated metal specimens. In an early experiment on this problem (Carnegie 2) two days irradiation at room temperature produced no perceptible change in ductility and strength of α-extruded or rolled material, but appeared to have caused a decline of 25 per cent in ductility and strength of β-extruded metal. In a second investigation (Carnegie 3) no changes were found in results of bending tests of uranium even after three weeks of irradiation.

In connection with the problem of the effect of fission products on the properties of uranium, the rate of diffusion of xenon through uranium was studied at Carnegie Institute. At first a lower limit of the diffusion coefficient at 600°C was found at $D \gtrsim 10^{-12}$ cm^2/sec (Carnegie 3). In a later investigation however, a much lower rate of diffusion was found, $D = 7.3 \times 10^{-15}$ cm^2/sec at 925°C (Carnegie 4). Extrapolation to 500°C gave a diffusion coefficient of the order of 10^{-20} to 10^{-19} cm^2/sec.

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CHAPTER VI

CHEMICAL PROPERTIES OF URANIUM METAL

1. Reactions with Nonmetallic Elements
2. Reactions with Compounds of the Nonmetallic Elements
3. Reactions with Aqueous Acid Solutions
4. Reactions with Aqueous Alkali Solutions
5. Reactions with Heavy Metal Salt Solutions
6. Miscellaneous Reactions

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CHAPTER VI

CHEMICAL PROPERTIES OF URANIUM METAL

In this chapter a summary of the chemical reactions of uranium metal is given. Little more than an enumeration of the various reactions observed can be included, because practically no quantitative data bearing on the kinetics of these reactions or their mechanisms are available. To avoid duplication, cross references are given to other chapters of this volume where more detailed information on the individual reactions can be found.

Uranium metal is highly reactive. It reacts readily with all of the nonmetallic elements and also forms numerous intermetallic compounds, as with Hg, Sn, Cu, Pb, Al, Bi, Fe, Ni, Mn, Co, Zn, and Be. These compounds are discussed in Chapter VII. The general chemical character of uranium is that of a strong reducing agent, particularly in aqueous systems. The position of uranium in the electromotive force series is not known exactly but appears to be close to that of beryllium.

The rates of reactions given below usually refer to massive cast uranium metal (99.9 per cent U) cleaned of oxide with dilute nitric acid. Finely divided uranium metal (such as that obtained by the decomposition of uranium hydride) often reacts much more rapidly than massive metal. Many reactions ascribed to uranium hydride (see chap. VIII), particularly those occurring above 400°-500°C, are actually reactions of finely divided uranium metal.

1. Reactions with Nonmetallic Elements

The elements are discussed below in the order in which they occur in the periodic table.

1.1 Hydrogen and Deuterium. (See chap. VIII.) Uranium turnings or lumps are converted to uranium hydride by gaseous hydrogen at or above 250°C:

$$(1) \qquad U + 3/2\ H_2 \longrightarrow UH_3$$

This reaction is discussed in considerable detail elsewhere in this volume (pp.   ).

1.2 Boron. (See chap. IX.) Finely divided uranium reacts with amorphous boron at the temperature of the electric furnace to give uranium boride (Wedekind, 1913).

1.3 Carbon. (See chap. IX.) By heating an intimate mixture of powdered uranium with the appropriate amount of powdered carbon to 800°-1200°C either of the two known uranium carbides UC or UC_2 can be obtained.

When uranium is melted in a graphite crucible, the crucible is protected by a film of uranium carbide formed at the interface. Therefore, the attack does not become serious until temperatures of 1500°-1650°C are reached.

1.4 Silicon. (See chap. IX.) Uranium and silicon form alloys when the powdered reactants are melted together. The phase diagram, which is very complex, indicates the existence of at least four uranium-silicon compounds.

1.5 Nitrogen. (See chap. IX.) At atmospheric pressure, uranium turnings react slowly with nitrogen at 450°C. At 700°C the reaction is rapid, and the compound $UN_{1.75}$ is formed. Reaction with powdered uranium is rapid even at 520°C. With higher nitrogen pressures, nitrides of the composition UN_2 can be prepared. If the reaction temperature is raised above 1300°C the mononitride UN is produced, since in this temperature region all the higher nitrides are unstable with respect to UN.

1.6 Phosphorus. (See chap. IX.) Finely divided uranium when heated with powdered phosphorus to 600°-1000°C forms U_3P_4 (Driggs, 1929).

1.7 Arsenic. (See chap. IX.) At least two compounds, U_2As and UA, have been identified as products of the reaction of arsenic and uranium.

1.8 Oxygen. (See chap. X.)(1) Uranium as turnings or small lumps burns brilliantly in oxygen at 700°-1000°C with the emission of white light.

$$(2) \qquad 3U + 4O_2 \longrightarrow U_3O_8$$

At very low partial pressures of oxygen ($< 10^{-4}$ atm) films of uranium monoxide UO are formed on uranium metal.

In air at room temperature massive uranium metal oxidizes slowly (Moore, 1923; Lely, 1914). It first assumes a yellow color; as the oxidation proceeds the film becomes darker, and at the end of 3 or 4 days the metal appears black. The oxide films which form on uranium in air do not protect the metal from further attack.

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(1) See Gmelin (1936) for references to older observations on impure metal.

Uranium turnings oxidize with moderate rapidity at 125°C. When ignited in air, they burn without a flame. Massive metal oxidizes slowly at 500°-700°C but complete oxidation is achieved within one hour when it is ignited at 700°-1000°C.(2)

Powdered uranium metal is usually pyrophoric and burns with a bright orange glow. Spectacular displays of sparks occur when metallic uranium is filed or held to a grindstone.

According to British observers (British 1), below 100°C only UO_2 is formed by the oxidation of uranium in air, while between 100° and 200°C both UO_2 and U_3O_8 are produced.

1.9 <u>Sulfur and Selenium</u>. (Peligot, 1842; Moissan, 1896; Zimmerman, 1882). (See chap. IX.) Uranium reacts slowly with molten sulfur at 250°-300°C. Uranium burns at 500°C in sulfur vapor. Depending on the exact conditions, the disulfide US_2, the sesquisulfide U_2S_3, or mixtures of the two are obtained. Selenium reacts in analogous fashion.

1.10 <u>Fluorine</u>. (See chap. XII, sec. 1.1) Fluorine reacts vigorously with metallic uranium at room temperature with the formation of uranium hexafluoride. The metal may easily become incandescent if it is finely divided.

1.11 <u>Chlorine</u>. (See chap. XIII, sec. 2.1) Chlorine reacts with massive uranium metal at a moderate rate at 500°-600°C. Finely divided metal burns in chlorine at 150°-180°C. The reaction products consist of UCl_4, UCl_5, and UCl_6. The chlorides sublime and collect in the cooler parts of the apparatus.

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(2) For a detailed survey of air oxidation see Nat. Bur. Standards 1, Montreal 1, MP Clinton 1, MP Chicago 1.

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1.12 Bromine. (See chap. XIV, sec. 2.1) At 650°C bromine reacts smoothly with uranium turnings to form uranium tetrabromide, which distills from the reaction zone:

$$(3) \quad U + 2Br_2 \longrightarrow UBr_4$$

When less bromine is used, uranium tribromide is obtained. (See chap. XIV, sec. 1.1).

1.13 Iodine. (See chap. XIV, sec. 3.1) Uranium metal is attacked by iodine vapor at 350°C. Either UI_3 or UI_4 may be obtained, depending on the experimental conditions chosen.

1.14 Noble Gases. (See chap. VIII, sec. 1) Because of its tendency to react with the usual impurities present in these gases, uranium metal can be used to prepare very pure helium, argon, or other gases (MP Ames 1).

2. Reactions with Compounds of the Nonmetallic Elements

2.1 Water. The behavior of uranium metal with water and steam has been very thoroughly studied (see Vols. 6A and B), but the data are too extensive to permit detailed consideration here. Boiling water attacks massive uranium slowly:

$$(4) \quad U + 2H_2O \longrightarrow UO_2 + 2H_2$$

Hydrogen accelerates the corrosion of uranium because of hydride formation. In aerated distilled water the rate of reaction is at first less than in hydrogen-saturated water, a phenomenon which is probably contingent on the formation of protective oxide films. Eventually the rate of reaction increases and approaches the value in hydrogen-saturated water. A corrosion rate of 2.7 mg/cm^2/hr has been found experimentally in boiling

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distilled water; a rate of about 0.067 $mg/cm^2/hr$ has been observed in hydrogenated distilled water at $50^\circ C$ (MP Chicago 2,3,4).

Steam reacts with uranium at 150°-$250^\circ C$. A division of opinion exists as to the products formed. American workers postulated the reaction:

$$(5) \quad 7U + 6H_2O_{(g)} \xrightarrow{250^\circ C} 3UO_2 + 4UH_3$$

At 600°-$700^\circ C$, the products were reported to be pure UO_2 and hydrogen; no U_3O_8 was formed even at $1000^\circ C$ (MP Ames 2, 3). British workers, however, claimed that U_3O_8 was the principal product of the reaction of steam and uranium at temperatures above $300^\circ C$ (British 1). No explanation is available for this discrepancy. All observers are agreed that attack by steam is much more vigorous than attack by oxygen (British 2; MP Chicago 5).

2.2 Hydrogen Fluoride. (See chap. XI, sec. 2.1) Powdered uranium metal reacts with anhydrous hydrogen fluoride at elevated temperatures to form uranium tetrafluoride:

$$(6) \quad U + 4HF \longrightarrow UF_4 + 2H_2$$

(With uranium hydride and hydrogen fluoride, production of UF_4 occurs in the temperature range 20°-$400^\circ C$.) By using a mixture of hydrogen and hydrogen fluoride, reaction with massive metal can be initiated at $250^\circ C$. Since hydrogen is produced in the reaction, the external source of hydrogen may be removed once the reaction has started, and the reaction will then proceed until all of the metal is consumed.

2.3 Hydrogen Chloride. (See chap. XIII, sec. 1.1) With finely divided uranium, hydrogen chloride forms uranium trichloride:

$$(7) \qquad U + 3HCl \qquad UCl_3 + 3/2\ H_2$$

This reaction is incomplete with massive metal.

2.4 Hydrogen Bromide and Hydrogen Iodide. (See chap. VIII.) The reactions of these compounds with uranium metal have not been studied. With the hydride, however, uranium tribromide is formed by treatment with hydrogen bromide. With hydrogen iodide and uranium hydride, apparently mixtures of UI_4 and UI_3 are formed.

2.5 Carbon Monoxide. (See chap. IX.) There is little reaction between powdered uranium metal and carbon monoxide below 400°C. Reaction definitely occurs with turnings at 750°C, and yields a mixture of uranium oxide and carbide. (MP Ames 4, 5).

2.6 Carbon Dioxide. (See chap. IX.) At 750°C, reaction between uranium and carbon dioxide is quite rapid and leads to the formation of uranium oxides and carbides. Finely powdered metal was occasionally observed to ignite spontaneously in carbon dioxide. (MP Ames 5).

2.7 Ammonia (See chap. IX.) Uranium powder rapidly reacts with ammonia at 400°C (uranium turnings react at 700°C) to form the nitride $UN_{1.75}$.

2.8 Nitric Oxide. Uranium in the form of turnings burns in NO at 400°-500°C to form U_3O_8 and nitrogen. (Emich, 1894).

3. Reactions with Aqueous Acids

3.1 Hydrofluoric Acid. Massive uranium metal is attacked only slowly by concentrated hydrofluoric acid even at 80°-90°C, presumably because of the formation of an insoluble coating of uranium tetrafluoride. The addition of oxidizing agents such as hydrogen peroxide does not appear to accelerate the reaction appreciably.

3.2 Hydrochloric Acid. Uranium metal is attacked by concentrated hydrochloric acid with remarkable rapidity. The rate is much slower in 1N acid than in 6N acid. The reaction appears to be complex, since variable amounts of the metal are converted into an insoluble black material. (It has been suggested that this product is a hydrated uranium oxide. (MP Ames 6)) With a large excess of acid only small amounts of the black material are formed; if smaller amounts of acid are used as much as 20 per cent of the metal may be converted to this product (MP Ames 7). The ratio of U(III) to U(IV) in the final solution also varies. In 12N acid practically all of the metal is oxidized to the tetravalent state, but in 6N acid the average valence state of the final product is between 3.2 and 3.4. The degree of oxidation depends upon acid strength, ratio of acid to metal, temperature, time, and probably other as yet unrecognized factors (MP Ames 8).

Mixtures of hydrochloric acid and oxidizing agents may be used to effect complete solution of uranium metal. Hydrogen peroxide, nitric acid, bromine water, ammonium persulfate, potassium chlorate, or perchloric acid may be so used. The presence of 0.05M fluosilicic acid also permits complete solution of uranium metal in concentrated hydrochloric acid without the formation of a black residue (MP Ames 9). No trivalent uranium is present in such a solution. Methanolic hydrogen chloride dissolves uranium at a moderate rate, but about 28 per cent of black residue remains. A violet solution stable for some time is formed (MP Ames 6).

3.3 <u>Hydrobromic Acid and Hydroiodic Acid</u>. Hydrobromic acid resembles hydrochloric acid in its effect on uranium, except that the reaction is slower. A black precipitate forms in this case also. Hydroiodic acid reacts even more slowly.

3.4 <u>Nitric Acid</u>. Massive uranium is dissolved with only moderate rapidity by dilute or concentrated nitric acid to form uranyl nitrate. Since nitric acid vapors or nitrogen dioxide can react with uranium with explosive violence, it is necessary to add finely divided uranium to the nitric acid in small portions in order to avoid accidents. A number of studies have been made to evaluate the best conditions for dissolving massive uranium in nitric acid (MP Chicago 6,7,8).

3.5 <u>Sulfuric Acid</u>. Dilute (6<u>N</u>) sulfuric acid does not attack uranium; at the boiling point the action is about that of boiling water alone. With hot concentrated sulfuric acid a slow reaction occurs with the formation of U(IV) acid sulfate, SO_2, S, H_2S, and other products. In conjunction with oxidizing agents such as hydrogen peroxide or nitric acid, dilute sulfuric acid will dissolve uranium. Electrolytic oxidation in sulfuric acid solution can also be used to achieve solution (MP Chicago 9).

3.6 <u>Phosphoric Acid</u>. Uranium is attacked slowly by cold 85 per cent phosphoric acid. On heating, the rate is at first only slightly increased. On further heating, sufficient water is driven off to raise the concentration of the phosphoric acid to the point where a rapid exothermic reaction takes place, and a green solution of U(IV) acid phosphate is formed. Prolonged heating of a phosphoric acid solution of U(IV) phosphate may result in the formation of glasses which are extremely resistant to further chemical action.

3.7 Perchloric Acid. Dilute perchloric acid is rather inert as far as action on uranium is concerned. As water is boiled off, a vigorous reaction ensues when the concentration of perchloric acid reaches 90 per cent. The oxidation is very vigorous; the use of this reagent with large quantities of metal is not recommended. Dilute perchloric acid dissolves uranium smoothly with the aid of oxidizing agents.

3.8 Organic Acids. While formic, acetic, propionic, or butyric acids (dilute or anhydrous) do not react with metallic uranium, rapid exothermic reactions occur in the presence of hydrogen chloride or hydrochloric acid which form the corresponding U(IV) salts (MP Ames 10). Uranium acetate can also be obtained by reaction of acetic anhydride or acetyl chloride on the metal. Uranium reacts with benzoic acid in ether solution to form U(IV) benzoate.

4. Reactions with Aqueous Alkali Solutions

Solutions of alkali metal hydroxides have little effect on uranium metal (MP Chicago 8; Zimmermann, 1882; Lely, 1914). Sodium hydroxide solutions (or sodium peroxide - water mixtures) containing hydrogen peroxide dissolve uranium. Soluble sodium peruranates are formed (MP Ames 6). (For a similar reaction with uranium oxide, see chap. .)

5. Reactions with Heavy Metal Salt Solutions

Uranium metal is a sufficiently powerful reducing agent to displace many metals from solutions of their salts. Solutions of $Hg(NO_3)_2$, $AgNO_3$, $CuSO_4$, $SuCl_2$, $PtCl_4$, and $AuCl_3$ yield precipitates of the corresponding metals when treated with metallic uranium (Zimmermann, 1882). This reaction has received considerable study in connection with the problem of devising a method for the determination of uranium in metallic materials. Procedures based on solution of uranium in hydrochloric acid and measurement of the hydrogen evolved have been proposed, but the complexity of this reaction (see p.) renders it unsuitable. Therefore, efforts have been made to determine uranium by measuring the amount of another metal displaced from solution; so far these attempts have met with only indifferent success.

5.1 **Silver Salts.** (MP Ames 6, 11) Solutions of silver sulfate react slowly with uranium. The surface of the uranium appears to become coated with silver which practically prevents further reaction. Solutions of silver perchlorate react much more vigorously. The reaction is complex, since not only is silver produced, but also silver chloride, owing to the simultaneous reduction of the perchlorate to chloride:

$$U + 6AgClO_4 + 2\ H_2O \longrightarrow 6Ag + UO_2(ClO_4)_2 + 4HClO_4 \quad (8)$$

$$U + 4AgClO_4 \longrightarrow U(ClO_4)_4 + 4Ag \quad (9)$$

$$2U + 5AgClO_4 \longrightarrow 4Ag + AgCl + 2\ UO_2\ (ClO_4)_2 \quad (10)$$

About 20 per cent of the uranium reacts according to Eq. (10), whereas less than 0.1 per cent reacts according to Eq. (9).

The simultaneous formation of silver and silver chloride in varying ratios makes it impossible to use this reaction for determining uranium. In toluene (in which silver perchlorate is very soluble) the reaction proceeds in the same way, with the formation of both silver and silver chloride.

5.2 Copper Salts (Willems, 1941; Riott, 1941; MP Chicago 10, 11, 12). Although uranium seems to be only slightly attacked by cupric sulfate (see however Zimmermann, 1882), it dissolves readily in solutions of copper ammonium chloride. Copper first separates but is redissolved on shaking by the excess ammonium chloride present in the solution. Since uranium carbides and oxides as well as uranium metal are soluble in this reagent to an appreciable extent, the method has little analytical significance.

6. Miscellaneous Reactions

6.1 Uranium Tetrafluoride. (See chap. XI, sec. 1.) Powdered uranium reduces uranium tetrafluoride to the trifluoride at 1100°C:

$$3UF_4 + U \longrightarrow 4UF_3$$

6.2 Uranium Dioxide. (See chap. X.) At 2400°C uranium metal reduces UO_2 to the monoxide, UO:

$$UO_2 + U \longrightarrow 2UO$$

6.3 Substances Containing Silica. Glass, porcelain, and silica ware are attacked by finely divided uranium metal at 700°-800°C with the formation of mixtures of uranium oxide and silicide.

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6.4 Boric Acid (MP Ames 12). Uranium metal is substantially inert to fusion with boric acid.

6.5 Solutions of Potassium and Ammonium Persulfate (Levi, 1908). Vigorous reaction is reported to occur when metallic uranium is treated with an aqueous solution of potassium persulfate. With ammonium persulfate the reaction is more sluggish.

6.6 Absolute Methanol (MP Ames 13). It has been reported that powdered uranium does not react with anhydrous methanol. This observation is in need of confirmation.

6.7 Chlorinated Hydrocarbons. At temperatures above 150°-200°C, the vapors of carbon tetrachloride, chloroform, and trichlorethylene react slowly with metallic uranium. Above 1000°C, the reaction with carbon tetrachloride is rapid. (Caution: finely divided uranium may react violently with liquid halogenated hydrocarbons, especially if the metal is prepared by hydride decomposition and still contains some hydride.)

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CHAPTER VII

INTERMETALLIC COMPOUNDS AND ALLOY SYSTEMS OF URANIUM

1. Preparation of Alloys and Intermetallic Compounds

2. Mutual Solubility of Uranium and Various Metals

3. Intermetallic Compounds

CHAPTER VII

INTERMETALLIC COMPOUNDS AND ALLOY SYSTEMS OF URANIUM

For a more detailed description of the various uranium alloy systems, the reader is referred to Volume 12 of this series. Here space permits only the discussion of certain aspects of the subject which have a particular chemical interest. These will include a brief survey of the mutual solubility of uranium and various metals and a description of some intermetallic compounds which have been recognized during the study of the phase relationships of the intermetallic systems.

1. Preparation of Alloys and Intermetallic Compounds

Almost invariably fusion of the component metals in a vacuum or in an inert atmosphere of argon or helium is required. Refractory crucibles of beryllia or zirconia are now often employed; alumina ones have also been used on occasion. A very good vacuum is required to prevent oxidation. Where one of the metals is particularly volatile, highly purified argon may be used to minimize losses by distillation. Heating is best carried out by induction; this is particularly desirable when metals of very different densities are to be alloyed, because of the stirring action obtained. For low melting metals such as lead or bismuth electrolytic procedures have been employed; uranium tetrachloride was dissolved in a molten mixture of sodium and calcium chlorides (m.p. 750°C) and electrolysed with a pool of lead or bismuth covering the steel cathode (British 1). For preparing mercury amalgams it is essential to utilize very pure uranium metal prepared by decomposition of the hydride. Some alloys have been prepared accidentally by the simultaneous reduction of uranium tetrafluoride and another metal fluoride. This procedure is not to be recommended for systematic studies, since it is difficult to control the final composition and structure of the alloy.

2. Mutual Solubility of Uranium and Various Metals

A considerable body of information is available on the solubility of uranium in various metals and the solubility of various metals in uranium. For the most part, the data are the results of the application of both x-ray and metallographic techniques. As was pointed out in Chapter V, α - uranium possesses an unusually complex crystal structure. This makes it difficult to apply the usual crystallographic chemical criteria of solid solubility (Hume-Rothery, 1933). As far as could be ascertained, no extensive solubility of any metal in α - uranium has been observed. However, a number of metals possess considerable solubility in γ - uranium, which is stable above 650°C. In the case of molybdenum, quenching to room temperature leads to the formation of solid solutions in which the γ - structure is retained. Table 1 summarizes the available solubility data.

The solubility of uranium in mercury deserves special mention (MP Ames 1). Prior to 1941, all investigators agreed that the solubility of uranium in liquid mercury at 25°C was negligibly small; values of the order of 0.00001 per cent were ordinarily quoted for it. Recent work has shown that this result must be attributed to the use of impure or oxide-coated uranium. It was found that pure finely divided uranium metal prepared in an oxide-free state by decomposition of uranium hydride readily amalgamated with mercury to form a silvery pasty mass quite similar in appearance to other metal-mercury amalgams. Amalgams containing up to 1 per cent uranium are liquid and fairly stable to air. Those having between 1 and 15 per cent uranium are gray pyrophoric solids. A number of intermetallic U-Hg compounds have been isolated and are described below. The solubility of uranium in mercury was determined by separating the solid phase from the liquid phase in the amalgam by centrifugation at various temperatures and measuring the uranium content of the liquid. The results are not very precise but indicate a solubility range from 0.001-.01 per cent at 25°C to 1.06 per cent at 350°C. Very little is known about the chemistry of these amalgams; even less is known about their physical properties. The stability of these amalgams is indicated by the observation that heat is evolved when finely divided uranium is liquefied by mercury.

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TABLE 1

MUTUAL SOLUBILITY OF URANIUM AND SOME METALS

Atomic No.	Metal	Solubility of Uranium in Metal (atom per cent)	Solubility of Metal in Uranium (atom per cent)			Reference
			α	β	γ	
13	Aluminum	-	Nil	Nil	4-5	CT-2721
23	Vanadium	-	Nil	-	-	N-1779
24	Chromium	Nil	Nil	<2.5	<4	CT-3335
25	Manganese	?	-	-	3-4	CT-2945
26	Iron	Nil in γ-Fe	Nil	Nil	1.5-2.0	CT-2945
28	Nickel	-	-	1	2	CT-3013
29	Copper	Nil	Nil	Nil	Nil	CT-1784
41	Columbium	-	<0.25	<0.25	3.6 at 656°C 85 at 1350°C	CT-3071
42	Molybdenum	1 at 900°C	Nil	-	35.8	CT-2946
47	Silver	-	Nil	-	-	CN-1048
50	Tin	<0.02 at 600°C	Nil	-	-	CN-1784
58	Cerium	-	Nil	-	Nil	CT-2619
73	Tantalum	-	Nil	-	-	N-1779
74	Tungsten	1	<1	-	-	CT-3375
79	Gold	-	2%	-	-	CT-2483
80	Mercury	0.001-0.01 at 25°C 1.25 at 350°C	Nil	-	-	CT-2960
83	Bismuth	Nil	Nil	-	-	CT-2961
90	Thorium	< 2	Nil	-	-	CT-2717

The solubility of uranium in other solid metals appears to be limited. The same seems to be true of liquid metals of low melting point. Thus, massive uranium is not appreciably attacked by liquid sodium at 500°C even after several days of exposure (MP Chicago 1). Uranium also appears to be insoluble in liquid sodium-potassium alloys (MP Chicago). No alloys or intermetallic compounds of uranium with any of the members of the alkali or alkaline earth metals are known (MP Ames 2), with the exception of beryllium for which an intermetallic compound with 93 atom per cent beryllium ($U\ Be_{12-13}$) appears probable (Montreal 1). The case of magnesium was of practical interest. However, it was shown at Ames that it is extremely difficult to prepare uranium containing more than a few parts per million of magnesium.

3. Intermetallic Compounds

A considerable number of intermetallic compounds of uranium have thus far been prepared and identified (chiefly by x-ray methods). In Table 2 are listed all of the intermetallic compounds for which x-ray structures are available. In addition to these, the existence of the compounds UAl_5, UNi, UNi_5, UBi, UBi_2, U_5Sn_4, and U_3Sn_5 has been indicated by either chemical analysis or microscopic examination. These latter have not been definitely identified as pure phases. Table 3 shows all of the melting or decomposition point data available at present.

The intermetallic compounds vary considerably in physical properties and chemical reactivity. Compounds of the type U_6M are found to be exceedingly brittle. They can be readily fractured by a hammer blow, but are not quite hard enough to scratch glass. U_6M compounds can be isolated conveniently by utilizing their inertness to nitric acid. Treatment with either dilute or concentrated nitric acid of iron, cobalt, or manganese alloys of the approximate composition U_6M results in the solution of any excess uranium present. The uranium-mercury, -tin, -lead, and -bismuth systems are practicularly noteworthy for their chemical reactivity. Amalgams containing up to 15 per cent uranium oxidize readily in air to form a black powder which contains both uranium and mercury; those containing above 15 per cent uranium are spontaneously inflammable in air. In the tin-uranium system, pyrophoric alloys are also encountered; the 50 per cent alloy is exceedingly inflammable in air. The same is true of the lead system. In the base of bismuth, both UBi and UBi_2 are highly reactive. They heat up in a few minutes in air and react with water, alcohols, mineral oil, kerosene, benzene, and carbon tetrachloride. Uranium-aluminum compounds, on the other hand, appear to be inert. No systematic investigation of the reactions of any of these intermetallic compounds has been conducted, and, as can be seen from the above, the available information is very fragmentary.

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TABLE 2*

CRYSTAL STRUCTURES OF SOME URANIUM INTERMETALLIC COMPOUNDS

Compound	Unit Cell	Lattice Dimensions (A)		Molecules per Unit Cell	Density	Space Group or Structure Type	Isomorphic with
		a_1	a_3				
UCo	Body centered cubic	6.3429 ± .0004		8	8.138	T^5	
UAl_2	Face centered cubic	7.795		8	8.138	O_h^7 or O^4	UCu_5
UAl_3	Cubic	4.278		1	6.70	O_h^1; Structure type L 12	USn_3
UCu_5	Face centered cubic	7.020 ± 0.005		4	10.61	TL^2 or T^2	UAl_2 $AuBe_5$ $PdBe_5$
UNi_5	Face centered cubic	6.7693 ± .0005		4	11.31		UCu_5
UHg_2	Hexagonal	4.976 ± 0.01	3.218 ± .005	1	15.29		
UHg_3	Hexagonal	3.320 ± .005	4.878 ± .005	1/2	14.88		
UHg_4	Pseudo unit is body centered cubic	3.62			14.5	True unit and structure are complex	

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TABLE 2 (continued)

Compound	Unit Cell	Lattice Dimensions (A)		Molecules per Unit Cell	Density	Space Group or Structure Type	Isomorphic with
		a_1	a_3				
USn_3	Simple cubic	4.626		1	10.0	O_h^1; L12	UAl_3
UMn_2	Face centered cubic	7.1484 ± 0.0014		8	12.57	C15$^{(a)}$	UAl_2
UFe_2	Face centered cubic	7.044		8	13.21	C15$^{(a)}$	UAl_2
UCo_2	Face centered cubic	6.9780 ± 0.0004		8	13.83	C15$^{(a)}$	UAl_2
UNi_2	Hexagonal	4.956 ± .005	8.253 ± .009	4	13.46	C14	$MgZn_2$
U_6Mn	Tetragonal body centered	10.265 ± 0.01	5.23 ± 0.02	4	17.8	D_4^9	
U_6Fe	Tetragonal body centered	10.29 ± 0.04	5.23 ± 0.02	4	17.7	D_4^9	
U_6Co	Tetragonal body centered	10.34 ± 0.02	5.20 ± 0.02	4	17.7	D_4^9	
U_6Ni	Tetragonal body centered	10.35 ± 0.04	5.20 ± 0.02	4	17.6	D_4^9	

*R. E. Rundle, N. C. Baenziger, A. S. Wilson, CC-2947, 8-15-45; N. Baenziger, A. Wilson, A. Snow, CC-3255, 6/15/46

(a) This is the Cu_2Mg structure. It is a parameterless structure with 8U at 000, 0 1/2 1/2, 1/2 0 1/2, 1/2 1/2 0 + (000), (1/4 1/4 1/4), 16Mn at 000, 0 1/2 1/2, 1/2 0 1/2, 1/2 1/2 0 + (5/8 5/8 5/8), (5/8 3/8 3/8)
UAl_2 has a similar and UCu_5 a closely related structure.

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TABLE 3

MELTING OR DECOMPOSITION POINTS OF INTERMETALLIC COMPOUNDS OF URANIUM

Compound	Melting or decomposition temperature (°C)	Compound	Melting or decomposition temperature (°C)
UAl_2	1590	U_6Fe	815*
UAl_3	1350*	UMn_2	1120
UAl_5	730*	U_6Mn	726*
UCu_5	1052*	UHg_4	360*
UNi_2	810*	UHg_3	390*
Uni_5	1295	UHg_2	450*
U_6Ni	754*	U_5Sn_4	1500
UFe_2	1235	USn_3	1350*

* Decomposes by peritectic reaction.

A great number of alloy systems have been studied for resistance to corrosion by water and air. More or less detailed studies have been made of the systems of uranium with: Na, K, Cu, Ag, An, Be, Mg, Zn, Cd, Hg, Al, Ga, In, Ce, La, Nd, Ti, Ge, Zr, Sn, Th, V, Ct, Ta, Bi, Cr, Mo, W, Mn, Re, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt. In most cases, the complete phase diagram has not been worked out, since the work usually was suspended when corrosion studies indicated undesirable features. Of all the alloys tested, only those with columbium, molybdenum, and zirconium showed an enhanced corrosion resistance to water. The ternary alloys U-Cb-Si, and U-Cb-Zr exhibited even more satisfactory properties. (For details, refer to Vol. of this series.)

REFERENCES FOR CHAPTER VII

Intermetallic Compounds and Alloy Systems of Uranium

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CHAPTER VIII

THE URANIUM-HYDROGEN SYSTEM

1. Solubility of Hydrogen in Solid and Liquid Uranium Metal

2. Uranium Hydride

    2.1 Decomposition Isothermals

    2.2 Composition of Uranium Hydride

    2.3 Hydrogen Pressure Curve and Thermodynamics of Formation of UH_3

    2.4 Kinetics of Formation and Decomposition of UH_3

    2.5 UH_3 Formation from Uranium Compounds or from Uranium and Water

    2.6 Physical Properties of Uranium Hydride

    2.7 Chemical Reactions of Uranium Hydride

    2.8 Uranium Hydride Amalgam (and Similar Systems) and the "Quasi Hydride"

    2.9 Uses of Uranium Hydride

3. Uranium Deuteride

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CHAPTER VIII

THE URANIUM-HYDROGEN SYSTEM

1. Solubility of Hydrogen in Solid and Liquid Uranium Metal

Formation of uranium hydride (see Sec. 2) prevents study of the solubility of hydrogen in uranium at low temperatures and high pressures. Under a partial pressure of one atmosphere of hydrogen, for example, the solubility can be measured only above 435°C, the decomposition temperature of the hydride under atmospheric pressure. The capacity of uranium to dissolve hydrogen is small compared to that of metals such as iron. However, it increases markedly with temperature, particularly in the liquid state. Consequently, considerable quantities of hydrogen which were dissolved in the melt may remain occluded in castings. The solubility, occlusion, and liberation of hydrogen from uranium have been studied in considerable detail by the Battelle group. (1)

In the earlier investigations the hydrogen content of uranium samples was determined by pumping off and collecting the gas which liberated by heating metal specimens to about 750°C in a vacuum. It was later found, however, that some hydrogen was formed in this procedure by the reduction of moisture present in the system. More recent determinations of occluded hydrogen therefore were carried out by heating the metal in a closed vessel and measuring the increase in pressure. A correction had to be applied for the solubility of hydrogen at the temperature of degassing, as determined by the first-named method. The analytical methods are described in more detail in Volume 13 A of this series.

The solution isobar for hydrogen pressure of 1 atm. is reproduced in Fig. 1. It shows that the equilibrium content of hydrogen in the α-phase uranium is about 2 ppm and changes but little with temperature. This corresponds to about 0.4 cc hydrogen per cc metal, or 1 atom hydrogen per 2000 atoms uranium. The α - β transformation at 660°C causes the solubility to increase from 2 to about 8 ppm, and the β - γ transformation, at about 770°C leads to another increase to 15 ppm. Melting, which occurs at 1132°C, increases the solubility from 17 to 28 ppm. and the hydrogen content of the liquid metal continues to increase rapidly with temperature, reaching 30 ppm at 1250°C.

When molten uranium is cooled in a hydrogen atmosphere, the dissolved gas escapes in bubbles. During solidification, 40 per cent of the hydrogen dissolved in the melt must come out, or the solid metal will contain a considerable amount of occlued gas. A large fraction of the gas occluded during solidification is likely to remain in the metal after cooling to room temperature; the exact amount depends on the size of the piece, the rate of cooling, and probably also on the formation of surface films of oxide or nitride. Since the solubility of hydrogen in uranium is proportional to the square root of pressure, the melt produced in an atmosphere containing 1 per cent hydrogen should contain 2.8 ppm hydrogen. The castings made from it will contain >2 ppm hydrogen if most of the dissolved gas is retained in the solid as a consequence of sudden soldification and rapid cooling. According to

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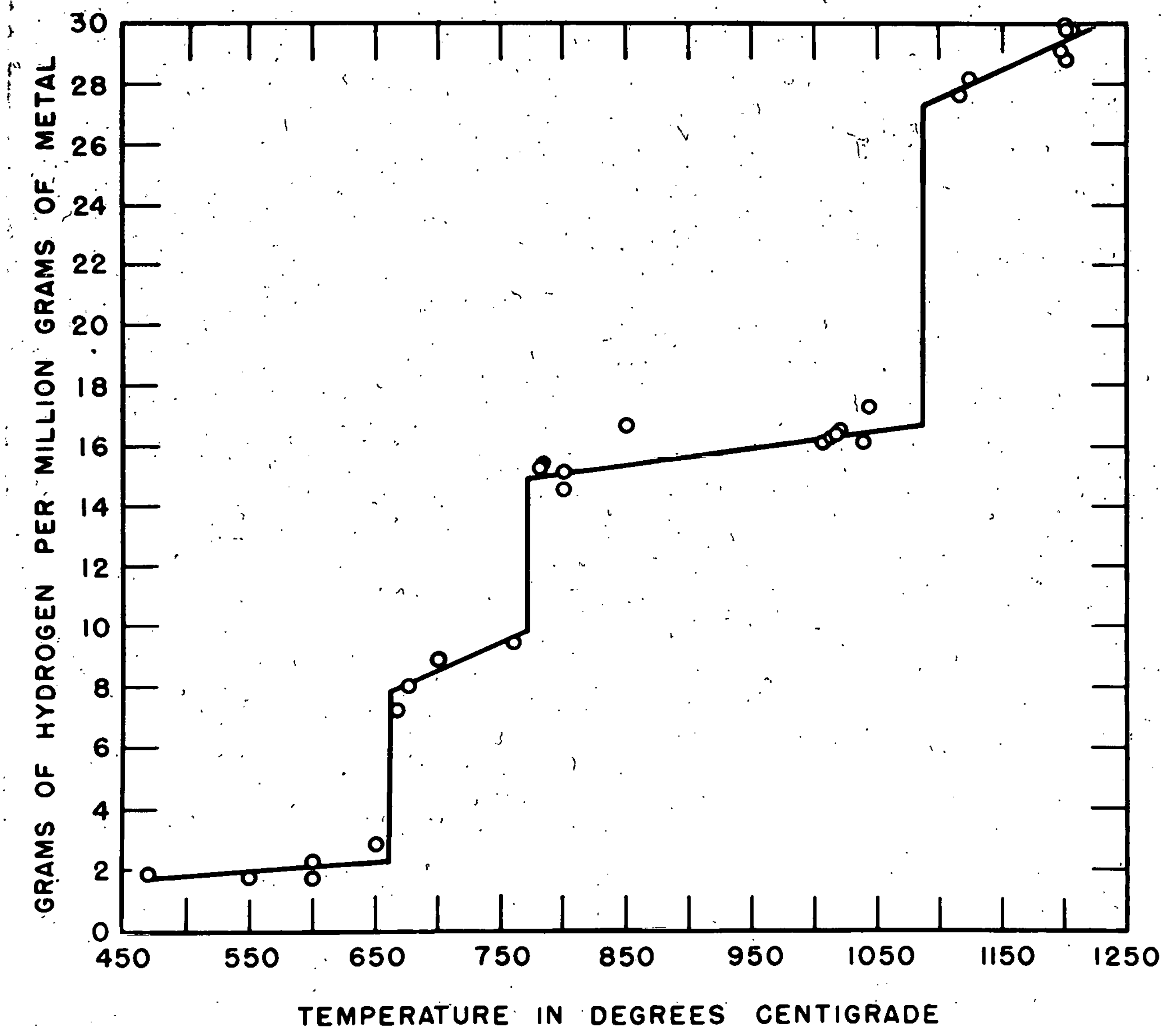

FIG. I. SOLUBILITY OF HYDROGEN IN THE METAL IN EQUILIBRIUM WITH HYDROGEN AT ATMOSPHERIC PRESSURE.

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Fig. 1 the equilibrium pressure corresponding to the content of 2 ppm hydrogen in α- uranium is 1 atm. When the uranium pieces become hot, the solution equilibrium is approached, and if the content of occluded hydrogen is >2 ppm, the pressure of liberated hydrogen will exceed 1 atm. Therefore 2 ppm occluded hydrogen is considered the danger limit. Since the hydrogen concentration of commercially cast or extruded metal often is above this limit, degassing may be a necessary precaution. The degassing process has been studied in detail at Battelle and is described in Vol. 12. From experiments on the rate of degassing rods of different sizes, the following values of the diffusion coefficient of hydrogen in α-uranium have been derived:

TABLE 1

Decomposition Pressure of Uranium Hydride (Berkley)

Temperature (°C)	Diffusion Coefficient (sq. in/hr)
566°	0.0040
593	0.0064
640	0.0125*

* extrapolated

The last value permits one to calculate that 6 hr heating to 640°C (in vacuum or in a stream of neutral gas) will reduce the hydrogen content of a rod 1.24 in. in diameter by 75 to 80 per cent. These are approximately the conditions of commercial outgassing.

As mentioned before, the solubility of hydrogen in uranium is proportional to the square root of the partial pressure of hydrogen. This is illustrated by Fig. 2 which shows that solution isothermals are straight lines if the square roots of the pressures are used as abscissae. The proportionality of solubility to the square root of pressure indicates that hydrogen is dissolved in uranium in the form of free atoms. The rule holds for all three solid uranium phases, α, β, and γ, since each of them is represented by an isothermal in Fig. 2.

2. Uranium Hydride

The existence of uranium hydride was discovered by Driggs (1929). He obtained the hydride by heating uranium powder in a hydrogen atmosphere to 225°C, and observed that it decomposed at 350°-400°C under 1 atm. partial pressure of hydrogen. A detailed study of uranium hydride has been carried out by the Ames group (MP Ames 1) since March, 1943. Some experiments with this compound also were made at Battelle (2), Los Alamos (MP Los Alamos 1), Clinton (MP Clinton 1) and UCRL(1).

Judged by the critera of simple stoichiometric composition and constant decomposition pressure at a given temperature, uranium hydride is a true chemical compound. If two bulbs containing uranium powder and uranium hydride powder, respectively, are kept in communication in an evacuated system for ten hours, no exchange of hydrogen between the two samples is observed at 269, 288, 300 or 325°C. (MP Ames 2). This behavior is typical of a true compound

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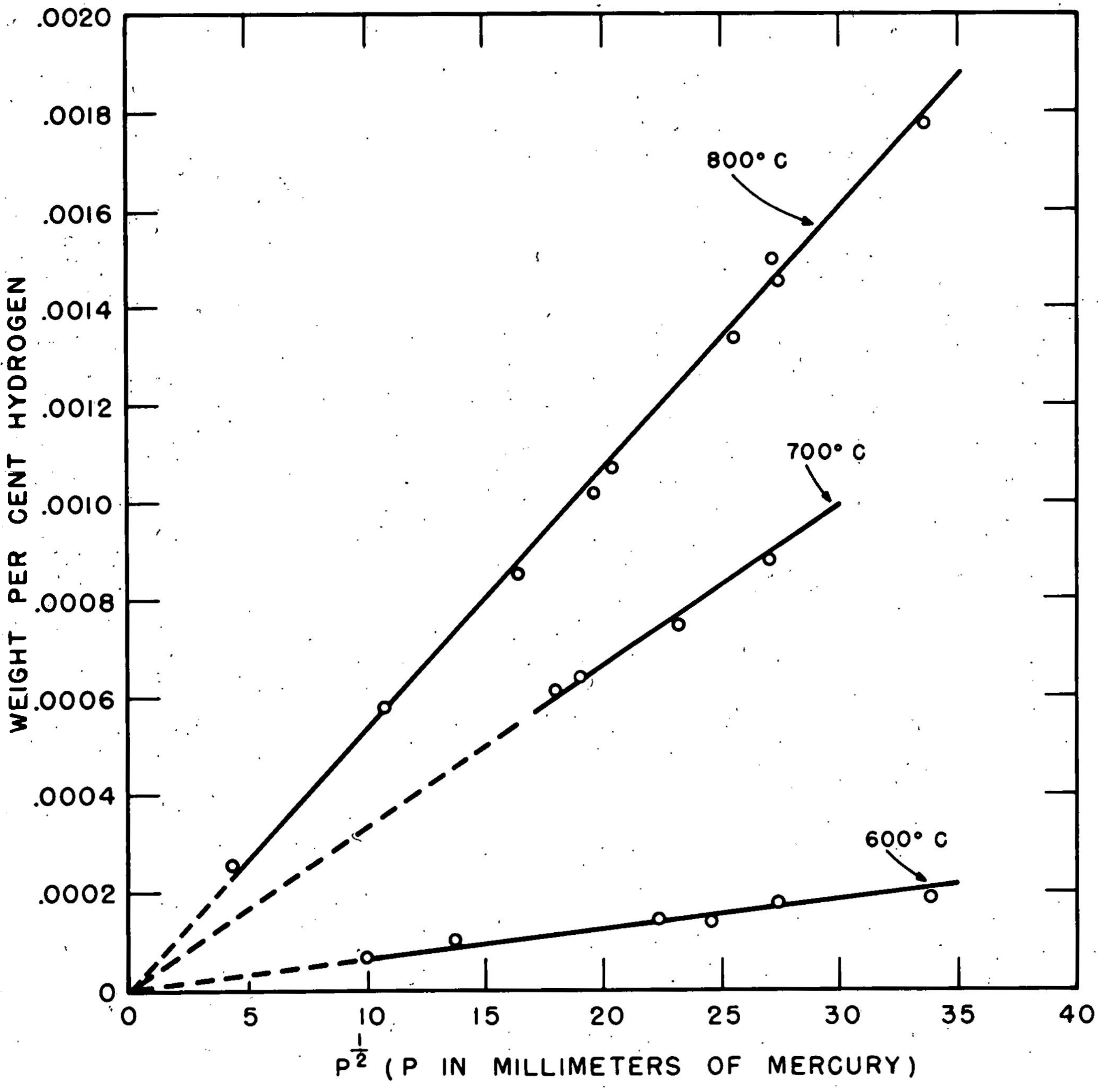

FIG. 2 SOLUBILITY OF HYDROGEN IN URANIUM METAL AS A FUNCTION OF HYDROGEN PRESSURE FOR 600°, 700°, AND 800° C.

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since even a slight dependence of equilibrium pressure on hydrogen concentration would cause hydrogen to diffuse from the hydride to the metal. On the other hand, the appearance and physical properties of uranium hydride resemble those of the "metal-like" hydrides of cerium, lanthanum and other rare earth metals. For all of these hydrides a more or less gradual change of decomposition pressure with content of hydrogen in the metal was observed in a series of investigations. Because of this variability of decomposition pressure, which, according to the phase rule, indicates that metal and hydrogen form a single solid phase of variable composition A. Sieverts (1925) interpreted the rare earth hydrides as "solid solutions." However, the decomposition isothermals of the rare earth hydrides, which all show a more or less extensive, even if not strictly horizontal plateau, are not typical of true solutions. One may perhaps suggest that similar to uranium hydride the rare earth hydrides, too, are true compounds of definite stoichiometric composition. The failure to obtain horizontal isothermals can then be attributed to the use of insufficiently pure and homogeneous metals. The metals used may have contained two or more solid phases, e.g., allotropic forms of the metal itself, alloys, oxides or carbides.

2.1. Decomposition Isothermals of Uranium Hydride. As mentioned above, the interpretation of uranium hydride as a chemical compound is based on the shape of its decomposition isothermals. These isothermals have been measured several times at Ames (MP Ames 3). The first measurements showed that equilibrium is established only very slowly. The 357°C isothermal, obtained by pumping hydrogen away from the hydride and waiting for 30 minutes, had a horizontal plateau at about 120 mm Hg pressure, while a similar isothermal, obtained by admitting hydrogen to the metal and waiting for the same length of time, had a plateau at about 170 mm Hg. This isothermal was redetermined later, waiting at each point until no pressure changes occurred in 24 hr; two days were usually necessary to reach this degree of constancy. The results are shown in Fig. 3. If the equilibrium is approached "from below", i.e. by the decomposition of hydride, the curve shows a plateau at 134 mm Hg which stretches from 5 to 90 per cent decomposition. A small but reproducible dip at 90 to 98 per cent hydrogenation, with a minimum at about 98 per cent UH_3, is the most remarkable feature of this curve. The points at the bottom of the dip are not changed even by 14 days waiting. In addition to the isothermal obtained at the temperature of boiling mercury (357°C) the dip could be observed also on dehydrogenation isothermals obtained at 440°C, (boiling sulfur), and 307°C (boiling benzophenone).

The hydrogenation isothermal (dotted line) shows no dip and its plateau extends from 5 to 95 per cent hydrogenation. Despite long waiting, this isothermal is still several mm Hg above the dehydrogenation isothermal, showing that perfect thermodynamic equilibrium has not been realized. The "pseudo-equilibrium"

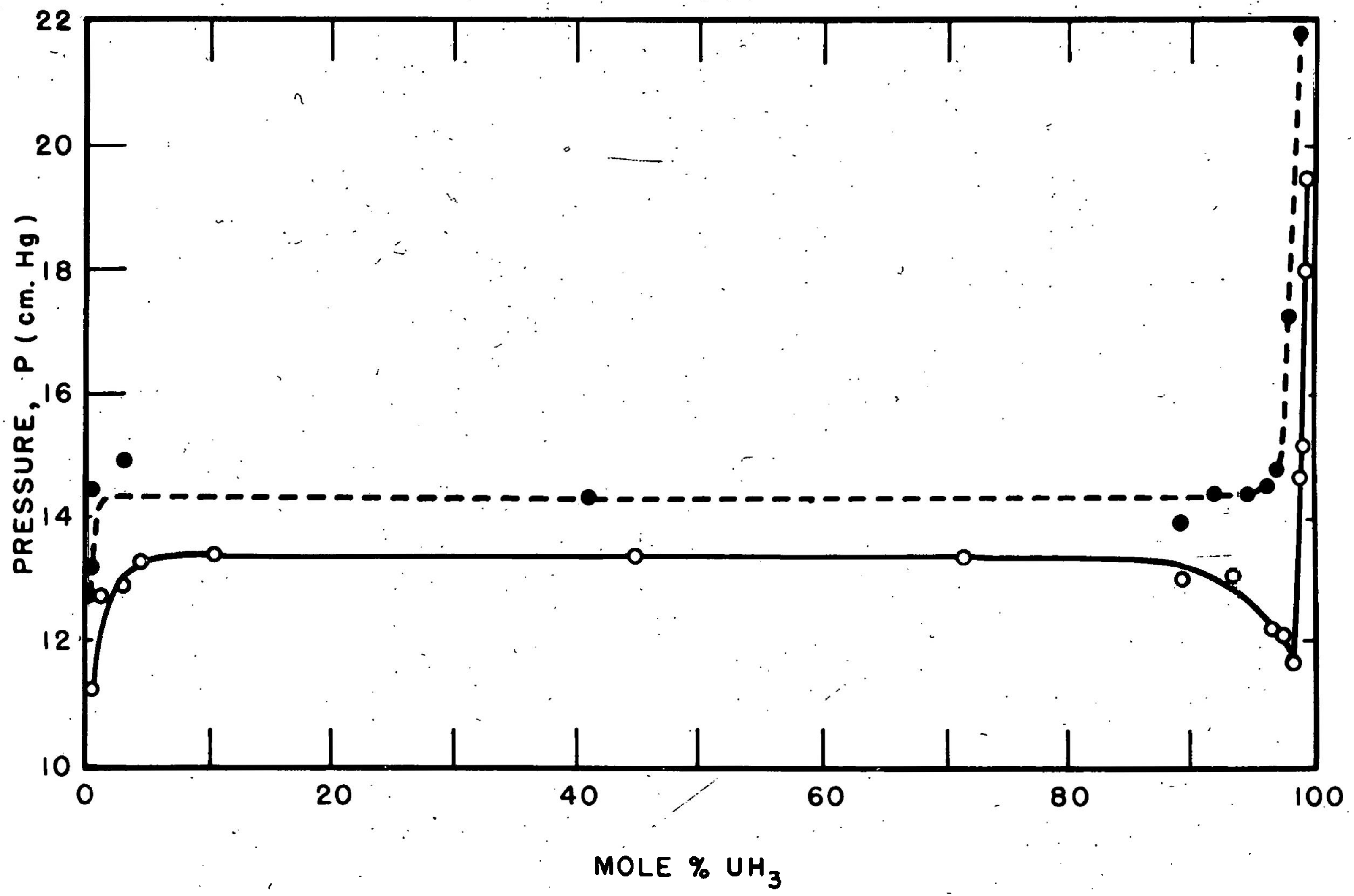

FIG. 3. PRESSURE-COMPOSITION ISOTHERM FOR THE URANIUM-URANIUM HYDRIDE-HYDROGEN SYSTEM AT 357°C. (○ = APPARENT EQUILIBRIUM UPON DECOMPOSITION, ● = APPARENT EQUILIBRIUM UPON FORMATION).

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field is particularly wide in the region of the dip. Experiments in which the uranium-uranium hydride mixture was carefully protected from mercury vapor showed that the dip was not due to a reaction with mercury. In the region of the dip the x-ray diagram showed only lines of uranium metal and of UH_3.

The origin of the dip remains unexplained. Assuming that the hydrogenation isothermal corresponds to true equilibrium while the dehydrogenation isothermal runs "too low" because of slow approach to the equilibrium, the dip seems to indicate that the delay is particularly long when hydrogenation is almost complete a fact which is not easy to understand. A similar effect noticeable at the opposite end of the isothermal between 0 and 5 per cent hydrogenation is less unexpected.

2.2 <u>The Composition of Uranium Hydride</u>. The composition at which the uranium-hydrogen isothermals bend sharply from horizontal to approximately vertical can be considered as that of the compound uranium hydride. If hydrogen were soluble in the uranium hydride lattice. the content of hydrogen in the solid phase would continue to increase with increasing hydrogen pressure beyond the value corresponding to the stoichiometric compound. It was thought at first at Ames that by using "supersaturating" pressures of hydrogen one could actually obtain solid phases containing a considerable excess of hydrogen (MP Ames 4). Later, however, it was demonstrated that the hydrogen content does not markedly increase even at hydrogen pressures as high as 2000 psi ($\sim$200 atm.) (MP Ames 5). This shows that beyond the saturation point the isothermals are practically vertical. The only visible result of high pressure on the hydride structure is crystal growth which could be observed at temperatures above 600°C. The X-ray diffraction lines were sharper and fibrous crystals could be noticed in the hydride powder obtained under high hydrogen pressure.

Since uranium hydride is a single compound and does not markedly dissolve hydrogen, its analysis gives the same composition regardless of the temperature and of the hydrogen pressure under which it was prepared. The first determinations at Ames gave compositions between $UH_{3.85}$ (cooled in vacuum) and $UH_{4.15}$ (cooled in hydrogen), so that a composition UH_4 was postulated (MP Ames 6). It was, however, soon found at Battelle(2) as well as at Ames (MP Ames 7) that these results were incorrect and that the true composition was close to UH_3. Thus, Battelle measurements gave $UH_{2.91}$ for material made at 300°C and at a series of hydrogen pressures from 253 to 1265 mm. At Ames compositions between $UH_{2.91}$ and $UH_{3.10}$ (average $UH_{2.99}$) were found by measuring the gain in weight of uranium turnings in hydrogen at 250°C and of uranium powder obtained by hydride decomposition at room temperature, as well as by determination of the volume of gas absorbed in hydrogenation or liberated in the decomposition of the hydride.

Six combustions of hydride prepared at 250°C, in which the weight of water formed from hydrogen produced by hydride decomposition was determined (MP Ames 8), gave compositions between $UH_{2.94}$ and $UH_{2.96}$. The product prepared at 420°C had the same composition. The deviations from the formula UH_3 found in this work although small, were beyond the limit of experimental error. However, they can be explained by the presence of oxides, carbides, or other impurities in uranium metal. For example, the presence of 0.14 per cent carbon as UC in the metal powder would reduce the hydrogen:uranium ratio to 2.91 if all UC remained unreduced by hydrogen (Battelle 2). At Ames (MP Ames 9) the known presence of 300 ppm carbon, 50 ppm iron, 50 ppm silicon, 30 ppm fluorine, 80 ppm oxygen, and 30 ppm nitrogen in a typical uranium sample was calculated to account exactly for the 2.97 hydrogen:uranium ratio observed in the formation of the hydride. At UCRL (1) a composition of $UH_{3.06}$ was calculated from reaction of a known amount of uranium with hydrogen at a constant volume by correcting the result for the known content of oxide in the metal which was as high as 11.7 per cent. At Los Alamos (MP Los Alamos 1), the following hydrogen:uranium ratios were found at different temperatures:

TABLE 2

RATIOS H:U

Temperature (°C)	150	175	200	225	250	275	300	350
Pressure (mm Hg)	3.03	2.99	2.96	3.04	3.03	3.03	2.99	2.92

Thus, the formula UH_3 is well established.

2.3. Hydrogen Pressure Curve and Thermodynamics of Formation of UH_3. Since UH_3 behaves as a true chemical compound (i.e., has a constant hydrogen pressure over a wide range of average hydrogen content of the solid phase), a unique decomposition pressure curve can be constructed and the heat of formation from the elements can be calculated from the slope of this curve. The first measurements were carried out at Ames (MP Ames 9) at 252 to 438°C; they gave pressures from 4 to 808 mm Hg; the pressure of 1 atm. was reached at 436°C. However, no exact thermodynamic equilibrium was reached in these measurements, as shown by considerable deviation between heating and cooling curves. According to a later review (MP Ames 9,10), the heating curve can be represented by the equation corresponding to $\Delta H = 31.0$ kcal /mole for the heat of decomposition.

(1) $\log p_{mm} = -4500/T + 9.23$

Similar measurements were carried out at Battelle$^{(2)}$. Fig. 4 shows the results. According to the summary report (MP Ames 10), the equation of the straight line in Fig. 4 is

(2) $\log p_{mm} = -4590/T + 9.39$;

The corresponding ΔH value is 31.5 kcal/mole. A rather rough direct calorimetric determination of ΔH gave 30.5 ± 0.5 kcal/mole in satisfactory agreement with the values calculated from the decomposition curves (MP Ames 11)

According to the Ames data (MP Ames 10) the decomposition pressures used in the above calculations are probably still too low because of incomplete equilibrium. Three points on the decomposition

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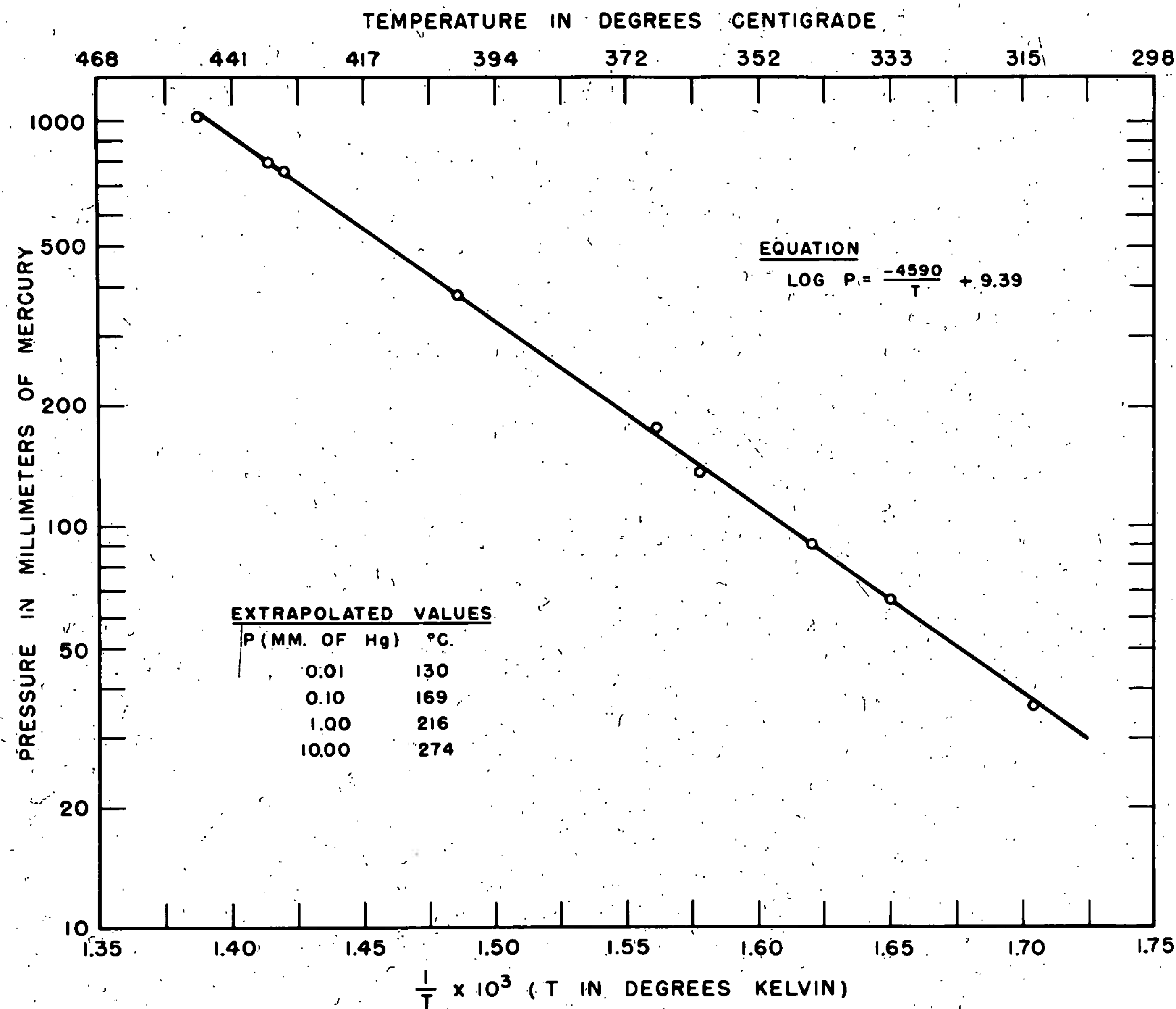

FIG. 4. EQUILIBRIUM PRESSURE AS A FUNCTION OF TEMPERATURE FOR THE SYSTEM. URANIUM HYDRIDE ⇌ URANIUM + HYDROGEN

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curve, determined more carefully by waiting several days at constant temperature were markedly higher than those obtained in more rapid experiments, but gave no significant change in the slope of the pressure-temperature curve and thus in the calculated value of ΔH. The equation of the straight line passing through these three points was

$$\log p_{mm} = \frac{-4500}{T} + 9.28 \quad (3)$$

Attempts to approach equilibrium from the side of the higher temperatures by hydrogenation of uranium rather than dehydrogenation of UH_3 gave less satisfactory results; the final values were not reached even after waiting for weeks.

At the UCRL (1,2), the following pressures were obtained, by approaching the equilibrium both from above and below:

Table 3

DECOMPOSITION PRESSURE OF URANIUM HYDRIDE (Berkeley)

Temperature (°C)	200	250	300	350	400	436
H_2 Pressure (mm Hg)	0.6	4.5	24.8	103.0	345	760*

* extrapolated

These results can be represented by the equation

$$\log_{10} p_{mm} = -\frac{4480}{T} + 9.20 \quad (4)$$

corresponding to a heat of decomposition of <u>30.7 kcal/mole.</u>

The calculation of ΔH, ΔF, and ΔS for the formation of UH_3 from the elements from this set of decomposition pressures was carried out at UCLR (2) and later revised (UCLR 3). It is based on an approximate value,

$$\Delta C_p = 1 \text{ cal/mole, for the reaction}$$

(5) $$UH_3 \longrightarrow U + 3/2\ H_2$$

This value was derived from Kopp's rule, and gives for the heat of decomposition:

(6) $$\Delta H = \Delta H_0 + 10^{-3} \times T \text{ kcal/mole}$$

$$\Delta H = 30.1 \text{ kcal/mole}$$

$$\Delta H_{298} = 30.4 \text{ kcal/mole}$$

Using the equation

(7) $$R \ln K = R \ln(p)^{3/2} = \Delta c_p \ln T - \frac{\Delta H_0}{T} + I$$

with

$\Delta C_p = 1$, one obtains

(8) $$3/2\ R \ln p = \ln T - \frac{\Delta H_0}{T} - I$$

MacWood obtained, from 17 individual measurements of decomposition pressure between 530° and 652°K, I-values between -35.5 and 36.4, with an average of I = -35.85. This gives, for the standard free energy of decomposition of UH_3,

(9) $$\Delta F^\circ = 30{,}100 - 2.303\ T \log T - 35.85\ T \text{ cal/mole}$$

and thus

$$\Delta F^\circ_{298} = 17.7 \text{ kcal/mole}$$

Combining the last value with $\Delta H_{298} = 30.4$ kcal, one obtains:

(10) $$\Delta S^\circ_{298} = 42.6 \text{ e.u.}$$

for the entropy of decomposition.

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The corresponding values for the formation of UH_3 from the elements are

$$\Delta H_{298} = -30.4 \text{ kcal/mole}$$

$$\Delta F^{o}_{298} = -17.7 \text{ kcal/mole}$$

$$\Delta S^{o}_{298} = -42.6 \text{ e.u.}$$

2.4. <u>Kinetics of Formation and Decomposition of Uranium Hydride</u> Driggs (1929) first obtained uranium hydride by heating uranium powder to 225°C or higher in oxygen atmosphere. Early experiments at Ames (MP Ames 12) confirmed that a temperature of 225°-250°C is best for rapid hydrogenation. As an example, 100 g uranium turnings could be completely hydrogenated in 30 minutes at 250°C and a 100 g lump of uranium metal, in two hours. Subsequently, the rate of hydrogenation was studied more closely in relation to temperature pressure and surface conditions at Ames (MP Ames 12), Clinton (MP Clinton 2) and Los Alamos (MP Los Alamos 1).

(a) <u>Effect of Temperature.</u> Rapid decline in the rate of hydrogenation at temperatures above 300°C is characteristic of the hydrogenation process independently of whether power or solid metal is used for the experiment. For example, uranium powder under one atmosphere partial pressure, took up no hydrogen in two days at 440°C, three days were required for complete hydrogenation at 306°-420°C (MP Ames 2), and less than one hour at 250°C. Similar results were obtained at Clinton (MP Clinton 2) for the rate of penetration of hydrogen into solid uranium.

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TABLE 4
Penetration Rate of Hydrogen Into Solid Uranium

Temperature (°C)	200	250	300
Rate of Penetration (cm/hr)	0.27	0.30	0.19

Figure 5 shows the temperature dependence of the rate of hydrogenation of uranium wire (0.0625 in. diam., Westinghouse electrolytic metal) as determined at Los Alamos(MP Los Alamos 1). The values plotted were the approximately constant rates prevailing after the termination of the induction period (See below) and before the slowing down of the process toward the end of hydrogenation. This curve, too, shows a maximum at 225°C.

The decline in reaction velocity at temperatures below 200°C depends on the state of the metal and the pressure of hydrogen. With turnings the reaction first becomes noticeable at 200°C under 1 atm. hydrogen pressure, at 150°C under 1000 psi, and at 130°C under 1800 psi. With finely powdered uranium as obtained by the decomposition of the hydride the hydrogen pickup remains very rapid even at 0°C, and marked, but slow, at -80°C; no reaction could be observed at the temperature of liquid air.

(b) <u>Effect of Pressure</u>. The decline of the rate of hydrogenation at temperatures above 250°C is associated with the fact that the rate becomes zero when the decomposition pressure reaches the

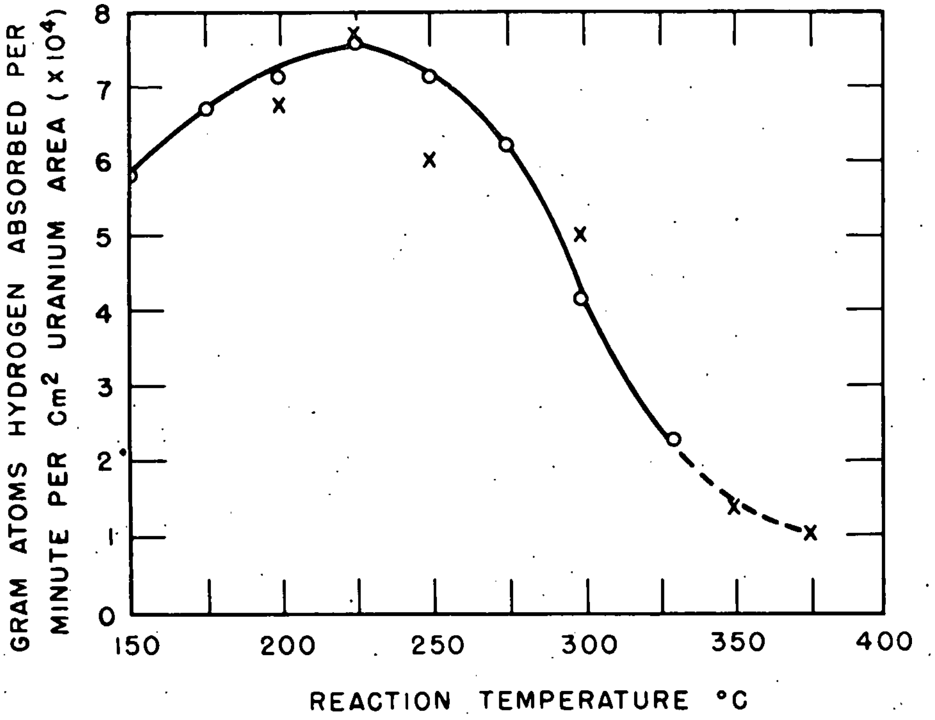

FIG. 5. EFFECT OF TEMPERATURE ON REACTION RATE
o – PURIFIED HYDROGEN x – TANK HYDROGEN

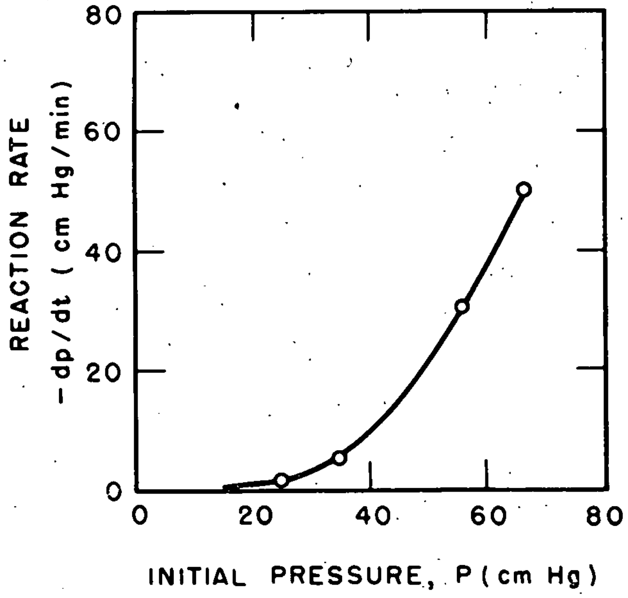

FIG. 6. EFFECT OF INITIAL HYDROGEN PRESSURE ON REACTION RATE OF HYDROGEN AND URANIUM AT 357°C.

external pressure of hydrogen. Thus, the rate of hydrogenation must be a function of the excess hydrogen pressure, that is, the difference between the external hydrogen pressure, p, and the decomposition pressure of the hydride, p_0. Rate measurements at constant temperature (357°C), carried out at Ames$^{\text{(MP Ames 14)}}$ have shown that the initial rate of hydrogenation of uranium powder (see Fig. 6) can be represented by the equation

$$(11) \qquad \dot{v}_0 = \left.\frac{dp}{dt}\right|_{t=0} = K(p - p_0)^{5/2}; \quad (p_0 = 134 \text{ mm Hg})$$

Integration of equation (9) indicates that the plot of $(p_t - p_0)^{3/2}$ against t must be linear. The quantity p_t is the residual hydrogen pressure after the hydrogenation has proceeded for the time t. This conclusion is confirmed by experiments. (See Fig. 7).

(c) Effect of Surface. According to Los Alamos measurements (MP Los Alamos 1) the slowing down of hydrogen consumption, which always occurs after hydrogenation has proceeded for a while, can be accounted for by the assumption that the rate is proportional to the active uranium surface. In the calculation of the active surface it was assumed that the hydrogenation of a wire progresses from the surface to the axis with the surface retaining its cylindrical shape. This assumption obviously cannot be exactly correct, but no other quantitative data on the relation between surface and hydrogenation velocity are available, apart from the trival observation that fine powder is hydrogenated much more rapidly than solid metal. It has been observed at Los Alamos that cold working of the wire reduced the rate of hydrogenation by as much as 50 per cent.

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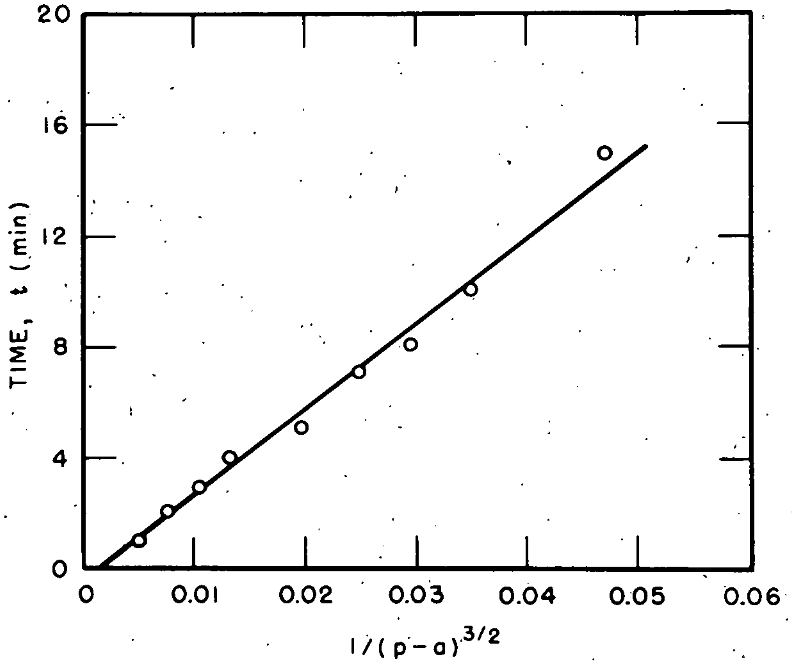

FIG. 7. RATE OF HYDROGENATION OF URANIUM POWDER AT 357°C.

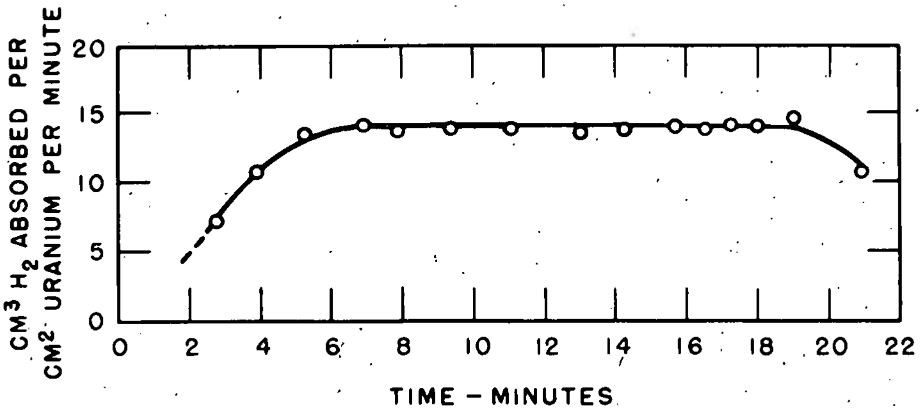

FIG. 8. RATE OF HYDROGEN ABSORPTION CORRECTED FOR SURFACE AREA OF URANIUM SPECIMEN. REACTION TEMPERATURE – 225°C.

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(d) Induction Period. It was suggested above that the decline of hydrogen consumption with progressing hydrogenation could be accounted for by calculating the rate for unit active surface. Fig. 8 shows that the specific rate calculated in this way remains constant throughout the process, except for a slight dip toward the very end of hydrogenation which is probably due to errors of method, and an induction period at the beginning of the process.

The duration of the induction period depends on the purity of the hydrogen; at 250°C it is as long as 28 min. in tank hydrogen, but drops to practically zero in hydrogen purified by hot uranium. At 150°C induction is noticeable even in most thoroughly purified hydrogen. Induction must be attributed to the formation of protective surface layers of oxide or nitride. It is noteworthy, however, that preliminary exposure of the metal to nitrogen or oxygen does not lead to an induction period in subsequent treatment by pure hydrogen.

After the induction period is over, the rate of hydrogenation is about the same in tank hydrogen as in pure hydrogen (MP Los Alamos 1).

An attempt was made at Ames (MP Ames 3) to prepare uranium hydride under an inert solvent mineral oil; however, the rate of hydrogenation at 250°C was only 1 per cent of the value obtained in hydrogen gas.

(e) Mechanism of Hydride Formation. The formation and decomposition of uranium hydride provides an interesting example for the study of kinetics of heterogeneous reactions. The occurrence of the difference $(p - p_0)$ in the rate versus pressure function seems to indicate that the rate is limited by a diffusion process, but no off-hand explanation can be given for the power 5/2 with which this factor occurs in equation (11). The same factor indirectly accounts for the drop in the rate of hydrogenation at high temperatures, where p_e approaches p.

(f) Kinetics of Decomposition. The rate of decomposition of the hydride also was studied at Ames (MP Ames 15). At 250°C about 50 per cent of a 6 to 7 g sample of hydride could be decomposed in one hour by evacuation at a pressure of ~ 0.1 mm. Systematic measurements were carried out at 294°, 367° and 405°C. (MP Ames 13) However, the temperature dropped by as much as 100°C immediately after the beginning of pumping, and returned only gradually to the initial level. Furthermore, the true pressure of hydrogen at the surface of the hydride is not known and may vary for different parts of the sample. Thus, the decomposition curves (Fig. 9) cannot be considered as having general significance. These curves indicate an approximately first order reaction and a rather slow increase in decomposition rate with temperature. For example 50 per cent decomposition is reached in 30 min. at 294°C and after 3 min. at 405°C. This slow increase may be due to the fact that the true hydrogen pressure at the surface of the hydride becomes higher with increasing temperature because of the limited rate of pumping.

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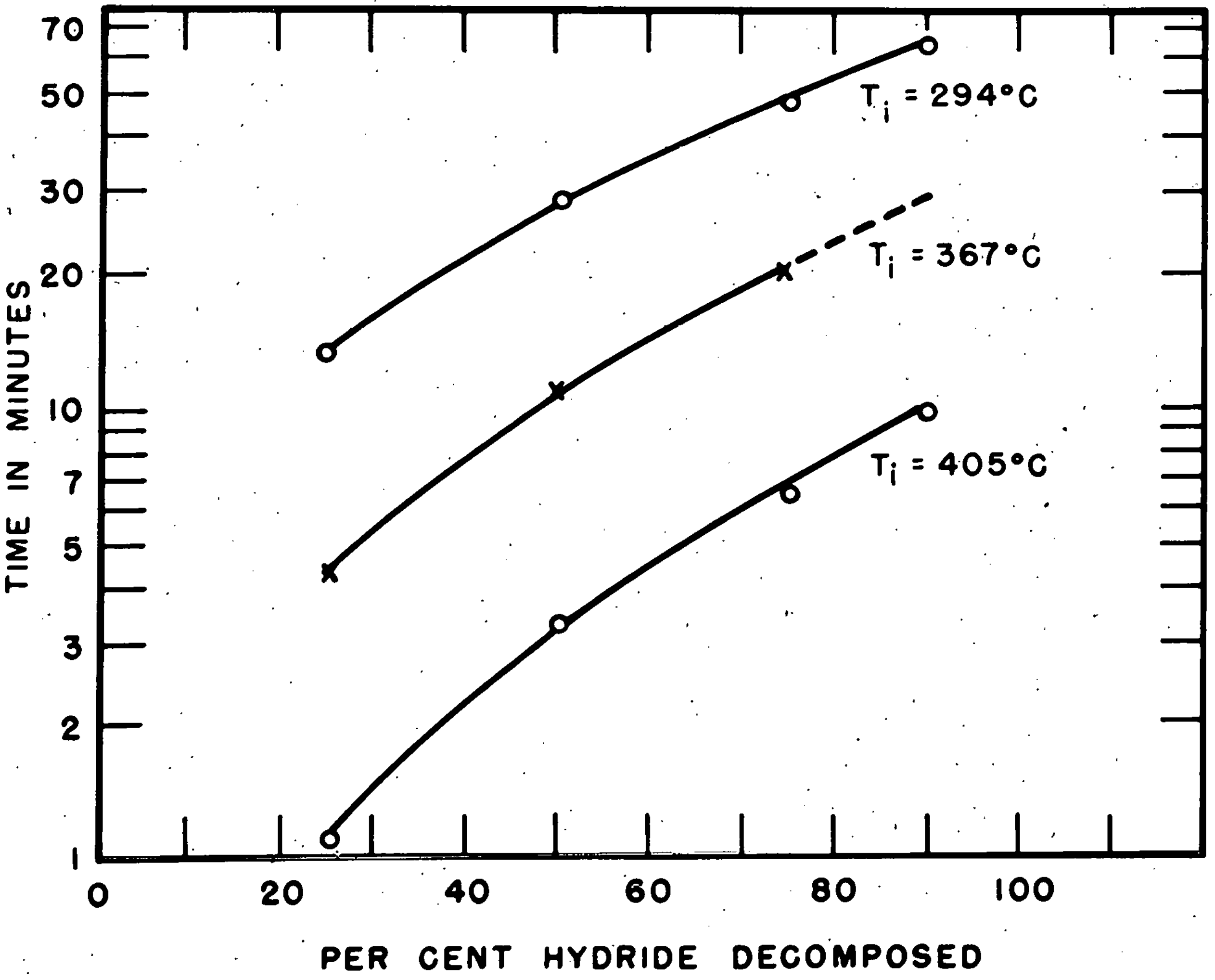

FIG. 9. DECOMPOSITION RATE OF URANIUM HYDRIDE WITH TEMPERATURE.

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8.5 Hydride Formation from Uranium Compounds or from Uranium and Water.

(a) Formation of Hydride from Uranium Compounds. According to the Ames group(MP Ames 12), no hydride is formed by heating uranium carbide or oxide in hydrogen. Uranium alloy with 20 per cent aluminum reacts with hydrogen giving a powder which apparently contains metallic uranium and a uranium-aluminum compound. Sodium hydroxide dissolves aluminum out of it at least partially. Uranium amalgam does not react with hydrogen (MP Ames 2).

(b) Hydride Formation from Uranium and Water Vapor. Water can be decomposed by uranium at 600-700°C and uranium hydride formed by reaction of hydrogen with uranium at 250°C, in one piece of apparatus (MP Ames 57). Considerable amounts of the hydride were also obtained by direct reaction of uranium with steam at 750°C (MP Ames 62).

2.6. Physical Properties of Uranium Hydride. The hydride is described as a brownish-black or brownish-gray, pyrophoric powder. It passes easily through 400 mesh sieve or silk bolting cloth. Prepared from metal, it contains shiny particles, probably oxide inclusions from the original metal. Screened, decomposed in vacuum, and re-synthesized the hydride appears more homogeneous and more grayish in color(MP Ames 10,12).

(a) Crystal Structure and Density. The first x-ray analysis of uranium hydride at Ames (MP Ames 16) showed that is has a simple cubic structure quite different from the three structures of uranium metal. The determination was repeated later with especially

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pure samples$^{\text{(MP Ames 17, 18)}}$. The samples prepared at 200-300°C and atmospheric pressure of hydrogen gave satisfactory but not very sharp reflections in the back reflection region of a symmetrical self-focusing camera of 5 cm radius with CuK radiation. The reason for diffuseness is that small size of the hydride particles. Hydride prepared under 1800 psi at 500-600°C consists of much larger crystals and gives very sharp maxima. The best value of the lattice spacing,

$$a_0 = 6.6310 \pm 0.0008 \text{ A},$$

has been obtained with such high-pressure preparations. The "low pressure" hydride gave the value

$$a_0 = 6.632 \pm 0.001 \text{ A}.$$

at Chicago$^{\text{(MP Chicago 1)}}$. In satisfactory agreement with Ames' result a lattice constant,

$$a_0 = 6.634 \pm 0.002 \text{ A}$$

was found.

The missing reflections in the diffraction diagram lead to the identification of O_h^3, O^2 and T_d^4 as the three possible space groups in the lattice of uranium hydride; final selection of the space group is impossible without knowledge of the positions of the hydrogen atoms. The elementary cell contains eight molecules; the positions of the eight uranium atoms can be divided into two groups: (a) two equivalent positions as 0, 0, 0, and ½, ½, ½, and (b) six equivalent positions at ¼, ½, 0; 0, ¼, ½; ½ 0, ¼; 3/4, ½, 0; ½, 0, 3/4, and 0, 3/4, ½. This arrangement is represented in Fig. 10. Each of the atoms of group (a) has twelve atoms of group

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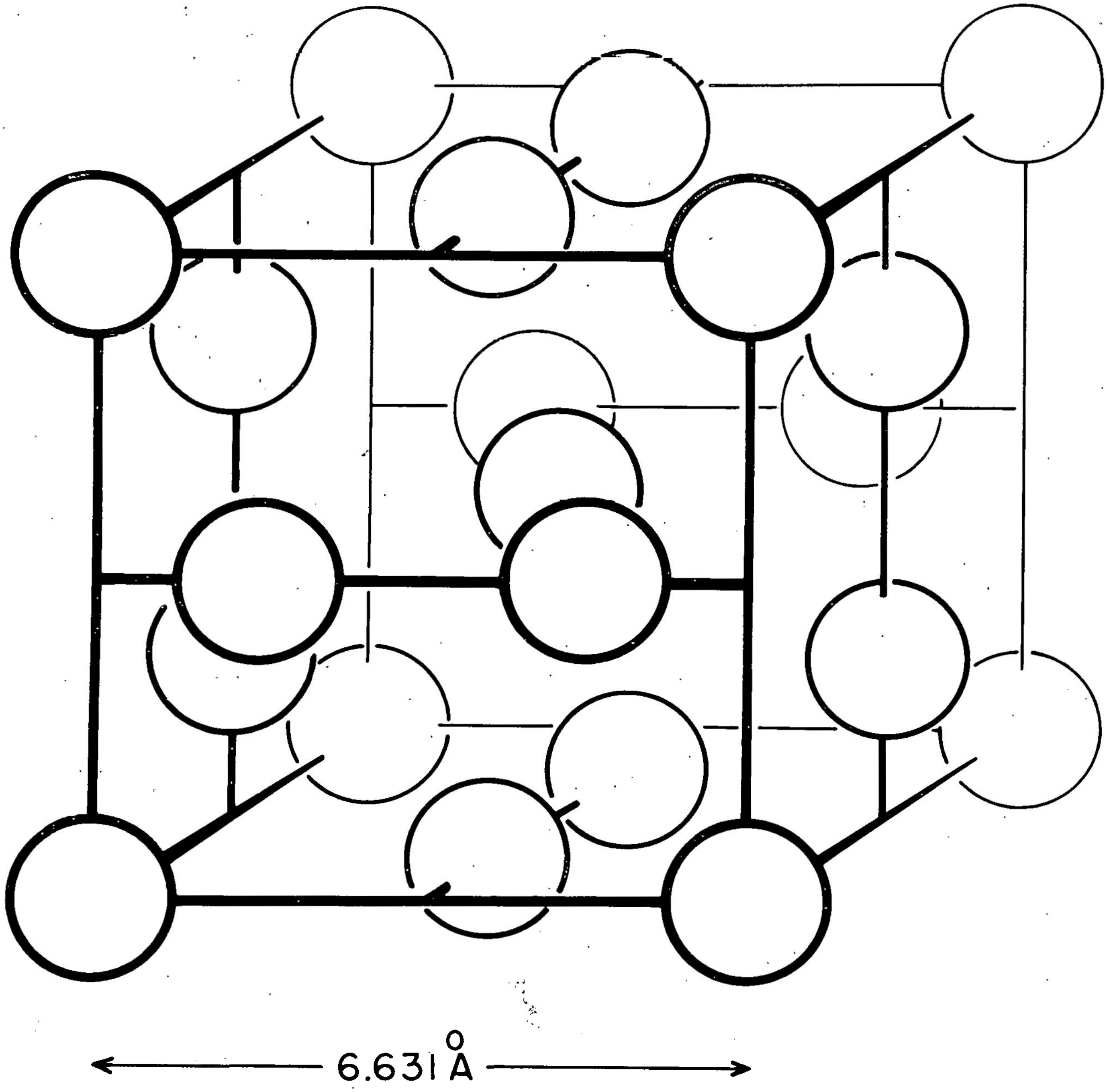

FIG. 10. THE STRUCTURE OF URANIUM HYDRIDE

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(b) as its nearest neighbors at a distance of 3.707 A; each atom of group (B) has two nearest neighbors of the same group at 3.316 A distance, four tetrahedrally arranged neighbors of group (a) at 3.707 A distance, and eight atoms of group (b) at a distance of 4.06 A.

The density of UH_3 calculated from the x-ray structure is 10.92 g/cc. This result is in excellent agreement with the experimental density determination by the helium displacement method(MP Ames 10,19), which gave 10.95 g/cc. Earlier, less precise density determinations (under hexane) gave a value of 11.4 g/cc. The bulk density of dry UH_3 powder is 3.4 g/cc; wetted with hexane it settles to 3.5 g/cc. Centrifugation increases the density to 4.0, pressure of 28 tons/sq.in., to 7.3, and pressure of 160 tons/sq.in. to 8.4 g/cc (MP Ames 10). Uranium hydride powder prepared at 700°-800°C under 1800 psi hydrogen pressure can be pressed to a bulk density of>9.0 g/cc (MP Ames 5).

The low bulk density of uranium hydride causes a large increase of the volume of the metal during hydrogenation; this swelling must be taken into account in the construction of apparatus for hydrogenation.

In partially decomposed or incompletely hydrogenated hydride samples, the density is within ± 1 per cent, a linear function of the hydrogen content(MP Chicago1). The lattice constant of the hydride was unchanged by heating a mixture of hydride with uranium metal; in a heated mixture of 1 part UH_3 with 1 part uranium, for example, the spacing was $a_0 = 6.630$ A ± 0.002 A. These results are typical of a mechanical mixture of two solid phases without mutual solubility. As mentioned before, a hydride sample made under 1800 psi of hydrogen showed no significant displacement of the x-ray diffraction maxima compared to their position in the diagram of hydride prepared under low hydrogen pressure. In other words, there was no indication of lattice distortion by dissolved or occluded hydrogen. The hydride separated from the uranium hydride amalgam by aeration (see Sec. 2.8) had the same lattice constant as ordinary hydride.

(b) Electrical Conductivity. Hydride powder tapped between electrodes showed metallic conductivity. The specific resistance was 0.47 Ω-cm, not very different from that of uranium metal powder obtained by the decomposition of the hydride (0.68 Ω-cm) (MP Ames 6). Pressed material conducted better than loose powder (MP Ames 10).

2.7 Chemical Reactions of Uranium Hydride. Uranium hydride is a very reactive substance and can be used for the preparation of numerous uranium compounds. In many cases the reaction probably proceeds through the intermediary of free uranium metal which is formed by the decomposition of the hydride into a very finely divided and chemically active state. The reactions of the hydride have been studied in a series of investigations at Ames (MP Ames 6,10,20,21). A few experiments also were performed at Clinton (MP Clinton 3) and M.I.T. (1).

(a) Reactions with Gases. Table 5 is a review of the reactions of uranium hydride with various gases (MP Ames 10,22). The hydride is often pyrophoric (MP Ames 12) and must be handled with care. Non-pyrophoric samples probably are protected by surface layers of oxide and can be obtained by first exposing the hydride to air at the temperature of dry ice. Carbon dioxide and nitrogen are safe atmospheres up to 200°-225°C; however, these gases, too, react with the hydride at higher temperatures. Once reaction with carbon dioxide or nitrogen has started, it cannot be stopped, but there is no risk of explosion as in the presence of oxygen. In open air the hydride burns smoothly to water and U_3O_8; UO_2 may be formed if the air supply is insufficient.

The rate of oxidation of UH_3 in air can be measured if ignition is avoided by careful initial exposure (MP Ames 23). The initial rate of oxygen pickup of a stable UH_3 sample was 0.25 mg per day per gram hydride; after 45 days the rate still was about half as large. So-called "quasi-hydride" (see Sec. 2.8) gained 0.83 mg/g per day initially and about one-fifth of this after 45 days.

Table 5 shows that the reaction of uranium hydride with HCl, HBr, PH_3 and NH_3 give compounds of trivalent uranium, while those with Cl_2, Br_2, H_2O, HF, $COCl_2$ and probably HI, lead to tetravalent uranium compounds.

The reaction of UH_3 with HF gas been studied in some detail at Clinton (MP Clinton 3). When UH_3 is treated with HF at 270°C, a surface layer of UF_4 is formed which prevents further penetration of the hydride by HF. No such caking occurs at 500°C, and all hydrides is converted to UF_4. According to Ames studies (MP Ames 29) a reaction of uranium with a mixture of equal volumes of HF and H_2 at 250°C gives a smooth conversion to UF_4; uranium hydride undoubtedly is an intermediate compound in this reaction.

TABLE 5

REACTION OF URANIUM HYDRIDE WITH GASES

Gas	Temperature (°C)	Product	Remarks.
		Elementary Gases	
N_2	225	$UN_{1.6}$	Reaction slow, incomplete.
	250		Pyrophoric nitrid rapidly formed (MP Ames 24).
	900	UN (?)	Chicago work 3.6% N; (UN theoretically 5.5%) (M.I.T.1)
O_2	(pyrophoric)	U_3O_8	UO_2 can be formed if air supply is insufficient.
Cl_2	200	UCl_4	Product melts during reaction.
Br_2	200-300	UBr_4	Brown, partly fused powder.
I_2	400	$UI_{(4)}$ (?)	Product unstable, analysis uncertain (MP Ames 25).
		Hydrides	
H_2O	350	UO_2	Black oxide, by weight gain $UO_{2.14}$ (MP Ames 6).(Excess over $UO_{2.0}$ probably due to air leakage).
	500	UO_2	Reaction mass glows.
H_2S	400-500	US_2	Black powder; U_2S_3 as intermediate can be isolated. Reaction slow.
NH_3*	100	UN (?)	"Low temperature" nitride, slow reaction.
	250		Pyrophoric (?) faster reaction.
PH_3	400	U_2P_3	Black Powder.

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TABLE 5

REACTION OF URANIUM HYDRIDE WITH GASES

Gas	Temperature (°C)	Product	Remark
		Hydrides	
HF	20-400	UF_4	Green dry powder, typical "green salt".
HCl	250-300	UCl_3	Dry powder, olive green at 25°C, reddish brown at higher temp.
HBr	200	UBr_3	Reddish brown dry powder. Best results obtained by conducting HBr through UH_3 from below at 250°-275°C. (MP Ames 26.
HI	300-400	UI_4 (?)	Product unstable, analysis UI_{3-4}
		Oxides	
CO	up to 400	U	No volatile carbonyl formed
CO_2	200	UO_2	Impure product (carbide). UH_3 burns once reaction started.
		Organic Gases*	
C_2H_4	500	UC (?)	Product not known, contains 1.6% C. Reaction probably incomplete.
HCN	400	carbide, nitride	Black powder, pyrophoric, contains no CN.
$COCl_2$	250	UCl	Yellow-green dry powder, slightly contaminated by carbon.
CH_3I	275-300	UI_3 (?)	Uncertain. Reaction moderately fast.
CCl_4	250	UCl_4+C(?)	CH_4 and C_2H_6 probable by-products (MP Ames 27, 28).

* For clarification of reaction of UH_3 with nitrogen and ammonia see the discussion of uranium nitrides in Chapter X.

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(b) **Reactions with Water and Aqueous Acids in Bases.** A small quantity of UH_3 powder disperses in water without reaction. Sometimes, however, ignition occurs; although once the powder is wetted, this danger is over (MP Ames 30). Large quantities always ignite unless water is added very slowly (MP Ames 31). UH_3 reacts slowly with water vapor at 200-300°C; the oxide formed is probably UO_2 (MP Ames 26).

Uranium hydride dissolves much more slowly than uranium metal in 6 N or 12 N hydrochloric acid giving a pale-green solution (MP Ames 30, 32). The hydride is easily dissolved in chloric acid ($KClO_3+H_2SO_4$) (MP Ames 33). Dilute percholric acid dissolves the hydride slowly if at all, but concentrated acid reacts upon heating to give uranyl perchlorate, $UO_2(ClO_4)_2$. This reaction is safe if performed on a small scale, but becomes dangerous with quantities exceeding 1 or 2 g (MP Ames 30). Dilute phosphoric acid does not react, although concentrated acid dissolves the hydride to form uranous phosphate. (MP Ames 30). Cold 8 N acetic acid does not react, but a brown suspension is formed upon boiling; this may be merely peptized hydride, or it may be a product of chemical transformation. Glacial acetic acid does not affect the hydride (MP Ames 30). Uranium hydride readily reduces 6 N or concentrated nitric acid to NO_2, while uranium, after passing through an intermediate green stage, forms yellow uranyl nitrate, (MP Ames 30) $UO_2(NO_3)_2$. Dilute sulfuric acid reacts very slowly, but hot concentrated acid is rapidly reduced to sulfur and hydrogen sulfide, while uranium is dissolved as uranous sulfate $U(SO_4)_2$ (MP Ames 30).

Hot or cold solutions of the <u>bases</u>, KOH, NaOH, NH_4OH, and NaCN, do not react with the hydride. Nor is the hydride dissolved by liquid ammonia (MP Ames 30).

(c) <u>Reactions with Organic Solvents.</u> Organic solvents containing no halogen (e.g., benzene, toluene, hexane, dioxane, alcohol, acetone, ethyl acetate) do not dissolve the hydride and do not react with it. (MP Ames 30). Halogenated solvents, on the other hand, are dangerous. Upon addition of hydride to carbon tetrachloride, for example, a violent explosion may ensue, producing UCl_4, HCl, hydrogen and carbon. Carbon tetrachloride <u>vapor</u> reacts with uranium hydride only above 200°C, producing UCl_3, UCl_4 and carbon (MP Ames 28).

(d) <u>Oxidation of Hydride by Weak Inorganic Oxidants.</u> Many weak inorganic oxidants oxidize UH_3 to U(IV) or U(VI) salts and liberate hydrogen. Particularly efficient are <u>silver salts</u> as in the following reactions: (MP Ames 34)

(12) $UH_3 + 4AgF \rightarrow UF_4 + 4Ag + 3/2\ H_2$ (vigorous reaction)

(13) $UH_3 + 6AgNO_3 \rightarrow 2H_2O + 6Ag + UO_2(NO_3)_2 + 4HNO_3 + 3/2\ H_2$

(very rapid reaction. Solution heats up to boiling, and color of resulting solution indicates complex formation)

(14) $UH_3 + Ag_2SO_4 \rightarrow 2H_2O + UO_2SO_4 + 6Ag + 2H_2SO_4 + 3/2\ H_2$

(This reaction is slower than the two preceding ones)

(15) $UH_3 + 2Ag(CH_3COO) \rightarrow UO_2(CH_3COO)_2 + \ldots\ldots$

(This reaction is slow)

(16) $UH_3 + Ag(OOCHCHOHCHOHCOO) \rightarrow UO_2(OOCHCHOHCHOHCOO) + \ldots\ldots$

(Still slower)

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Three parallel reactions occur with silver perchlorate:

(17) $UH_3 + 6\ AgClO_4 + 2H_2O \longrightarrow 6Ag + UO_2\ (ClO_4)_2 + 4HClO_4 + 3/2H_2$ (80%)

(18) $UH_3 + 4\ AgClO_4 \longrightarrow 4Ag + U(ClO_4)_4 + 3/2\ H_2$ ($<$ 0.1%)

(19) $UH_3 + 5\ AgClO_4 \longrightarrow 4Ag + AgCl + 2UO_2(ClO_4)_2 + 3/2H_2$ (20%)

In toluene, the reaction of UH_3 with $AgClO_4$ gives silver and AgCl, perhaps according to the equation (MP Ames 35):

(20) $2UH_3 + 6AgClO_4 \longrightarrow 2Ag + 2AgCl + Ag_2O + 2UO_2\ (ClO_4)_2 + 3H_2O$

Similar reactions occur with mercuric salts. Mercuric chloride reacts vigorously giving UCl_4 (15%) UO_2Cl_2 (35%); the rest of uranium is found in the grey Hg Hg_2Cl_2 precipitate. Mercuric nitrate also reacts rapidly giving uranyl nitrate and mercury. Antimonous chloride in 3N HCl oxidizes UH_3 to UCl_4 and liberates H_2:

(21) $4SbCl_3 + 3UH_3 \longrightarrow 4Sb + 3UCl_4 + 9/2H_2$.

Cupric sulfate does not react at room temperature, but is reduced slowly at 80°-90°C, giving copper and $U(SO_4)_2$. Cupric chloride and NH_4Cl evolve hydrogen rapidly, and gives a green solution$^{(MP\ Ames\ 33)}$.

Ferrous sulfate oxidizes UH_3 to UO_2^{++} upon heating(MP Ames 34). No reaction is observed with bismuth or lead salts$^{(MP\ Ames\ 34)}$.

(e) Oxidation of Hydride by Strong Oxidants. The effect of saturated sodium hypochlorite (NaOCl)solution on UH_3 is slight$^{(MP\ Ames\ 33)}$ A 30 per cent solution of hydrogen peroxide reacts vigorously with sparking and formation of black oxide$^{(MP\ Ames\ 36)}$. The reaction of hydrogen peroxide with suspension of UH_3 in HCl gives UO_2Cl_2. This reaction is slower in H_2SO_4. In the presence of organic acids H_2O_2 produces the corresponding uranyl salts; with excess peroxide peruranic acid may be formed. Ceric salts oxidize the uranium in UH_3 to the

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hexavalent state and release hydrogen. Dichromate reacts only upon heating giving uranyl salt. Cold permanganate does not react without acid, but reacts rapidly in the presence of acid giving uranyl salt. The same is true of bromate (MP Ames 10). Reactions with perchloric, nitric and sulfuric acid were mentioned in Section 2.7 (b).

2.8 The Uranium Hydride Amalgam and Similar Systems, and the "Quasi Hydride." Uranium hydride can be dispersed in mercury(MP Ames 10,37) without marked heat liberation or hydrogen evolution. The resulting "amalgam" is fluid up to 10 per cent UH_3, and wets glass pasty at 30 per cent and semi-solid at 40 per cent. Above 60 per cent UH_3 takes up mercury as sawdust takes up oil. The 90 per cent amalgam is a grey pyrophoric powder.

Filtration through alundum or sintered glass separates the amalgam into practically pure mercury and a residue which looks like more concentrated amalgam. Pure mercury can also be squeezed out from 35 per cent amalgam by pressure of 40 tons/sq in.(MP Ames 38). These results indicate that the amalgam is a colloidal system rather than a true molecular solution or a chemical compound.

The behavior of the amalgam in air supports the interpretation of its being a capillary system. Uranium hydride which has been exposed to air ceases to be wetted by mercury. Aeration of the amalgam prepared under exclusion of air causes a precipitation of the hydride. In the course of this precipitation partial oxidation takes place, causing the precipitate to be somewhat different from the original hydride, and leading to its designation as "Quasi-hydride". (MP Ames 39) Its x-ray diffraction picture is the same as that of the true hydride, but it is brown in color and a typical analysis

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shows 97.4 per cent uranium and 1.15 per cent hydrogen, the rest probably being oxygen. This corresponds to the composition $UH_{2.82}O_{0.2}$; therefore the quasi hydride is probably an intimate mixture of UH_3 and uranium oxide. The quasi hydride is sometimes stable and sometimes pyrophoric.

Because of partial oxidation by air, of the hydride during its precipitation from mercury, some water is formed in this process(MP Ames 40); the absorption of oxygen and formation of water lead to liberation of heat. If the amalgam is exposed to quiet or slowly circulating air in an open vessel, the pickup of oxygen and the formation of water are rapid the first day, and continues at a diminishing rate for months or even years(MP Ames 38).

Freshly precipitated, the quasi hydride carries a large proportion of finely dispersed mercury. It can be freed from mercury by suspension in hexane or petroleum ether and filtering through sintered glass(MP Ames 41). Amalgamation of UH_3 by mercury is not affected by the presence of magnesium in mercury(MP Ames 42).

The hydride disperses not only in mercury, but also in other low-melting metals and alloys. For example, 2 g UH_3 could be "dissolved" in 20 cc of liquid sodium-potassium alloy(MP Ames 43). In this case, too, the heat effect is negligible. Treatment of uranium hydride with liquid Woods metal or pure tin leads to the formation of a spongy mass. Hydrogen is liberated and intermetallic compounds are formed in this reaction(MP Ames 38). Some experiments were made with a hydride formed from uranium-iron alloy (MP Ames 42). The product probably contained UH_3 together with an unchanged uranium-iron compound.

2.9. <u>Uses of Uranium Hydride</u>. The first and most obvious use of uranium hydride is the preparation of pure, finely dispersed uranium metal (MP Ames 12). This metal is reactive and can be used for the preparation of alloys and other compounds such as uranium carbide (MP Ames 44). Pure hydrogen and deuterium also can be obtained by synthesis and decomposition of uranium hydride, a method regularly in use at Ames (MP Ames 10). Intermetallic or related compounds of uranium do not react with hydrogen, so inclusions can be separated from uranium metal by hydrogenation and sifting. This method has been applied to uranium-aluminum alloys (MP Ames 45). Uranium alloys can be etched by hydride formation (MP Ames 51).

The preparation of various trivalent and tetravalent compounds of uranium from uranium hydride has been suggested (MP Ames 52), and many of these procedures, based on results summarized in Table 5 have actually been utilized. One of these methods is the preparation of UF_4 by reaction between UH_3 and HF (MP Ames 53), or simultaneous action of hydrogen and HF on uranium (MP Ames 29, 54). Preparation of certain uranyl salts also can be achieved by using uranium hydride as starting material (MP Ames 10), for example:

(21) $Ag_2SiF_6 + UH_3 + 2Ag_2O \longrightarrow UO_2SiF_6 + 6Ag + 3/2H_2$

(22) $(CH_3CHOHCOO)\,Ag + UH_3 + 2Ag_2O \longrightarrow (CH_3CHOHCOO)_2\,UO_2 + 6Ag + 3/2H_2$

Attempts to use uranium as a hydrogenation catalyst (with naphthalene and maleic acid as H-acceptors) were unsuccessful (MP Ames 55).

The formation and decomposition of the hydride and volumetric determination of hydrogen formed has been suggested as an analytical method for the determination of uranium (MP Ames 56) (See also Vol 13). A similar procedure has been used for the conversion of water and hydrogen and deuterium in the analysis of heavy water (MP Ames 10).

3. The Uranium Deuteride

The uranium deuteride, UD_3, has been prepared at Ames, and studied especially from the point of view of its possible use for the separation of deuterium from hydrogen.

3.1 **Preparation.** Uranium deuteride can be prepared by decomposing heavy water with uranium at 600°-700°C, and reacting the deuterium produced in this way with uranium at 250°C:

$$U + 2D_2O \xrightarrow{600^\circ\text{-}700^\circ C} UO_2 + 2D_2 \quad (23)$$

$$U + 3/2\ D_2 \xrightarrow{250^\circ C} UD_3 \quad (24)$$

The two operations can be carried out successively in the same piece of apparatus (MP Ames 57).

The decomposition pressure of UH_3-UD_3 mixtures between 20 and 80 per cent UH_3 was measured at 357°C (MP Ames 58). The results indicate that this system behaves as a perfect solution, that is, the pressure is a linear function of composition. (See Fig. 11). The decomposition pressure of pure UD_3 at 357°C is 186 mm Hg, and thus considerably higher than that of UH_3 (134 mm Hg). The ratio $P_D(UH_3)$ is constant (about 1.4) in the temperature range 250°-430°C (MP Ames 59). The decomposition pressure equation is:

$$\log P_{mm} = -4500/T + 9.43 \text{ (see Eq. 3).} \quad (25)$$

The heat of formation of UD_3 is 31 kcal/mole the same as that of UH_3.

The **rate of formation** of UD_3 from uranium and deuterium at

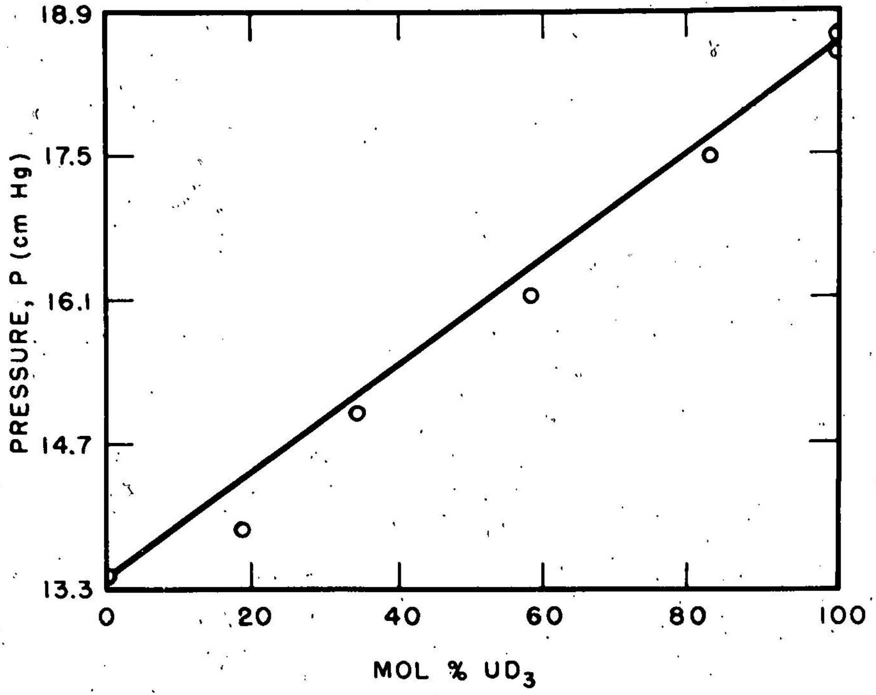

FIG. 11. EQUILIBRIUM PRESSURES OF HYDROGEN AND DEUTERIUM OVER UH_3-UD_3 MIXTURES AT 357°C.

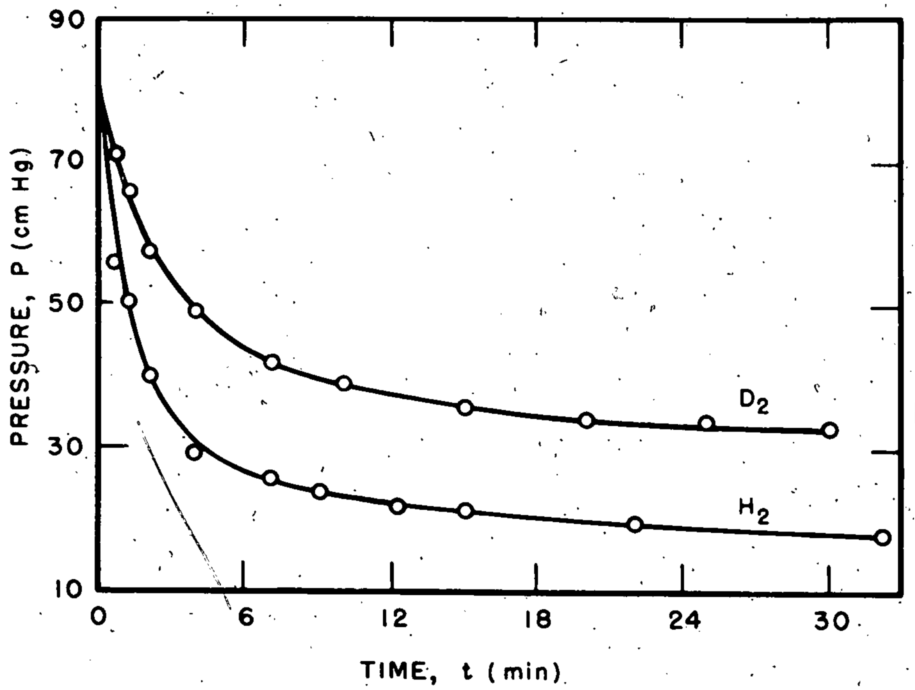

FIG. 12. REACTION RATES OF HYDROGEN AND DEUTERIUM WITH POWDERED URANIUM AT 375°C.

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356°C is much slower than that of UH_3 (Fig.12) (MP Ames 14), a difference which can be explained by the larger zero point energy of the hydrogen molecule as compared to the deuterium molecule. However, contrary to expectation, this difference is not enhanced but rather diminished if the synthesis is carried out at low temperature. Measurements at -76°C were rather erratic (MP Ames 60), but the rate of consumption of both hydrogen and deuterium was about the same, 7 cc gas per hour per gram uranium, compared to an initial rate of about 30 cc hydrogen per min. at 357°C.

The slower formation of the deuteride and its higher decomposition pressure appeared to offer a way for the separation of hydrogen and deuterium. However, experiments on decomposition of $UH_3 + DH_3$ mixtures at Ames (MP Ames 61) lead only to a slight enrichment of deuterium in the gas phase. For example, with a solid material containing 19.8 mol per cent deuterium in total hydrogen, the ratio $[D_2] / [H_2]) / ([UD_3] / [UH_3])$ was equal to 1.2. The first gaseous fraction out of ten contained 23.2 per cent deuterium and the last one 16.8 per cent deuterium. The difference in the rate of formation of UH_3 and UD_3 cannot be utilized for separation because the isotopic exchange between hydride and gas is very rapid with complete exchange occurring in 5 min. at 300°C (MP Ames 61).

Some experiments were carried out with the hydride and deuteride amalgams. In this case, the isotopic exchange between gas phase and liquid phase was found to be slow. For example, when hydrogen was heated with a 25 per cent DH_3 and 75 per cent UH_3 mixture, the concentration of deuterium in the gas was only 2.7 per cent after

15 min. and 10.3 per cent after 2 hours. The reverse replacement of hydrogen in UH_3 by deuterium from the gas phase was even slower. This slow exchange prevents the use of an amalgam column for effective separation of deuterium and hydrogen.

The <u>lattice constant</u> of uranium deuteride (MP Ames 39) is $a_0 = 6.625$ A, that is, 0.025 A smaller than that of the hydride. The calculated density is 11.16 g/cc compared with 10.91 g/cc for UH_3.

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CHAPTER 9

URANIUM BORIDES, CARBIDES, AND SILICIDES

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1. Uranium - Boron System

Two uranium borides have been described in the literature. Wedekind and Jochein (1913) obtained uranium diboride, UB_2, by forming electrodes from uranium powder pressed with amorphous boron under 200 atm. pressure at 1000°C. These electrodes were melted in an electric arc, and the silver grey product obtained was washed with dilute nitric acid. The diboride proved resistant to aqueous alkalis and acids with the exception of nitric acid and hydrofluoric acid. It dissolved in melted alkali with liberation of hydrogen.

Andrieux (1929) electrolyzed at about 1000°C a melt of U_3O_8 and B_2O_3 to which alkaline earth oxides and fluorides were added as flux and obtained crystals with metallic lustre, the composition of which was determined as UB_4. This uranium tetraboride dissolves in cold hydrofluoric or hydrochloric acid, reduces concentrated sulfuric acid, and dissolves easily in nitric acid and concentrated hydrogen peroxide. It is rapidly decomposed by melting with hydroxides and carbonates and reacts vigorously with peroxides.

2. Uranium - Carbon System

Existence of a uranium carbide was discovered by Moissan (1896) who obtained it from heating U_3O_8 and carbon in an electric furnace. Moissan and later Rideal (1913) ascribed to this compound the formula U_2C_3, while Lebeau (1911) and Heusler (1925) favored the formula UC_2. Recent investigations proved the existence of a uranium monocarbide, UC, in addition to comfirming that of the dicarbide, UC_2. The monocarbide is thermodynamically stable at room temperature, the dicarbide probably only at high temperatures. The existence at high temperatures ($>$2000°C) of true sesqui-carbide, U_2C_3, has been postulated, but is as yet quite uncertain. (See Vol. 12 A.)

2.1 Phase Relationships in the Uranium - Carbon System. The solubility of pure carbon (graphite) in liquid uranium was determined at Ames by heating the metal in graphite crucibles and maintaining constant temperature long enough to attain equilibrium between the melt and the graphite. The following values were obtained (MI Ames 1,2):

TABLE 1

SOLUBILITY OF CARBON (or UC) IN LIQUID URANIUM

Temperature (°C)	Per Cent Carbon by weight	Atom C/Atom U
1350 - 1400	0.10	0.02
1450 - 1500	0.17	0.034
1550 - 1600	0.36	0.072
1650 - 1700	0.42	0.084
1750 - 1800	0.51	0.102
1850 - 1900	1.60	0.325
1950 - 2000	1.74	0.354
2080 - 2130	2.92	0.592

Maximum Temperature (°C)	Time (Minutes)	Per Cent Carbon by weight
1375	40	0.137
1400	20	0.168
1500	60	0.385
1600	20	0.626
1800	30	0.775
1900	30	1.20
2000	30	1.50

The solubility of carbon in solid uranium was studied at Battelle (1,2,3,); it is less than in the liquid. In the γ-phase (> 770°C) the solubility may be of the order of 0.05 per cent (1 atom per cent C) although metal containing 0.05 per cent carbon even in the form of fairly small carbide particles does not show complete dissolution of the carbide even when annealed 96 hours at 1000°C. The upper limit of the solubility of carbon in β-uranium (660°-770°C) is of the order of 0.03 per cent (0.6 atom per cent C), while in the α-phase (> 660°C) the solubility is much greater than 0.01 per cent (0.2 atom per cent C). The temperatures of the α - β and β - γ transitions appear not to be markedly affected by saturation of uranium with carbon (MP Ames 2,3). According to Ames x-ray data obtained from samples quenched at 2000°C the solubility of both carbon and uranium in the uranium monocarbide phase appears negligible. (MP Ames 4,5).

The uranium carbon phase diagram between UC (4.8 per cent carbon) and UC_2 (13.07 per cent carbon) also was studied at Ames (MP Ames 6). (See Fig. 1.) Evidence for the existence of a high temperature compound, U_2C_3, is slight. Widmanstätten patterns of alloys between U_2C_3 and UC_2 have been interpreted as indicating the existence of solid solutions of δ U_2C_3 and ϵ UC_2. No carbides with more than two carbon atoms per uranium atom seem to exist. There is some x-ray evidence however, for solubility of carbon in the UC_2 lattice, particularly at temperatures near the melting point (2375°C).

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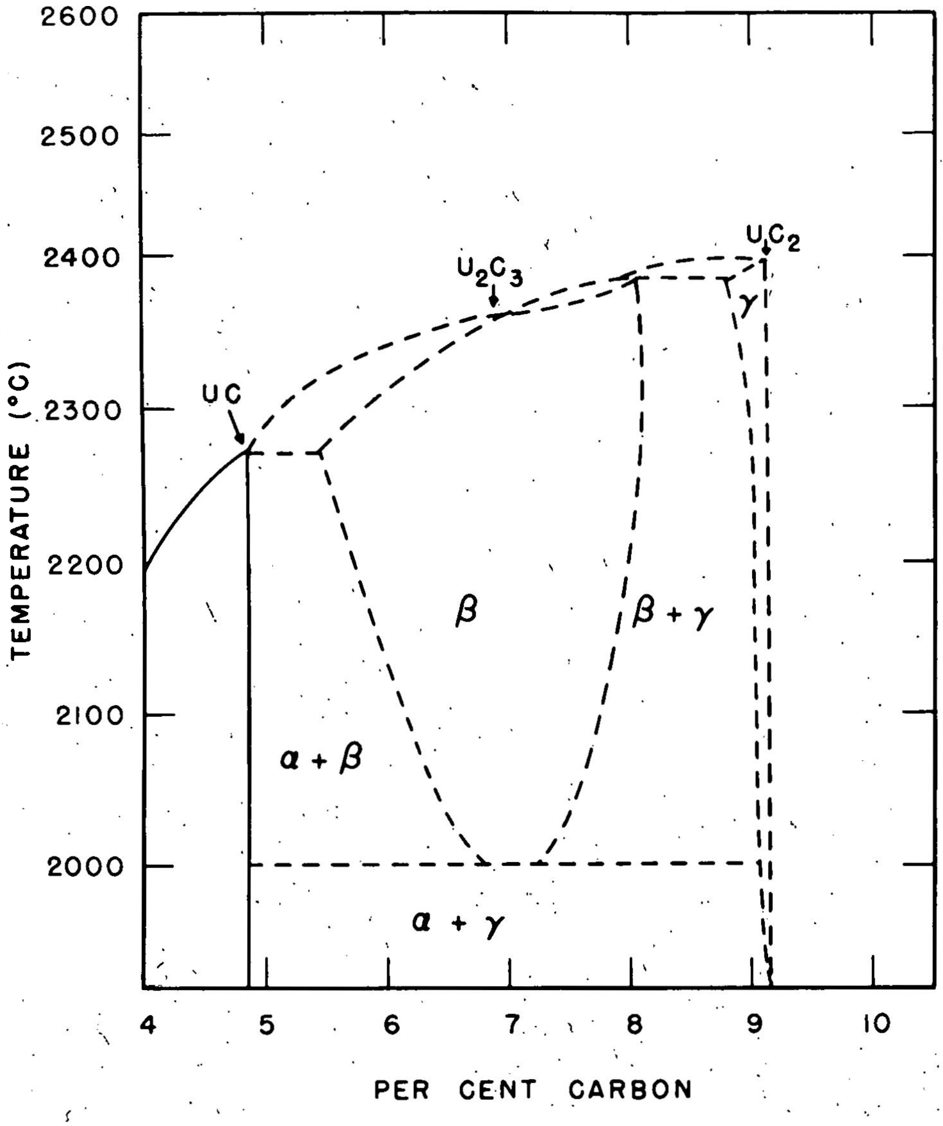

FIG. I. URANIUM CARBON SYSTEM 4.8 – 9.16 PER CENT CARBON.

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2.2 Physical Properties of Uranium Carbides.

(a) U + UC Uranium-carbon alloys with less than 4.8 per cent carbon are mixtures of uranium (containing less than 0.01 per cent carbon) with UC. Because of this inhomogeneous character, determinations of physical constants of these alloys give variable results. The following hardness figures were obtained at Ames (MF Ames 1,7):

TABLE 2

HARDNESS OF URANIUM-CARBON ALLOYS

Per Cent Carbon	Rockwell A	 B
0.06	-	88
0.08	-	88
0.168	-	91
0.25	-	95
0.30	-	95
0.7	-	93
1.99	-	111
0.17	52.8*	-
0.36	54.8	-
0.42	56.0	-
0.51	58.7	-
1.60	63.1	-
1.74	63.8	-
2.92	63.6	-

*Average of several measurements in various parts of the surface of the test piece.

At the Metallurgical Laboratory a carbide preparation with a composition corresponding to the formula U_3C_2 was found to have a density of 10.52 g/cc and a thermal conductivity of 0.082

cal/(cm sec °C) at 56°C (MP Chicago 1,2).

(b) <u>UC. Crystal Structure.</u> Uranium monocarbide forms cubic face-centered crystals (probably NaCl-structure), isomorphous with those of UN and UO. The lattice constant was determined at Ames with the following results:

TABLE 3

LATTICE CONSTANT AND X-RAY DENSITY OF UC

a_1 (Å)	Density (g/cc)	Reference
4.98	--	(MP Ames 8)
4.966 ± 0.005	13.56	(MP Ames 9)
4.948 ± 0.001	13.66	(MP Ames 10)
4.948 to 4.951	--	(MP Ames 11)
4.94	--	(British 1)

According to Ames observations carbon in UC can be replaced by oxygen or nitrogen with a slight decrease in lattice constant (as low as 4.936 when UO_2 is also found). Therefore the most reliable value of the lattice constant is the highest one obtained (4.951 Å). As mentioned above, the lattice constant of UC does not markedly depend upon the presence of excess uranium or carbon, thus indicating low solubility of both components in the carbide.

If one assumes the usual value of 0.77 Å for the radius of the carbon atom, one obtains a value of 2.71 Å for the

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radius of the uranium atom from a lattice constant of 4.94 Å for UC.

Melting Point. Evidence of melting of UC was observed at Ames at 2250°C (MP Ames 6,11).

(c) U_2C_3. X-ray studies of carbide samples with the composition U:C = 2:3 showed that they always consisted of UC and UC_2 (MP Ames 12). Evidence in favor of the existence of a compound U_2C_3 at high temperatures was derived from the fact that apparent single, cubic crystals are formed by quenching an alloy corresponding to U_2C_3 from high temperature even though x-rays prove these single crystals to be diphasic. Microscopic examination of the single crystals revealed a Widmanstätten structure. Therefore, it appears that U_2C_3 is a cubic phase stable somewhere above 2400°C, which has not yet been successfully quenched. A sample with the composition U_2C_3 was brittle and hardness could be determined only approximately as Rockwell 396 (MP Ames 13). The melting point of a carbide sample with 6.95 per cent carbon (U_2C_3 contains 7.04 per cent carbon) was found at Ames to be the same as that of UC_2 (2350°-2400°C) (MP Ames 11).

(d) UC_2. Crystal Structure. Moissan described uranium dicarbide, UC_2, as metallic, dense, and fine crystalline with a density of 11.28 g/cc (Moissan, 1897). The crystal structure of UC_2 was first studied by Hagg (1931), who found it to be face-centered tetragonal in pairs. This was confirmed at Ames (MP Ames 14). The structure is similar to that of LaC_2 with two molecules per unit cell with the lattice constants:

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$$a_1 = 3.517\ \text{Å} \pm 0.001$$
$$a_3 = 5.987\ \text{Å} \pm 0.001$$

Dissolution of carbon in the UC_2 lattice seems to decrease the lattice constant to about $a_1 = 3.505$ Å and $a_3 = 5.951$ Å. The Ames investigators consider this decrease an indication that UC_2 is not an "interstitial solid solution" of carbon in uranium. They suggest that UC_2 is built of small positive U-ions and large negative C_2-ions, with uranium in the interstices of the anion lattice, and that in alloys with $UC_{>2}$ some uranium ions are missing. As discussed in Chapter 11 in connection with a similar interpretation of the decrease in lattice dimensions from $UO_{2.0}$ to $UO_{2.3}$, this interpretation seems to require a marked decrease in density. This was not found in the case of the oxides; no systematic density measurements are available for carbides. The calculated x-ray density is 11.68 g/cc. At the Metallurgical Laboratory a density of only 9.97 g/cc ± 2% was found by Ilott and Raeth (MP Chicago 1,2).

<u>Melting and Boiling Point.</u> An uranium-carbon sample containing 9.18 per cent carbon (UC_2 has 9.16 per cent carbon) showed signs of melting at 2350°-2400°C (MP Ames 6,11). An estimate of the boiling point as 4370°C at 760 mm Hg was made by Mott (1918). Ruff and co-workers (1911, 1919) gave 2425°C for the melting point of UC_2. Tiede and Birnbräuer (1914) found the melting point to be 2200°C in an electric vacuum furnace and 2260°C in a cathode ray furnace.

<u>Specific Heat.</u> At UCRL (1), the specific heat of UC_2 was estimated as

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$$(1) \quad C_p = 8.92 + 3.25 \times 10^{-3}\ T \text{ cal/g mole}$$

At Chicago (MP Chicago 3) an estimate of C_p was made by extrapolation from the known values for other carbides, particularly TaC. The latter is 75 per cent of the Dulong-Petit value at 21.3°C. Assuming that in the case of UC_2 the corresponding value is 80 per cent, one obtains

C_p (UC_2) = 15 cal/g mole for 1940°K.

Thermal Conductivity. At the Metallurgical Laboratory (MP Chicago 2) a thermal conductivity of 0.082 cal/(cm sec °C) was found for a UC_2 sample with a density of 10 g/cc (see crystal structure).

2.3 Preparation of Uranium Carbides

(a) Thermodynamics of UC-Formation. At Berkeley the heat of formation of UC from the elements was estimated at -30 kcal/mole, but this estimate was based entirely on the observation that UC_2 decomposes into U and UC at low temperatures. (MP Berkeley 1).

(b) Thermodynamics of UC_2-Formation. At Chicago (MP Chicago 1), estimates were made of the energy and free energy of the reaction

$$(2) \quad UO_2 + 4C \xrightarrow[\text{(graphite)}]{} UC_2 + 2CO$$

The required experimental data were taken from Heusler's equilibrium measurements of the reaction. Heusler (1926) measured the CO- equilibrium pressure over UO_2-carbon mixture at 1480°-1801°C. Figure 2 shows that the pressures ranged from 18 mm to 1 atm., and that the T logp vs T plot was approximately linear. The equation

$$(3) \quad \log p = -19100\ T^{-1} + 12.09$$

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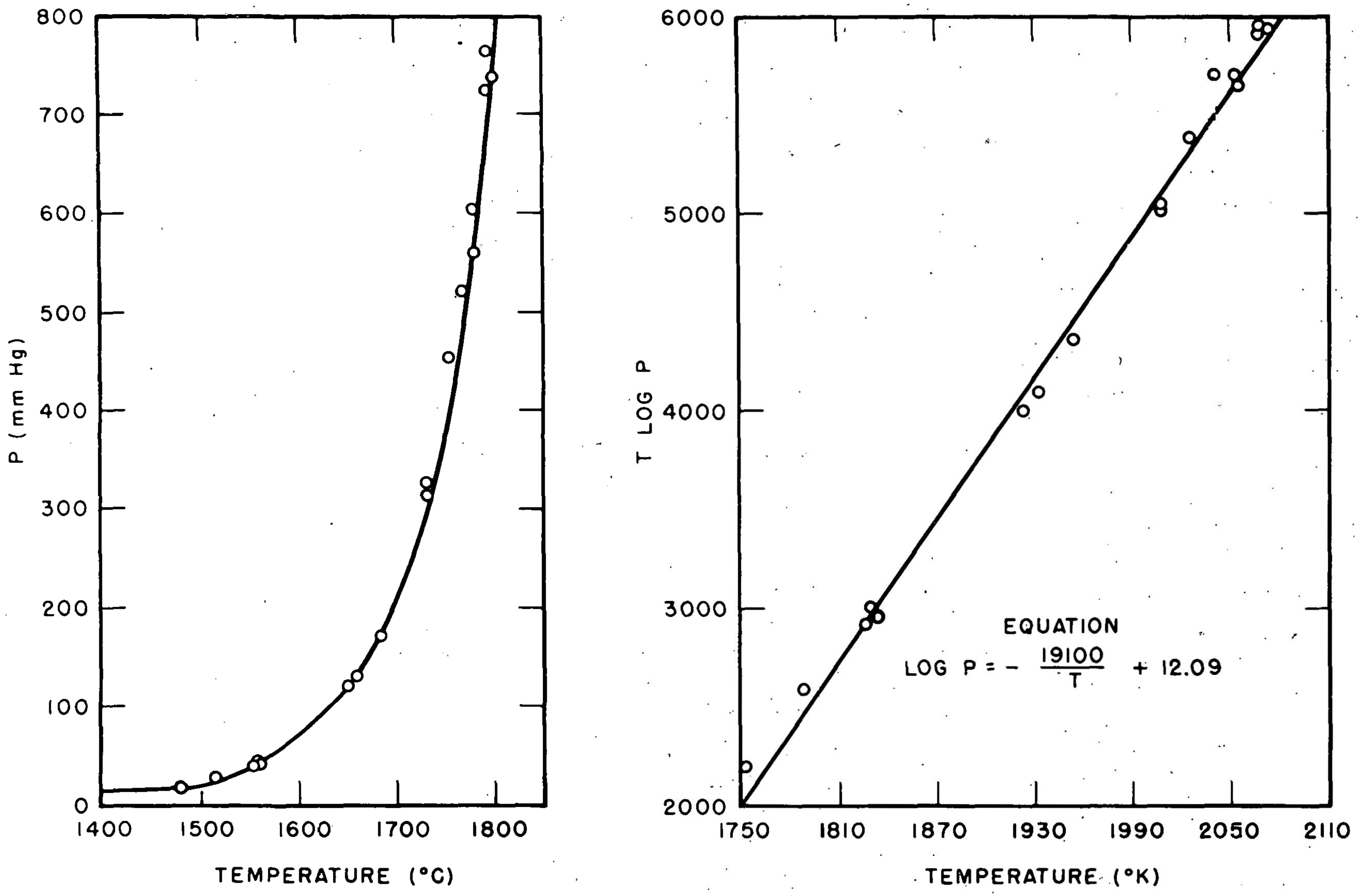

FIG. 2. CARBON MONOXIDE EQUILIBRIUM PRESSURE OVER URANIUM DIOXIDE−CARBON MIXTURE. (AFTER O. HEUSLER, Z. ANORG. ALLGEM. CHEM., <u>154</u>, 364 (1926)).

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represents the results approximately, but not exactly; ΔH apparently changes markedly with temperature. According to Equation 3 the average value of $-\Delta H$ in the region studied is 174.6 kcal/gram atom U. At Chicago (MP Chicago 1) an estimate also was made of ΔC_p for the reaction in Equation 2:

(4) $\Delta C_p = 0.8 - 8.1 \times 10^{-3} T + 4.68 \times 10^{5} T^{-2}$

Combining this equation with the results of Heusler, the following thermodynamic equations were obtained for the reaction of Equation 2:

(5) $-\Delta H = -188{,}540 - 0.8 T + 4.05 \times 10^{-3} T^{2} + 4.68 \times 10^{5} T^{-1}$ cal/gram atom U.

(6) $-\Delta F = -188{,}540 + 1.842 T \log T - 4.05 \times 10^{-3} T^{2} + 2.34 \times 10^{5} T^{-1} + 93.4 T$ cal/gram atom U.

For the entropy change for the reaction one obtains:

$\Delta S^{o}_{298} = 93.8$ e.u.

Using the known entropy values for UO_2, C, and CO, one obtains for the entropy of formation of UC_2:

$S^{o}_{298} (UC_2) = 23.6$ e.u.

At Berkeley (MP Berkeley 2) the free energy and entropy of formation of UC_2 were estimated as follows:

$-\Delta F_{298} = 8.8$ kcal/ gram atom U; $S^{o}_{298} = 15.1$ e.u.

At the UCRL (1) similar estimates were made, using the C_p Equation 1 for UC_2 and the equilbrium data of Heusler. The resulting thermodynamic equations for Reaction 2 were:

(7) $-\Delta F_{o} = -202{,}500 - 16.17 T \log T - 2.77_{5} \times 10^{-3} T^{2} + 3.475 \times 10^{5} T^{-1} + 156.74 T$ kcal/gram atom U

(8) $-\Delta H_{298} = -199.0$ kcal/gram atom U

$-\Delta F_{298} = -166.8$ kcal/gram atom U

$\Delta S^{o}_{298} = 108.0$ e.u.

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For the formation of UC_2 from the elements,

(9) $U + 2C \longrightarrow UC_2$

The same authors derived the following free energy equation:

$$(10) \quad -\Delta F_o = 3925 + 6.3\,T \log T - 3.48 \times 10^{-3}\,T^2 + 7.545 \times 10^4\,T^{-1} + 19.85\,T \text{ cal/g at U}$$

From this equation they calculated the thermodynamic functions of UC_2 at 298°K to be:

$$-\Delta H_{298} = 3.92 \text{ kcal/gram atom U}$$

$$-\Delta F_{298} = 9.83 \text{ kcal/gram atom U}$$

$$S^o_{298} = 19.8 \text{ e.u.}$$

It will be noted that UC_2 is thermodynamically unstable at room temperature (in respect to $UC + C$); UC_2 probably decomposes slowly into UC and C below about 2400°C. Quenching of the dicarbide from > 2400°C produces pure UC_2, while quenching from 1000°C or slow cooling results in UC_2 containing both UC and C, independently of an excess component in the melt.

(c) Preparation of Uranium from Uranium Metal and Carbon. At Ames (MP Ames 13,15) it was noticed that when uranium metal was heated to 1800°-1900°C in graphite crucibles, the crucible walls were attacked and a hard, brittle carbide was formed. The formation of the carbide seems to occur by penetration of uranium into graphite rather than by penetration of graphite into uranium. Therefore the reaction takes place in the presence of excess carbon and leads to the carbon-rich compound, UC_2 (MP Ames 3). Alternatively graphite powder can be dissolved in molten uranium or can be pressed with uranium turnings before melting (MP Ames 7).

Sintering of powdered metal mixed with excess carbon was recommended at Ames for the preparation of uranium-carbon alloys with high carbon content (MP Ames 8). This method (pressing at 50 tons, sintering at 1800-2000°C in vacuum) was used at Ames to prepare alloys with carbon-content between 0.174 per cent and 8.54 per cent by weight (MP Ames 12). In England uranium carbide was prepared by heating uranium turnings with pure carbon to 1200°-1600°C (British 1).

All uranium-carbon alloys obtained in this way are inhomogeneous; they contain dendritic carbide inclusions in a matrix of a saturated carbon solution in uranium. The inclusions can be separated from the matrix by dissolving the latter in 3 N HCl containing some peroxide. The residue is found both by x-ray and chemical analysis (4.70 per cent C) to be practically pure monocarbide, UC. Uranium monocarbide can also be obtained by heating uranium and UC_2 above 1800°C.

(d) Preparation of Uranium Carbide from Uranium Metal and Carbon Monoxide. At Battelle carbon monoxide was admitted to an outgassed uranium slug and the latter heated to 1200°C. Reaction was rapid at first, then slowed down. After forty-five minutes when the liquid metal was still slowly taking up carbon monoxide, it was cooled and examined. A black flaky crust was found on the surface; x-ray examination showed it to consist of UO_2 and UC (Battelle 4).

(e) Preparation of Uranium Carbide from Uranium Oxides. Moissan (1897) mixed U_3O_8 (50 g) and sugar carbon (50 g) in a graphite crucible and heated the mixture eight to ten minutes in an electric furnace (45,000 joule). According to Lebeau (1911)

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[redacted]

the product obtained in this way always contains graphite. Ruff and Heinzelmann (1911) heated UO_2 with sugar carbon in a vacuum furnace slowly to 2450°C. The reaction is less violent than with U_3O_8, and the product almost free from graphite. Heusler (1926a) carried out the reaction of UO_2 with excess carbon in a vacuum furnace at 1800°C, without melting a while pumping away the liberated carbon monoxide.

At Ames mixtures of 1 part Acheson graphite and 5 to 7 parts U_3O_8 were heated in graphite crucibles in a hydrogen atmosphere to produce carbide (MP Ames 16, 17). Later (MP Ames 13, 18) it was determined that with an UO_2:C weight ratio between 5 and 6.4 the product was UC_2 (9.15 per cent carbon compared to 9.16 per cent in UC_2). With a UO_2:C ratio of 7 and 8 the product had a composition close to U_2C_3 (7.21 per cent carbon compared to 7.03 per cent in U_2C_3).

No pure UC could be obtained from UO_2 and carbon. Attempts made at Ames to prepare uranium carbide by reduction of mixtures of UF_4 and carbon with calcium lead to no success. Heating of UO_2 with UC_2 gave the monocarbide, UC, but the product obtained in this way was not very pure.

2.4 Chemical Properties of Uranium Carbides. The data on the chemical behavior of uranium carbide refer to products whose composition is given either as UC_2 or as U_2C_3. It was repeatedly stated above that the existence of a homogeneous phase of the latter composition is highly doubtful, except perhaps at high temperatures.

(a). UC_2 and O_2. Uranium carbide is pyrophoric. Dropping it

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on a hard surface or striking it with a hammer produces a spray of sparks (Tiede and Birnbräuer, 1914a; Moissan, 1897). Crushing in an agate mortar may cause ignition (Moissan). According to Rideal (1913), the carbide ignites in air at 400°C. Moissan (1897) found it to ignite in oxygen at 370°C and burn to U_3O_8 and CO_2. According to Ames observers UC_2 decomposes completely within a week in air in all probability by primary reaction with water vapor (MP Ames 15).

At Ames it was observed that UC_2 did not oxidize at 300°C but oxidized completely within four hours in an air stream at 400°C and 500°C (MP Ames 17). A sample with the composition U_2C_3 was merely covered with a black film after the same treatment. After 5½ hours at 600°C the U_2C_3 sample was found to have disintegrated into granules still containing metallic-appearing material inside.

(b) <u>UC_2 and N_2.</u> According to Moissan (1897) nitrogen reacts with uranium carbide at 1100°C. Heusler (1926a) found the reaction was rapid at 1180°C. At this temperature after 12 hours the carbide takes up nitrogen until saturation is reached, all carbide being converted to nitride.

(c) <u>UC_2 and F_2.</u> Moissan (1897) reported no reaction at room temperature; but slight heating was enough to cause explosive reaction.

(d) <u>UC_2 and Cl_2.</u> Moissan (1897) found that the carbide ignites with chlorine at 350°C giving a volatile chloride. At Ames it was observed that $UO_2 + UC_2$ mixtures react with chlorine at 600°C to form UCl_4, but a large residue is left (MP Ames 19).

At 800°C and 1000°C higher uranium-chlorides are produced.

(e) UC_2 and Br_2. Moissan (1897) found that uranium carbide ignites in bromine vapor at 390°C. At Ames UC_2 was found to react with bromine above 300°C; at 900°C, the reaction gave UBr_4 (MP Ames 20). Later, the same reaction,

$$(11) \quad UC_2 + 2Br_2 \rightarrow UBr_4 + 2C$$

was observed at 800°C at Ames (MP Ames 21). The carbon produced is finely dispersed and difficult to separate. Most construction materials are attacked in this reaction.

(f) UC_2 and I_2. According to Moissan (1897) uranium carbide reacts with iodine below red heat without ignition. At Ames a carbide with the composition U_2C_3 was observed to react with iodine at 600°C giving uranium iodide (MP Ames 20). At UCRL it was observed that when iodine vapor at a partial pressure of 100 mm is passed over UC_2 at 500°C, UI_4 is formed (U.C.R.L. 1). It was suggested that the carbide may be a satisfactory material for the preparation of UI_3 or UI_4.

(g) UC_2 and S or Se. Moissan (1897) found that the uranium carbide burns in sulfur vapor giving uranium sulfide and carbon disulfide. Similar reaction occurs with selenium.

(h) UC_2 and H_2O. According to Moissan (1897) uranium carbide decomposes water slowly at room temperature, rapidly when heated. In the absence of air a green hydroxide is produced; whereas in the presence of air the product is greyish black. The carbon content is converted to gaseous (one-third), and liquid and solid hydrocarbons (two-thirds).

For composition see Lebeau and Damiens (1913, 1914, 1917). The mechanism of formation of hydrocarbons other than acetylene (which could be expected as the main product because the crystal structure of UC_2 is analogous to that of CaC_2) was discussed by Schmidt (1934). He attributed the multiplicity of products to the changes in uranium valency during decomposition.

The carbide reacts with water vapor at dark red heat with ignition to form a black oxide (Moissan, 1897). According to Ames observations uranium carbide decomposes completely in moist air within a week (MP Ames 15).

(i) UC_2 and NH_3. Moissan (1897) observed an incomplete decomposition of UC_2 by ammonia at red heat.

(j) UC_2 and H_2S Moissan (1897) found that UC_2 ignited in hydrogen sulfide at 600°C, and produced a sulfide.

(k) UC_2 and HCl. Moissan (1897) observed ignition of UC_2 in HCl at 600°C, and the formation of a chloride which was decomposed by water.

(l) UC_2 and Acids. Diluted HCl, HNO_3 and H_2SO_4 acids decomposed UC_2 as did water giving yellow solutions. Concentrated acids (except HNO_3) reacted only slowly at room temperature, but very vigorously when heated. At Ames UC_2 and U_2C_3 were treated with 85 per cent H_3PO_4; reaction was slow at room temperature but vigorous when heated, giving a mixture of gaseous, liquid and solid hydrocarbons (MP Ames 12).

(m) UC$_2$ and Alkalis. According to Rideal (1913) the carbide is readily decomposed by alkalis.

(n) UC$_2$ and Salts. Melting of UC$_2$ with KNO_3 or $KClO_4$ causes ignition and produces uranate.

At Ames $Na_2UO_2Cl_4$ was obtained by heating a mixture of NaCl, UC$_2$ and UO$_2$ to 1000°C (MP Ames 19).

(o) UC$_2$ and Bi. At the Metallurgical Laboratory no reaction was observed when uranium carbide was heated at 600°C for three hours in vacuum in contact with bismuth (MP Ames 23,24). The carbide was not wetted by molten bismuth. Later, at Ames samples of carbide wereimmersed in molten bismuth for four hours at 600°C and cooled slowly (MP Ames 17). Cross-sections showed intimate contact between bismuth and either UC$_2$ or U_2C_3 but no evidence of reaction.

3. Uranium-Silicon System

The uranium-silicon system has been investigated at the Massachussetts Institute of Technology by thermal, microscopic and x-ray methods and found to be of considerable complexity. (M.I.T. 1). The phase diagram given in Figure 3 shows five compounds: U_5Si_3, USi, U_2Si_3, USi_2 and USi_3. A sixth, formed by peritectoid reaction between carbon-free γ-uranium and U_5Si_3 at 940°C, has been found at MIT between 4 and 28 atom per cent silicon. (M.I.T. 2). In addition to this peritectoid compound the uranium-silicon system has three eutectic and three peritectic compounds.

The pentauranium trisilicide, U_5Si_3, has been identified by x-ray analysis and its formula made reasonably certain by

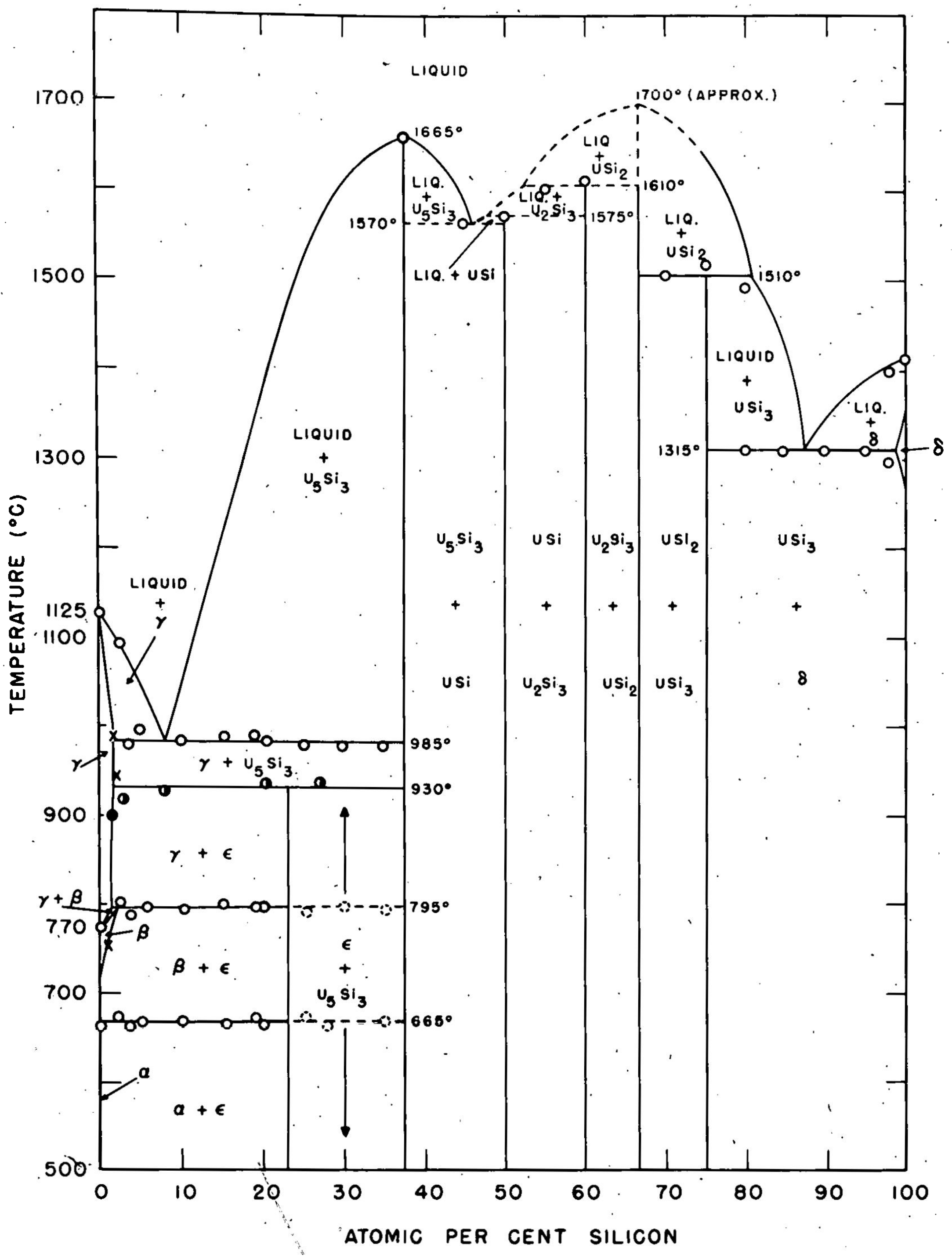

FIG. 3. URANIUM-SILICON PHASE DIAGRAM.

○ - THERMAL ARREST OBTAINED ON HEATING.
x - TWO-PHASE ALLOY BY MICROSCOPIC EXAMINATION.
● - ONE-PHASE ALLOY BY MICROSCOPIC EXAMINATION.
◐ - EPSILON PERITECTOID TEMPERATURE.

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microscopic examination. Its melting point has been derived from an arrest on cooling curves.

The eutectic at 1570°C between U_5Si_3 and USi has been established by microstructure analysis and located at 47 atom per cent silicon. The eutectic between γ-uranium and U_5Si_3 has been found at 9 atom per cent silicon at 985°C. The maximum solubility of silicon in γ-uranium is about 1.75 atom per cent at 980°C; solubility in β-uranium is less than 1 atom per cent. The β - γ transformation temperature of uranium is somewhat increased by silicon from 770°C to about 795°C; the α - β transformation temperature appears unchanged at 660°C.

The existence of the compound U_2Si_3, uranium sesquisilicide, has been indicated by x-ray data but the formula, assigned from microscopic investigation, is not very certain. The peritectic decomposition at 1610°C was derived from a rather indistinct thermal arrest.

The compound USi_2, uranium disilicide, was first described by Defacqz (1908), who prepared it by aluminothermy in the form of a light grey metallic mocroscopically crystalline (cubic) powder. It is insoluble in cold or hot concentrated HCl, HNO_3, H_2SO_4 or aqua regie but soluble in concentrated HF. It is converted to silicate and uranate by molten alkalis or alkali carbonates at red heat, and is slowly attacked by molten $KHSO_4$. It burns in oxygen at 800°C and reacts with chlorine at 500°C. This silicide has been studied at Chicago (MP Chicago 4,5) by x-rays and found to have body-centered tetragonal crystals

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isomorphous with $CeSi_2$ with four molecules per unit cell and the dimensions, $a_1 = 3.97$ Å ± 0.03, $a_2 = 13.71$ Å ± 0.08, giving a calculated density of 9.98 g/cc. The interatomic distances are uranium-silicon = 3.03 Å, and silicon-silicon = 2.29 Å. No melting was found up to 1700°C.

The compound USi_3, uranium trisilicide, was identified by microscopic and x-ray analysis; it decomposes peritectically at about 1515°C. Its crystal structure is simple cubic, a = 4.03 Å. An eutectic is formed between USi_3 and Si (containing very little dissolved uranium) at 1315°C and 86 atom per cent silicon.

The high temperature region between 35 and 75 atom per cent silicon in uranium in Figure 3 is uncertain. The region between U and U_5Si_3 as shown in Figure 3 represents metastable equilibrium since it does not show the above-mentioned peritectoid reaction between 4 and 28 atom per cent silicon at 940°C.

Alloys containing greater than 30 atom per cent silicon are brittle and difficult to polish.

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CHAPTER X

URANIUM COMPOUNDS WITH ELEMENTS OF GROUP V

1. Uranium Nitrides
2. Uranium Phosphides
3. Uranium Arsenides and Antimonides

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CHAPTER X

URANIUM COMPOUNDS WITH ELEMENTS OF GROUP V

1. Uranium Nitrides

The reaction of metallic uranium with free nitrogen was discovered by Moissan (1896), who found that the two elements form a yellow nitride at 1000°C. Fifty years earlier Rammelsberg (1842) observed that a brown uranium-nitrogen compound is formed when UCl_4 is heated to red heat in an atmosphere of ammonia, and Uhrlaub (1859) determined the composition of this product as U_3N_4. The same composition was found by Heusler (1926) for the nitride obtained by Moissan's method of direct reaction between uranium and nitrogen. On the basis of these results U_3N_4 was considered until recently as the main uranium nitride with a rational proportion of uranium to nitrogen.

New methods of preparation and the chemical and physical properties of this compound were described by Kohlshütter (1901), Colani (1903, 1907) Hardtung (1912), Miner (1922), and H. Herzer (1927). According to Herzer the nitride is a dark brown or black powder which decomposes above 1400°C and has a density of 10.09 g/cc.

O. Heusler (1926) asserted that a lower nitride with the composition U_5N_4 is formed when U_3N_4 is decomposed in vacuum at 1650°C. According to the same author decomposition at 1900°C lead to a still lower nitride, U_5N_2. Lorenz and Woolcock (1928) denied the existence of these compounds. They observed that the nitrogen pressure over the nitride (at 1280°C and 1480°C) changes gradually and without discontinuity with changing uranium-nitrogen ratio in the range from $UN_{0.1}$ to $UN_{1.0}$, and suggested that products with less than one nitrogen atom per uranium atom are solid solutions of uranium nitride in metallic uranium.

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All these observations have to be re-evaluated in the light of x-ray studies carried out recently at Ames (MP Ames 1) and Battelle (1). These studies showed that a compound U_3N_4 does not exist. The uranium nitride phase with the lowest nitrogen content is the mononitride UN. Between uranium and UN, there are neither intermediate stoichiometric compounds nor extensive solid solubility. (Lorenz, 1928)The mononitride has no appreciable nitrogen decomposition pressure at the temperatures used in the investigation of Lorenz and Woolcock; therefore, the nitrogen pressures measured by these investigators could not have been equilibrium decomposition pressures of UN_x- systems with $x < 1$.

Between UN and the next highest uranium-nitrogen compound, the sesquinitride U_2N_3, the uranium-nitrogen system is inhomogeneous. It consists of the two separate phases, UN and U_2N_3. From U_2N_3 up to the dinitride UN_2, which is the third "stoichiometric" nitride of uranium, the system is homogeneous; in other words, the U_2N_3 crystal structure is transformed gradually, without discontinuity, with increasing nitrogen content into the UN_2 structure.

When uranium nitride is prepared by reaction of N_2 or NH_3 with uranium under atmospheric pressure the product is a single phase system with a composition between $UN_{1.5}$ and $UN_{1.8}$ depending upon temperature (formation of UN_2 does not occur except under high pressure). The uranium nitrides described by earlier investigators must have been such half-way products

1.1 Crystal Structure and Phase Relationships.

(a) The Range Uranium to UN; the Mononitride. The Solubility of nitrogen in metallic uranium has not been studied in detail, but was reported by Ames investigators as "slight" (1). Because of the stability of UN, the system uranium + dissolved nitrogen is metastable except at very high temperatures. The measurement of solubility is made difficult by the fact

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that the rate of formation of the nitride is already high at 600°-700°C with massive uranium and at 300°-350°C with fine uranium powder obtained by the decomposition of the hydride. Also according to Ames observations the solubility of uranium in UN cannot be large, because the lattice spacing of the UN crystals does not change appreciably with the ratio of uranium to nitrogen in preparations made by fusing uranium and UN at high temperature. The small observed variations (e.g., $a_0 \cong 4.899$A instead of $a_0 \cong 880$A) probably are due to partial replacement of nitrogen by oxygen or carbon rather than to uranium content of UN lattice. The solubility of UN in uranium probably is small also at least in the solid state. The presence of nitride and also oxide has been observed to increase the viscosity of uranium melts. (Mallinckrodt 1).

The mononitride UN is a light grey powder (MP Ames 2) having face-centered cubic structure with a lattice constant of 4.880 ± 0.001A (MP Ames 1, MP Ames 3, Battelle 1). Four uranium atoms are contained in a unit cell. The structure is of the rock salt rather than of the zinc sulfied type; this is indicated by the fact that on powder diagrams the (420) reflection is markedly more intense than the (331) reflection. (MP-Ames 3) The density of UN calculated from x-ray data is 14.31 g/cc.

If uranium nitride is prepared by the action of nitrogen on uranium at temperatures up to 1300°C, the reaction does not stop or slow down at the composition UN, but proceeds to the composition of the $(U_2N_3 + UN_2)$ phase which is in equilibrium with the nitrogen atmosphere under the conditions of the experiment. Pure mononitride can be prepared by decomposing the higher nitrides at temperatures $>$ 1200°C, and if the heating is carried out slowly, nitrogen is evolved smoothly. Traces of oxygen must be avoided since otherwise UO and UO_2 can be formed. The UN remaining after the decomposition of U_2N_3 is a very stable compound. It does not markedly decompose at 1700°C.

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(MP Ames 4) According to Battelle(1) the decomposition pressure ~~UN~~ UN at 1200°C is $< 10^{-6}$ mm. UN has been observed to sinter at 2300°C and to melt in an atomic hydrogen arc at about 2630°±50°C. (MP-Ames 5).

(b) <u>The Range UN to U_2N_3, the Sesquinitride</u>. Systems containing between 1 and $1\frac{1}{2}$ nitrogen atoms per uranium atom are two-phase systems according to x-ray evidence. The second phase, U_2N_3, is also cubic but is body-centered and has a lattice constant of 10.678A. (MP Ames 6; Battelle 1, 2) ((6.21) If only strong maxima in the diffraction pattern are considered, the U_2N_3 lattice appears face-centered with a lattice constant of ~5.3A. Consideration of the weaker maxima leads to a body-centered lattice with a lattice constant twice as large. This structure ($D5_3$) is known for Mn_2O_3 and some rare earth oxides and is closely related to the fluorite structure. It allows a smooth transition from the U_2N_3 lattice to the fluorite-type lattice of UN_2. (MP Ames 1)

The positions of the uranium atoms in the elementary cell of U_2N_3 which contains 16 molecules per unit cell, are as follows:

Eight UI atoms in positions:

$$(000),\ (\tfrac{1}{2},\ \tfrac{1}{2},\ \tfrac{1}{2}) + (\tfrac{1}{4},\ \tfrac{1}{4},\ \tfrac{1}{4});\ (\tfrac{1}{4},\ 3/4,\ 3/4);\ \text{etc.}$$

Twenty-four UII atoms in positions:

$$\pm\ (x,\ 0,\ \tfrac{1}{4});\ (x,\ \tfrac{1}{2},\ \tfrac{1}{4}),\ \text{etc. with } x = 0.288\ \text{(24 UII atoms).}$$

The positions of the 48 nitrogen atoms are

$$\pm\ (xyz);\ (\tfrac{1}{2}-x,\ y,\ \bar{z})$$
$$(\bar{x},\ \bar{y},\ \tfrac{1}{2}-z);\ (\bar{x},\ \tfrac{1}{2}-y,\ z)\ \text{etc.}$$

The nitrogen atom parameters x, y, z cannot be obtained from the pattern because of the comparative weakness of scattering by nitrogen atoms. In Mn_2O_3 the oxygen parameters are $x = 0.385$, $y = 0.145$, and $z = 0.380$.

The density of U_2N_3 calculated from x-ray data is 11.24 g/cc. The spacing in U_2N_3 and UN remain constant with changing uranium:nitrogen ratio showing lack of mutual solubility of these two phases.

(c) <u>The Range U_2N_3 to UN_2, the Dinitride.</u> The gradual conversion of U_2N_3 to UN_2 without a discontinuous phase transition is possible because the Mn_2O_3 structure of U_2N_3 can be interpreted as a distorted fluorite structure in which UN_2 crystallizes. In the latter compound the metal atoms are in the positions 000, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, and $\frac{1}{2}\frac{1}{2}0$, and the nitrogen atoms in the positions $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, 3/4, 314, $\frac{1}{4}$, etc. 3/4 3/4, 3/4, $\frac{1}{4}$, $\frac{1}{4}$, 3/4, etc. In reference to the eight times as large body-centered unit the 000 metal atoms are in positions 000, $0\frac{1}{2}0$, etc., $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$, etc. In the transition to U_2N_3 structure these uranium atoms remain fixed; the other 24 metal atoms are displaced slightly from the four-fold axes, thus destroying the small face-centered cell. The gradual change in cell dimensions is illustrated by Table 1.

TABLE 1

LATTICE CONSTANTS OF U_2N_3 AND UN_2

Composition	Lattice Constant		Density (g/cc)
	Body centered Cell (A)	Face-Centered pseudo-cell (A)	
$UN_{1.435}$	10.678±0.006	5.339±0.003	--
$UN_{1.52}$	10.658±0.005	5.329±0.003	11.24
$UN_{1.75}$	10.580±0.005	5.290±0.003	--
UN_2	--	5.31±0.01	11.73

As the nitrogen content increases the weak diffraction maxima indicating the distortion of the face-centered unit disappear. The distribution of the nitrogen atoms in the intermediate products between U_2N_3 and UN_2 remains unknown, since the whole pattern analyzed is due to the spacial arrangement

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of the much heavier uranium atoms.

It will be noted that U_2N_3 ($\rho = 11.24$) is less dense than UN_2 ($\rho = 11.73$) and particularly UN ($\rho = 14.31$). Consequently, U_2N_3 dismutates under high pressures into $UN + UN_2$.

Although UN is stable in vacuum up to 1800°C and higher, U_2N_3 loses nitrogen in vacuum at temperatures above 700°-800°C, and UN_2 cannot be prepared at all except under high nitrogen pressures. The equilibrium pressure of nitrogen over the higher nitrides is a smooth function of temperature and of the nitrogen content x in the solid ($1.5 < x < 2$). According to Ames data the pressure increases vary rapidly with x, and has at $x = 1.712$ a value of 4 mm at 450°C and about 400 mm at 800°C. The slope of the decomposition pressure curve indicates a heat of nitrogenation of 16.0 kcal/mole. The equilibrium is established rapidly and reversibly (MP-Ames 7). More extensive measurements were carried out at Battelle, (1, 3) where the equilibrium was found to be established within an hour at 658°C-1048°C but required up to 2 days at 492°C. Here, too, the rapid change of pressure with composition was noted. For example, at 1048°C the pressure was 50 mm for $UN_{1.52}$ and 825 mm for $UN_{1.56}$; at 492°C it was 50 mm for $UN_{1.65}$ and 825 mm for $UN_{1.68}$. Fig. 1 shows equilibrium curves, $\log p = f(1/T)$, for three nitrogen contents.

The above-mentioned Ames value (400 mm at 800°C at $UN_{1.70}$) does not agree well with Fig. 1; this difference was ascribed to errors of nitrogen determination. According to Ames the decomposition of UN_x, rapid at $x > 1.5$, slows down perceptibly after the composition U_2N_3 has been reached.

1.2 The Preparation of Uranium Nitrides. Two methods of preparation of the nitride were mentioned above:

(1) Direct reaction of uranium with nitrogen at or below 1000°C (Meissan 1896).

(2) Reaction of UCl_4 with ammonia at red heat (Rammelsberg, 1842)

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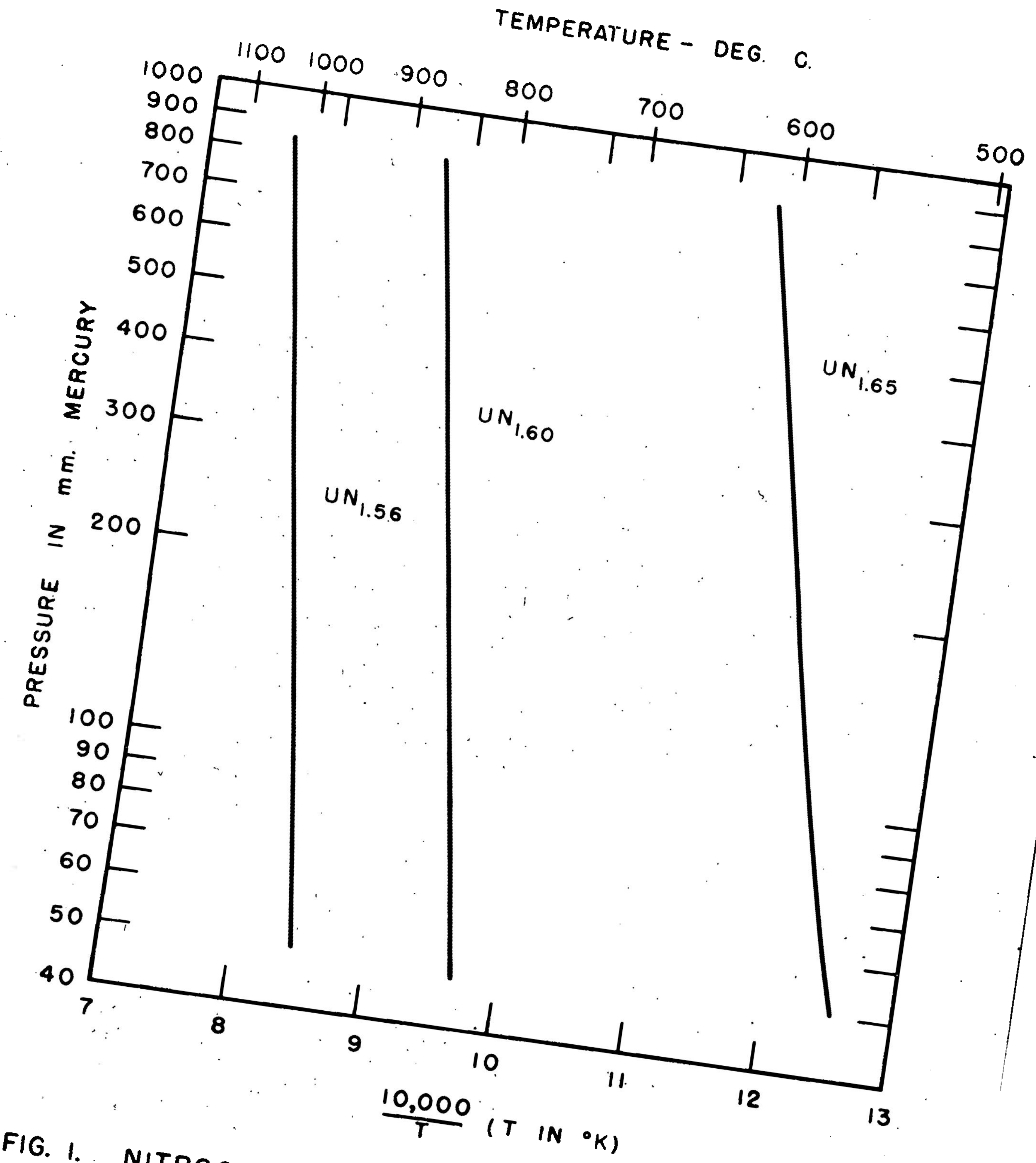

FIG. 1. NITROGEN PRESSURE IN EQUILIBRIUM WITH THREE DIFFERENT COMPOSITIONS OF URANIUM NITRIDE AT VARIOUS TEMPERATURES.

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The following methods are described in subsequent literature:

(3) Reaction of U_3O_8 with magnesium in a nitrogen stream (Kohlschütter, 1901).

(4) Reaction of $2NaCl.UCl_4$ with ammonia at red heat (Colani, 1907).

(5) Reaction of uranium powder with ammonia at or below 1000°C (Hardtung, 1912).

(6) Reaction of uranium metal or its alloys with Mg_3N in vacuum (Miner, 1922).

(7) Reaction of UC_2 with nitrogen at 1180°C (Heusler, 1926).

(8) Reaction of UH_3 with ammonia at 200°C (MP Ames 1).

(9) Reaction of UH_3 with nitrogen at 350°C (MP Ames 1).

According to the last authors only the reactions of uranium, UH_3, or UCl_4 with nitrogen or ammonia are likely to produce nitride not contaminated by other solids which are difficult to remove. To avoid oxide contamination oxygen must be carefully excluded from all reactants.

According to the phase relationships discussed in Sec. 1.1 (see Fig. 1), the preparation of nitride under atmospheric pressure of nitrogen must lead to mixed crystals of $U_2N_3 + UN_2$, with an average composition between $UN_{1.5}$ and $UN_{1.8}$ depending on temperature of the reaction. The same result is obtained when ammonia is used instead of nitrogen. The fact that earlier analyses gave lower nitrogen values (U_3N_4, i.e. $UN_{1.33}$) can be attributed to the presence of oxides, or to errors in nitrogen determination by the method of Dumas.

The <u>reaction of uranium metal with nitrogen</u> has recently been studied in some detail. At Ames massive uranium and uranium powder prepared by decomposition of UH_3 were used. As an example of preparations of the first type, uranium turnings cleaned in 8<u>N</u> HNO_3 were converted to $UN_{1.712}$

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(a steel-gray powder, ρ = 11.3 g/cc) by heating at 450°C at one atmosphere of nitrogen (MP Ames 7). As an example of the use of metal powder, a compound UN$_{1.75}$ was obtained by heating uranium powder for 3 days to 520°C in a stream of pure nitrogen. (MP Ames 8) It was observed at Ames (MP Ames 9) that a nitride layer is formed around the bright metal core when thick uranium turnings are partly oxidized by ignition in air. At Chicago (MP Chicago 1) it was found that the rate of nitrogenation of uranium increases with temperature particularly rapid around 800°C, probably in consequence of the $\beta \rightarrow \gamma$ transformation of the metal. According to Battelle observations (Battelle 4) the reaction of massive uranium with nitrogen begins to be rapid above 450°C.

At the National Bureau of Standards, the uranium-nitrogen reaction was found (Nat. Bur. Standards 1) to be slight at 400°C, to become marked at 500°-600°C, and to proceed rapidly above 800°C. At or below 750°C, the specimen becomes covered by a black adherent scale with a metallic luster. Small bits of this scale pop off upon cooling. When all of this scale was removed by grinding, the nitrogen content of the bright core was found to be 0.012 per cent compared to 0.003 per cent before the reaction. At or above 800°C a dark grey or black, non-metallic powder is formed instead of the scale; analysis gave the composition UN$_{1.6}$ for both scale and powder. It was observed at the National Bureau of Standards that a nitride scale will protect uranium from oxidation at 300°C, but that an oxide scale affords no protection from nitrogen.

The reaction of uranium metal with ammonia, also studied at Ames (MP Ames 1), begins at about 400°C. With turnings a temperature in excess of 700°C is required for rapid conversion. The product, UN$_{1.747}$, was obtained by heating uranium in an ammonia atmosphere at 800°C for 24 hours.

The reaction of uranium hydride with nitrogen occurs even at 200°C. (MP Ames 10) It, too, gives a product of approximate composition $UN_{1.75}$. The reaction requires 10 to 12 hours at 250°C and 1 to 2 hours at 350°C.

The reaction of uranium hydride with ammonia (MP Ames 1) occurs slowly even at 100°C (1.5 mg nitrogen taken up by 5g uranium in 1 hour), and becomes rapid above 200°C (316 mg nitrogen taken up by 5 g uranium in 1 hour). This is perhaps the easiest way to obtain the nitride. The product is an exceedingly fine powder (bulk density 3.4 g/cc, true density 11.3 g/cc). Contrary to what was thought for a while, (MP Ames 11) low-temperature reactions of UH_3 with nitrogen and ammonia do not stop or slow down at the composition UN, but proceed to U_2N_3 and beyond. It is doubtful whether the mononitride is formed at all as an intermediate in low temperature nitrogenation. (MP Ames 13) As mentioned before, the way to prepare the mononitride is to decompose the higher nitrides in vacuum above 1300°C. For example, at Ames (MP Ames 2) UN was obtained by heating $UN_{1.67}$ to 1650°C in vacuum in a graphite crucible.

The dinitride UN_2 has not yet been obtained in the pure state. A mixture of $UN + UN_2$ is obtained (as shown by x-ray evidence) when uranium is combined with nitrogen under 1800 psi at 600°C (MP Ames 14). Although the average composition of this product ($UN_{1.75}$) is the same as that of the nitride obtained under atmospheric pressure, its x-ray diagram proves the absence of U_2N_3. As mentioned in Section 1. 1(c), the dismutation of U_2N_3 into UN UN_2 under high pressure is plausible because of the greater density of UN_2 and particularly of UN, as compared to U_2N_3.

1.3 The Physical and Chemical Properties of Uranium Nitrides. The nitrides have been described as dark brown, steel gray, dark grey, and black powders. Their x-ray structure was discussed in Section 1.1. The densities calculated from x-ray data are 14.31 g/cc for UN, 11.24 g/cc for U_2N_3, and 11.73 g/cc for UN_2. The directly determined density of analyzed $UN_{1.8}$ (as obtained from UH_3 and ammonia) was 11.3 g/cc. This product had a bulk density of 3.4 g/cc and an electrical resistivity, without compression, of about 200 ohm-cm. (MP Ames 12)

The heats of formation are not well known. Neumann, Kroger and Haebler (1932) found that 68.5 kcal are liberated per gram atom absorbed nitrogen in the formation of a nitride containing 3.5 per cent nitrogen. This is a much lower nitrogen content than even that of UN (5.55% N). It is thus quite uncertain what phase was actually formed, but we may assume tentatively that it was U_2N_3 and that the low nitrogen content was due to the presence of uranium or unreacted metal in the product. With this assumption, one calculates 256 kcal/mole as the heat of the reaction

$$2U + 3/2N_2 \longrightarrow U_2N_3.$$

The slopes of the three straight lines lead to the following values for the integral heats of decomposition of UN_x into UN and $(x-1)/2\ N_2$:

$UN_{1.65}$ $\Delta H = 15.69$ kcal/ gram atom U
$UN_{1.60}$ $\Delta H = 18.79$ kcal/gram atom U
$UN_{1.56}$ $\Delta H = 19.55$ kcal/gram atom U

The change in ΔH is not linear with x, and the extrapolation to $x = 1.5$ is uncertain. The Battelle report (3.49) gives $\Delta H = 21.9$ as the result of this extrapolation, leading to the thermochemical equation

$$2UN + \tfrac{1}{2}N_2 = U_2N_3 + 43.8 \text{ kcal.}$$

If the trend of ΔH vs x shown by the above figures is correct, the nitrogenation of U_2N_3 is an endothermal process. Therefore UN_2 can be expected to be more stable at the higher temperatures.

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From the above-estimated heat values (256 kcal for U_2N_3 and 44 kcal for the difference $U_2N_3 - 2UN$) one obtains 106 kcal/mole for the heat of formation of UN, a value which may explain the stability of this product. We thus have the following preliminary estimates:

$$U + \tfrac{1}{2}N_2 \longrightarrow UN + 106\ \text{kcal}$$

$$2UN + \tfrac{1}{2}N_2 \longrightarrow U_2N_3 + 44\ \text{kcal}$$

$$U_2N_3 + \tfrac{1}{2}N_2 \longrightarrow UN_2 + x\ \text{kcal (endothermal)}$$

Estimates of ΔF and ΔS of nitride formation (MP Chicago 2; Mp Berkley 1) were made on the assumption that U_3N_4 is the nitride formed and are thus obsolete. There seems to be little justification in attempting to correct these estimates for UN and U_2N_3 because of the absence of any reliable thermochemical data.

1.4 <u>The Chemical Reactions of Uranium Nitrides.</u> The thermal decomposition of the higher uranium nitrides, U_2N_3 and UN_2, was discussed in Section 1.3. These nitrides also can be reducte by hydrogen, a reaction which was studied at Ames. (MP Ames 8) The formation of ammonia from $UN_{1.75}$ and hydrogen could be noticed even at 100°C. At 500°C 10 per cent of the nitrogen content was lost after 4 hours. At 800°C $UN_{1.75}$ was reduced to UN_{152} after one hour heating in hydrogen; continuation of the treatment for another 18 hours lead to a product with the composition $UN_{1.43}$. At this last temperature, however, thermal decomposition may have played an important part in addition to the reduction by hydrogen.

The nitride is easily oxidized. It is not normally pyrophoric, although the finely powdered product obtained from UH_3 has occasionally been described as such (MP Ames 2). It will ignite in air at 150° to 200°C and burn to form UO_2 (or U_3O_8) and nitrogen (but no nitrogen oxides) (MP Ames 12). The formation of ammonia in this process (from reaction of

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nitride with moisture?) also was noticed; (MP Chicago 3). Kohlschütter (1901) had long ago described the decomposition of the nitride by heating with water vapor. The same author has observed the oxidation of the nitride by various oxidizing agents such as CuO, $PbCrO_4$, F_2O_3, UO_2 (see also MP Ames 15), $KClO_3$, and KNO_3.

The nitride is slowly oxidized by concentrated nitric acid. It is not attacked by hot or cold hydrocholoric or sulfuric acid, or by sodium hydroxide solution. (Kohlschütter, 1901; MP Ames 1) However, it reacts with molten alkali, liberating ammonia (Kohlschutter, 1901), and with gaseous hydrogen choloride (MP Ames 16). The reaction with HCl gas at 400°-500°C gave NH_4Cl and converted $UN_{1.75}$ into a hard hygroscopic sinter of green and brown color which contained, by x-ray evidence, UCl_4, U_3O_8, UO_2, and an unknown phase perhaps the double salt $(NH_4)_2\ UCl_6$. Analysis showed the presence of 2% NH_4. A similay treatment of UN gave a product with $<$ 1% NH_4. The nitride reacts readily with hot 85 per cent H_3PO_4 to form uranous phosphate and with fuming $HClO_4$ to form uranyl percholorate (MP Ames 1).

The chenical properties of the mononitride have not been studied in detail but descrived as "similar to those of the higher nitrides." The mononitride was found to react with carbon (finely divided graphite) at 2250°C and with uranium dioxide at about 2300°C, (MP Ames 15) but the reaction products are unknown.

2. Uranium Phosphides

Rammelsberg (1872) supposed uranium monophosphide was produced by decomposition of $UO_2(H_2PO_2)\ H_2O$. At Ames (MP Ames 17) a uranium monophosphide phase was identified by x-ray analysis. It has a NaCl structure with $a_o =$ 5.689 A.

A triuranium tetraphosphide U_3P_4 was described by Colani (1907). This product was obtained in small yield, when PH_3 reacted with $2NaCl \cdot UCl_4$. This could be achieved by passing a stream of dry hydrogen over a melt containing aluminum phosphide and excess $2NaCl \cdot UCl_4$. The product is leached with water and hydrochloric acid and washed with water, alcohol, and ether. The residue is a fine black crystalline powder containing some aluminum. It slowly oxidizes in air to yellow uranyl phosphate. It burns in air and is attacked slowly by water particularly if air is present. Dilute HCl has no effect, but boiling concentrated HNO_3, aqua regia, or molten NaOH decompose the phosphide instantaneously.

Lilliendahl and Driggs (1929) suggested, as a commercial method of preparation of uranium phosphide, heating of 3 parts of finely powdered metal with 1 part phosphorous powder to 600°-1000°C. Unreacted phosphorous is leached out by alcohol and ether or distilled away.

3. Uranium Arsenides and Antimonides

Colani (1907a) prepared uranium arsenide and antimonide by methods similar to that he used for the preparation of phosphide. To obtain the arsenide he passed dry hydrogen charged with arsenic vapor over $2NaCl \cdot UCl_4$. A small quantity of square or hexagonal, black, lustrous tablets was obtained. Melting of Na_3As with excess arsenic and $2NaCl \cdot UCl_4$ in a stream of dry hydrogen gave a steel gray, mocrocrystalline arsenide. Ignition of a mixture of arsenic powder, arsenous oxide, uranium trioxide and aluminum also could be used, although no success was obtained with the aluminothermic method in the case of uranium phosphide preparation. The uranium arsenide, whose composition Colani determined as U_3As_4, is hardly attacked at all by dry air, but somewhat more by moist air. It is easily soluble in nitric acid, and burns in the flame of a Busnen Burner.

The uranium-arsenic system was studied by x-ray analysis at Ames.

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(MP Ames 17). Two compounds were identified: a monoarsenide UAs (cubic, NaCl structure, a_0 = 5.767A, $\cong$ 10.77 g/cc, and U_2As (prepared at Ames by Figard) (MP Ames 18) The latter gives a new x-ray pattern which is different from those of uranium, UO_2, or UAS.

The uranium antimonide was obtained by Colani (1907) by ignition of dry 2NaCl. UCl_4 with an equivalent mixture of antimony and aluminum in a stream of hydrogen. Analysis of the (aluminum-free) product gave 58 per cent antimony and 42 per cent uranium corresponding to an approximate formula U_3Sb_8. Heating this product in a stream of hydrogen caused a gradual loss of antimony, but the composition U_3Sb_4, which Colani expected by analogy with his formulae for phosphide and arsenide, was not reached. The antimonide was attacked by concentrated hydrochloric acid and dissolved by concentrated nitric acid with the formation of an antimony oxide.

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