80
3-15-66

MASTER RFP-688

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

CRITICAL TEMPERATURE OF
PLUTONIUM-CHLORINATED SOLVENT REACTIONS

by

S. H. Pitts, Jr.

THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80402
U. S. ATOMIC ENERGY COMMISSION
CONTRACT AT(29-1)-1106

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in USA. Price \$1. Available from the Clearinghouse for Federal
Scientific and Technical Information, National Bureau of Standards,
U. S. Department of Commerce, Springfield, Virginia

18 February 1966

RFP-688

UC-4 CHEMISTRY

TID-4500 (46th Ed.)

RELEASED FOR ANNOUNCEMENT

IN NUCLEAR SCIENCE ABSTRACTS

CRITICAL TEMPERATURE OF
PLUTONIUM-CHLORINATED SOLVENT REACTIONS

by

S. H. Pitts, Jr.

THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80402
U. S. ATOMIC ENERGY COMMISSION
CONTRACT AT(29-1)-1106

INTRODUCTION

in plutonium production machining and handling operations, a potential hazard exists in the compatibility of plutonium and certain chlorinated solvents. Burning plutonium, at 750-800°C, readily and violently reacts with carbon tetrachloride but not with some other chlorinated solvents. A previous report⁽¹⁾ dealt with the comparison of the relative intensities of the reactions of burning plutonium with various solvents. Irregularities in the initiation of the reaction emphasized the need for more quantitative information. This prompted the following study of the temperature at which the plutonium-chlorinated solvent reaction occurs (critical temperature), the effect of surface area on this temperature, and the effect of cutting oil addition to CCl₄.

SUMMARY AND CONCLUSIONS

Critical temperatures were determined for some plutonium-chlorinated solvent reactions. The critical temperature, as used here, is defined as the lowest temperature at which plutonium reacts with the solvent to yield an exothermic reaction accompanied by light emission. These temperatures were determined by heating plutonium samples to a known temperature in argon and dropping them into various solvents while visually watching for a reaction.

A correlation was established between the critical temperature and surface area for unalloyed and 1 w/o gallium alloyed plutonium in several chlorinated solvents. The critical temperature decreases as the specific surface area is increased.

A previous investigation⁽¹⁾ indicated that burning plutonium does not react with 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, and 1,1,2-trichloro-1,2,2-trifluoroethane. This implied that a burning coupon would be extinguished and the reaction was not self sustaining. For these critical temperature measurements a reaction was defined as any exothermic reaction accompanied by a flash of light. The light emission needed only to be bright and long enough to be visible with the naked eye. The reaction may or may not go to completion. By this definition, the above

(1) Pitts, Jr., S. H., Preliminary Studies on Reactions of Burning Plutonium in Various Solvents, The Dow Chemical Company, Rocky Flats Division, July 19, 1965, RFP-566.

four solvents do react with plutonium. However, the reaction is milder and seldom goes to completion as it does in CCl_4 . CCl_4 consistently had the lowest critical temperatures. Chlorothene®* and Freon®** TB-1 solvents had essentially the same critical temperature which was lower than for perchloroethylene and 1,1,2-trichloroethylene. Of the solvents studied, trichloroethylene was the least reactive and therefore the safest under these test conditions.

In general, unalloyed plutonium exhibited a lower critical temperature than gallium stabilized delta phase plutonium.

The critical temperature of plutonium in CCl_4 was increased by the addition of Texaco Regal®*** cutting oil. The addition of plutonium oxide, plutonium chloride, water, or chlorine to CCl_4 did not lower the critical temperature of plutonium. Both acetone and methanol added to CCl_4 suppressed the reaction and increased the critical temperature.

EXPERIMENTAL

Apparatus

Figure 1 shows the experimental apparatus. It consists of a Vycor®**** glass tube containing a beaker of solvent in the bottom and a heated side-arm near the top. Opposite the side-arm was a second side-arm through which a loosely-fitted spoon of Vycor® with an internal thermocouple was inserted. An inert atmosphere was maintained by an argon purge entering near the bottom and leaving through a small hole in the gravity-held blow-out plug on the top.

Procedure

A typical run was made by loading 0.5-1.0 gram of plutonium onto the spoon, inserting it into the furnace tube, and heating it while purging with argon. An inert gas atmosphere is necessary to prevent plutonium ignition. Upon reaching the desired temperature, the spoon is quickly withdrawn from the furnace and rotated to drop the plutonium into 5-7 ml of room-temperature solvent. A reaction was easily recognized by the emission of a bright orange light and vigorous boiling of the solution.

* - Trademark The Dow Chemical Company
** - Trademark E. I. du Pont de Nemours & Co., Inc.
*** - Trademark Texaco, Inc.
**** - Trademark Corning Glass Works

Critical temperatures were determined by running a series of tests above and below the estimated actual value. Temperatures above the critical temperature were decreased and those below the critical temperature were increased until the actual value was within a 10°C range. Because of the broad unit division of the recorder chart paper and the uncertainty of reaction near the critical temperature (operator judgment), the critical temperatures were estimated to be accurate within $\pm 10^{\circ}\text{C}$.

Reagents

Commercial grade solvents were used in most of these tests. There was no detectable difference in the critical temperature determinations when using either commercial or reagent grade CCl_4 . Inhibited and non-inhibited 1,1,1-trichloroethane also gave similar temperatures.

The plutonium samples were made from cast and rolled metal. The alpha phase plutonium was approximately 99.3 percent pure and the delta phase metal 98.9 percent pure. Table I gives a typical analysis for the type of alpha and delta phase plutonium used. Filings were manually prepared using a double cut, coarse bastard file for the coarse filings and a single cut, mill bastard file for the fine filings.

RESULTS AND DISCUSSION

The data presented in Tables II and III are the results of several hundred individual experiments. The number of runs to establish any one critical

Figure 1. REACTION CHAMBER FOR CRITICAL TEMPERATURE DETERMINATIONS

TABLE I

TYPICAL ANALYSIS OF PLUTONIUM USED
IN CRITICAL TEMPERATURE DETERMINATIONS

	Alpha Phase	Delta Phase
Pu (assay)	99.30%	98.90%
Pu ²⁴⁰ (mass spec.)	5.935	5.901
Ga	--	1.002
Impurities, ppm		
Al	37	54
Cr	28	73
Fe	184	491
Ga	28	--
Ni	74	121
Si	42	54
U	75	57
C	150	182
Am	90	247

TABLE II

EFFECT OF SURFACE AREA ON THE CRITICAL TEMPERATURE
FOR THE Pu-CHLORINATED SOLVENT REACTION

Pu Sample	Specific Surface Area, m ² /g	Critical Temperature, °C ± 10°				
		Trichloro- ethylene	Perchloro- ethylene	Chloroethene (1)	Freon TB-1. (2)	Carbon Tetrachloride
delta phase coupon	0.00011	755	745	750	745	645
delta phase coarse filings	0.6	655	605	565	565	425
delta phase fine filings	1.2	615	505	405	405	370
alpha phase coupon	0.00011	745	700	715	715	625
alpha phase coarse filings	0.6	660	465	465	455	395
alpha phase fine filings	1.2	525	385	355	365	305

(1) Inhibited 1,1,1-trichloroethane, The Dow Chemical Company

(2) 1,1,2-trichloro-1,2,2-trifluoroethane + ethylene glycol monobutyl ether, E. I Du Pont Co.

NOTE: Approximate Pu sample wt. = 0.6-0.8 g, approximate solvent volume = 5-7 ml.

TABLE III

EFFECT OF TEXACO REGAL CUTTING OIL ON THE CRITICAL
TEMPERATURE OF THE Pu-CCl₄ REACTION

Pu Sample	Specific Surface Area, m ² /g	CCl ₄	Volume Ratio CCl ₄ /Oil					Texaco Regal 2A Cutting Oil	50 Trichloroethylene 50 Oil
			90 10	70 30	50 50	40 60	20 80		
delta phase coupon	0.00011	645	645	650	650	665	765	No reaction up to 865°C	--
delta phase coarse filings	0.6	425	425	485	485	535	565		655
delta phase fine filings	1.2	370	370	370	380	400	470		--
alpha phase coupon	0.00011	625	625	625	655	655	755		--
alpha phase coarse filings	0.6	395	410	--	435	--	520		655
alpha phase fine filings	1.2	305	310	--	340	--	390		--

NOTE: Approximate Pu sample wt. = 0.6-0.8 g; approximate solvent volume = 5-7 ml.

temperature was unimportant since only the two temperatures immediately above and below it were necessary. The critical temperatures given here are the best values when all of the sources of error were considered.

The major source of experimental error was attributed to particle size. Due to the method of preparation and absence of screening techniques, the particle size varied considerably within batches. A batch containing an unusual amount of finer particles would yield a lower temperature.

Other sources of variation were due to the amount of splatter of molten samples, temperature variation of the solvents, and temperature variations of the particles when dropped through the argon purge. Some uncertainty existed in the surface area of the particles at temperatures near the melting point of plutonium due to partial agglomeration.

Table II summarizes the relationship of surface area and critical temperature of the plutonium-chlorinated solvent reactions. It also gives a relative comparison of the ease of reaction initiation between each of these various solvents and plutonium.

Several apparent conclusions are:

1. The critical temperature decreases as the specific surface area of the plutonium increases.
2. The critical temperature for unalloyed plutonium is lower than for alloyed plutonium of similar surface area. This difference is more pronounced with smaller particles.
3. CCl_4 consistently gave the lowest critical temperature for any particular surface area.
4. Chlorothene® and Freon® TB-1 have essentially the same critical temperatures for plutonium.
5. Trichloroethylene had the highest critical temperature with plutonium. The more pronounced differences were in the smaller particles.

Figures 2 and 3 graphically illustrate the difference in critical temperature of alpha and delta phase plutonium in various solvents with surface

Figure 2. EFFECT OF SURFACE AREA ON THE CRITICAL TEMPERATURE OF DELTA-PHASE PLUTONIUM IN VARIOUS SOLVENTS

Figure 3. EFFECT OF SURFACE AREA ON THE CRITICAL TEMPERATURE OF ALPHA-PHASE PLUTONIUM IN VARIOUS SOLVENTS

area. It is postulated that if the critical temperatures were known for samples with still smaller and larger specific surface areas, an S type curve would result. A minimum temperature should exist where the surface area is theoretically infinite. A maximum temperature is apparently approached for large, bulk samples.

The large experimental difference in activity of CCl_4 and 1,1,1-trichloroethane with heated plutonium is not understood. This difference is not indicated by thermodynamic calculations of the heat of reactions and the free energy. In an oxygen free system at 500°K , thermodynamic calculations give the following:

Reaction	ΔH	ΔF
$4\text{Pu} + 4\text{CH}_3\text{CCl}_3 \rightarrow 4\text{PuCl}_3 + 8\text{C} + 2\text{H}_2$	-762.0 Kcal	-752.4 Kcal
$4\text{Pu} + 3\text{CCl}_4 \rightarrow 4\text{PuCl}_3 + 6\text{C}$	-831.1 Kcal	-771.5 Kcal

This suggests that the plutonium-1,1,1-trichloroethane reaction sequence has a higher activation energy. The reaction ceases when the temperature falls below the critical temperature.

The effect of adding Texaco Regal[®] cutting oil to CCl_4 is shown in Table II and Figure 4. The oil itself was non-reactive up to 865°C . As the concentration of the oil in CCl_4 was increased from 10 to 80 percent, the critical temperature increased erratically. In no case was a lower temperature obtained through the use of oil. This was further verified by the two spot checks with a 1:1 trichloroethylene/oil mixture.

The contaminants suspected in a plutonium-chlorinated solvent system are PuCl_3 , PuO_2 , H_2O , and Cl_2 . There was

Figure 4. EFFECT OF OIL ON THE CRITICAL TEMPERATURE OF PLUTONIUM WITH VARIOUS SURFACE AREAS IN CCl_4

no indication that any of these compounds would lower the critical temperature of plutonium when mixed with CCl_4 . This was determined by making runs slightly below the critical temperature for plutonium in pure CCl_4 . The solutions contained an excess, but unmeasured amount of the PuCl_3 , PuO_2 , H_2O (estimated 0.5-2.0 w/o), or were nearly saturated with chlorine. No reaction was obtained in any of these runs. Since the exact critical temperature was not determined with these solutions, the temperature increasing effects, if any, were not established.

A suppressive effect on the reaction was observed by the addition of acetone or methanol to CCl_4 . Acetone was more effective than methanol. A one-percent solution of acetone in CCl_4 gave a shorter, less intense reaction with a plutonium coupon at 670°C than does CCl_4 alone. A similar effect was obtained with a 4-percent solution of methanol in CCl_4 . The normal intensity of the plutonium- CCl_4 reaction could be restored with these solutions by increasing the metal temperature to greater than 700°C . Ten-percent solutions of either acetone or methanol in CCl_4 did not give a sustained reaction at 700°C .

The suppressive effect of acetone or methanol on the plutonium- CCl_4 reaction is directly proportional to the amount used. It is postulated that a competing plutonium surface reaction (such as oxidation) occurs with the additive, and the resulting product acts as a barrier to the CCl_4 . It was demonstrated that PuO_2 does not visibly react with either CCl_4 or 1,1,1-trichloroethane up to 850°C as does plutonium under these test conditions.

RECOMMENDATIONS

The lowering of the critical temperature of the plutonium- CCl_4 reaction by smaller plutonium particles should be considered in operations involving plutonium- CCl_4 contact. A normally safe operation is made unsafe through generation of small, active particles and heat. The heat generated from a small plutonium- CCl_4 reaction could conceivably activate a larger reaction. Consequently, the heating of unalloyed plutonium with a specific surface area of $1.2 \text{ m}^2/\text{g}$ to 305°C and alloyed plutonium to 370°C in CCl_4 should be avoided. This work suggests that plutonium with a larger specific surface area would react at even a lower temperature.

The use of acetone or methanol to prevent a self-sustaining plutonium- CCl_4 reaction is possible, but more than catalytic amounts would be required. Between a 4- and 10-percent concentration is necessary to increase the critical temperature 30-40°C.

From the standpoint of critical temperature, trichloroethylene is the safest solvent of those evaluated for plutonium use. It should be considered as a replacement for CCl_4 providing that other criteria such as solvent properties, recovery, and economics are satisfied. Perchloroethylene, Chlorothene[®] and Freon[®] TB-1 are also less reactive than CCl_4 .

Cutting oils that become contaminated with appreciable quantities of chlorinated solvents should be treated as the solvents themselves insofar as safety is concerned.

THE DOW CHEMICAL COMPANY

ROCKY FLATS DIVISION

P. O. BOX 938

GOLDEN, COLORADO 80402