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# THERMODYNAMIC CALCULATIONS RELATING TO CHLORIDE VOLATILITY PROCESSING OF NUCLEAR FUELS. II. THE CAPACITY OF CHLORINE FOR TRANSPORTING PLUTONIUM TETRACHLORIDE VAPOR DURING REACTION OF $U_3O_8$-$PuO_2$ WITH CARBON TETRACHLORIDE

T. A. Gens

**OAK RIDGE NATIONAL LABORATORY**
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ORNL-3693

Contract No. W-7405-eng-26
Chemical Development Section B
CHEMICAL TECHNOLOGY DIVISION

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OCTOBER 1964

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# THERMODYNAMIC CALCULATIONS RELATING TO CHLORIDE VOLATILITY PROCESSING OF NUCLEAR FUELS. II. THE CAPACITY OF CHLORINE FOR TRANSPORTING PLUTONIUM TETRACHLORIDE VAPOR DURING REACTION OF $U_3O_8$-$PuO_2$ WITH CARBON TETRACHLORIDE

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## ABSTRACT

The capacity of chlorine gas for transporting plutonium tetrachloride vapor in the presence of $UCl_5$ and $UCl_6$ formed in the reaction of $U_3O_8$-$PuO_2$ with carbon tetrachloride vapor at 1 atm was estimated from free-energy data as a function of temperature between 500 and 1050°K and the amounts of chlorine and inert gas introduced. It was determined that the presence of $UCl_5$ and $UCl_6$ has little effect on the capacity of chlorine for transporting $PuCl_4$. This capacity can be estimated closely from the capacity in the $PuCl_3$-$Cl_2$ system in the absence of uranium chlorides, where it increases from about $3 \times 10^{-6}$ to $10^{-2}$ mole of $PuCl_4$ per mole of chlorine as the temperature increases from 700 to 1000°K. The capacity is sufficient to transport the plutonium produced by neutron irradiation of natural or slightly enriched uranium oxide fuels, where the maximum plutonium content expected after long-term irradiation exposure is less than 1 wt %. Thus, simultaneous volatilization and transportation of plutonium and uranium should be feasible. Equations were developed for calculating the capacity of chlorine for transporting $PuCl_4$ for all compositions of $PuO_2$ in uranium oxide, but calculations were made only for fuels containing up to 1.7 wt % $PuO_2$. Based on these calculations, a practical set of operating conditions for volatilization of uranium and plutonium from uranium oxide fuels containing up to 1 wt % $PuO_2$ would be reaction at 550°C with $Cl_2$ saturated with $CCl_4$ vapor at room temperature (85 vol % $Cl_2$--15 vol % $CCl_4$).


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## 1. INTRODUCTION

One of the methods being considered for recovering uranium and plutonium from spent uranium oxide reactor fuel includes converting the uranium and plutonium oxides to volatile chlorides with mixtures of carbon tetrachloride and chlorine vapors.[1,2] Carbon tetrachloride is the preferred chlorinating agent, although other reagents such as $COCl_2$ may be used.[3] Phosgene is undesirable because of its toxicity, while pure chlorine does not react significantly with uranium oxides at tem-

peratures below 950°K. By volatilizing the uranium and plutonium chlorides, a separation from fission products having less-volatile chlorides may be possible. Calculations were made to estimate the amount of chlorine gas necessary to transport the $PuCl_4$ formed from $UO_2$ fuels under conditions where the $PuCl_4$ is at equilibrium with $UCl_5$, $UCl_6$, $PuCl_3$, and $Cl_2$.

The calculations indicate, for example, that the $PuCl_4$ formed from uranium oxide fuels containing 0.8 wt % $PuO_2$ would be volatilized along with the $UCl_5$ and $UCl_6$ at 550°C, when 20 moles of $Cl_2$ per mole of $UO_2$ are used. The results of such calculations indicate only that the proposed process is thermodynamically possible. It is not known with certainty that the rates of the reactions involved are rapid enough so that it is possible to approach the equilibrium conditions closely under practical operation conditions. Also, saturation of the gas stream with $PuCl_4$ would be necessary to achieve the predicted results.

Thermodynamic calculations were made to estimate the minimum amounts of chlorine required during chlorination of $U_3O_8$ with $CCl_4$ to form volatile uranium penta- and hexachlorides, and very little nonvolatile uranium tetrachloride. Calculations pertaining to the transport of $PuCl_4$ were then made by using values for the amount of chlorine present that were high enough so that the formation of $UCl_4$ did not have to be considered.

Plutonium trichloride is produced by chlorinating plutonium oxide with phosgene in a process being developed at the Hanford Atomic Products Operations.[3] The volatilization of plutonium during the reaction of uranium and plutonium oxides with $CCl_4$ has been observed by several workers,[5-8] and the equilibrium constants for the reaction $PuCl_{3(s)} + 1/2\ Cl_{2(g)} \longrightarrow PuCl_{4(g)}$ have been determined by a transpiration method.[9]

The equations developed in this report could be used to calculate the capacity of chlorine for transporting $PuCl_4$ for all compositions of $PuO_2$ in uranium oxide, but calculations were made only for fuels not enriched with $PuO_2$. Extension of the calculations to fuels enriched with plutonium would be desirable. However, the calculations are based on the assumption, which is probably valid when the weight percentage of $PuO_2$ is low, that

the $PuO_2$ chlorinates as rapidly as it becomes exposed at the reaction surface. The maximum $PuO_2$ content for which this assumption is valid remains to be determined experimentally.

## 2. CHEMICAL REACTIONS

In the proposed process,[1,2] the sintered uranium dioxide is first oxidized to form $U_3O_8$ powder,

$$3UO_2 + O_2 \longrightarrow U_3O_8 \ . \tag{1}$$

Oxidation increases both the valence state of the uranium and the reaction surface area, so that the subsequent chlorination can take place at a satisfactory rate. Uranium dioxide containing as much as 40% $PuO_2$ has been observed to oxidize rapidly at temperatures as low as 450°C, although not as rapidly as pure $UO_2$.[10]

The $U_3O_8$ is converted to chlorides:

$$U_3O_8 + 4\ CCl_4 \longrightarrow 2UCl_{5(gas)} + UCl_{6(gas)} + CO_2 \ , \tag{2}$$

and, for the purpose of the calculations, it was assumed that reaction (2) goes to completion and that the plutonium oxide is converted to the trichloride as rapidly as it is exposed:

$$PuO_2 + CCl_4 \longrightarrow PuCl_{3(solid)} + 1/2Cl_2 + CO_2 \ . \tag{3}$$

The oxides do not react appreciably with chlorine below about 950°K.[4] In the absence of chlorine, nonvolatile[11] $PuCl_3$ is formed rather than volatile $PuCl_4$.[6,12] Therefore, chlorine is introduced to the system to drive the reaction:

$$PuCl_{3(solid)} + 1/2Cl_2 \longrightarrow PuCl_{4(gas)} \ . \tag{4}$$

Although some workers apparently have produced $PuCl_4$ by using only $CCl_4$ with no added $Cl_2$,[7,8] their experiments were performed under conditions where some cracking of $CCl_4$ occurs, and chlorine formed from this cracking probably caused the formation of $PuCl_4$ by reaction (4). In addition,

chlorine is liberated by the decomposition of $UCl_6$ (reverse of reactions (5) below. This decomposition to liberate chlorine is discussed in detail later in the report.) The amount of $PuCl_4$ that can be transported by a given amount of saturated chlorine, i.e., the capacity, can be calculated easily using the equilibrium constants for reaction (4) obtained from the literature.[9] This was done, and the results are shown later (Sec 3.1, Fig. 5). The purpose of the calculations given in this report was to determine if this capacity is altered significantly by the presence of gaseous uranium chlorides. The effect of the reaction,

$$UCl_{5(gas)} + 1/2Cl_2 \longrightarrow UCl_{6(gas)} , \qquad (5)$$

on the amount of chlorine available for the chlorination of solid $PuCl_3$ must be considered. Reaction (5) can, under certain conditions, cause the amount of chlorine present at equilibrium to be either greater or smaller than the amount introduced, depending on whether the uranium chloride products from reactions (2) and (5) are preponderantly $UCl_5$ or $UCl_6$, respectively. In addition, the effect of the reaction,

$$UCl_{5(gas)} \longrightarrow UCl_{4(solid)} + 1/2Cl_2 , \qquad (6)$$

must be considered. In practice, reaction (6) cannot be allowed to occur to any great extent because the volatilization of uranium chlorides is desirable. Therefore, calculations were made to determine the minimum amount of chlorine needed to ensure that less than 1% of the uranium, at equilibrium, would be in the form of the nonvolatile tetrachloride (Sec 6). Calculations of the capacity of chlorine for transporting $PuCl_4$ were made by using conditions where enough chlorine was present so that reaction (6) could be disregarded. This not only simplifies the calculations but also eliminates from consideration conditions where the capacity for transporting $PuCl_4$ is very small.

Consideration of reactions (2) and (5) indicates (without calculation) that the presence of uranium chlorides cannot greatly affect reaction (4) unless less than about 10 moles of chlorine are introduced per mole of $U_3O_8$ chlorinated, since the maximum amount of chlorine that can be used

up if all the $UCl_5$ formed by reaction (2) is converted to $UCl_6$ is only 1 mole per mole of $U_3O_8$.

Although calculations were made considering reaction temperatures of up to 1050°K (Sec 5), the decomposition of $CCl_4$ at elevated temperatures (which has been observed at temperatures as low as 900°K in this laboratory) would significantly alter the equilibrium composition of the gases at high temperatures. The calculations at temperatures over 900°K, therefore, are of value mainly as an indication of trends, rather than as a method of determining equilibrium amounts of the various products.

## 2.1 Interfering Reactions

A question of major importance in attempting to apply the results of these calculations is whether or not the stoichiometry of reaction (2) is approached closely during chlorination of $U_3O_8$ with $CCl_4$. In experimental studies made in this system,[13] a number of interfering reactions, which might change the stoichiometry shown by reaction (2), were considered. It was concluded that, at the probable operating temperature of 500 to 600°C, the only interfering reactions of importance are those leading to formation of uranyl chloride, $UO_2Cl_2$, and the only important results of these reactions is that they decrease the efficiency of $CCl_4$ in reaction (2), that is, the amount of $CCl_4$ introduced which is used up according to reaction (2). Therefore, it was necessary (see Sec 3.2) to consider the efficiency of $CCl_4$ during chlorination of $U_3O_8$.

A second important question is whether or not very small quantities of plutonium chloride will behave according to reaction (4) or become involved in other types of reactions, such as sorption on vessel walls. That the kinetics of reaction (4) are quite rapid has already been shown.[9] However, during reaction of $CCl_4$ with $U_3O_8$ containing small amounts of $PuO_2$,[2] the chlorine introduced with the $CCl_4$ caused the volatilization of much less plutonium than would be predicted from the results of calculations in this report. The lower the $PuO_2$ content of the $U_3O_8$-$PuO_2$ mixture, the greater was the discrepancy. A possible explanation of this discrepancy is that when only small amounts of $PuO_2$ are present, the equilibrium,

$$PuCl_{4(gas)} \longrightarrow PuCl_{4(adsorbed)}, \qquad (7)$$

becomes relatively more important than reaction (4). In expression (7), $PuCl_{4(adsorbed)}$ denotes the plutonium chloride vapor that adsorbs on the vessel walls. Since the condensed form is unstable, adsorbed $PuCl_4$ presumably decomposes to $PuCl_3$. Chemisorption on vessel walls, as well as physical adsorption, apparently can impede the transfer of small amounts of volatile transuranium chlorides.[6] Therefore, for small amounts of plutonium chloride, equilibrium constants for expression (7) as well as for (4), would be needed. The calculations in this report apply only to systems where the amount of $PuCl_4$ formed is much greater than the amounts adsorbed on the vessel wall, or to systems in which the adsorbed and gaseous $PuCl_4$ are already equilibrated. Only experiments on a larger scale can determine if the amount of plutonium chloride vapor adsorbed would be significant on a process basis.

### 2.2 Assumptions Required in Calculations

The simplifying assumptions needed to set up the problem are discussed in various places in this report. Work reported in the chemical literature has been cited, and discussion is included to support the assumptions. These assumptions are listed here for easy reference.

1. The products of the reaction of $CCl_4$ and $U_3O_8$ are only $UCl_5$, $UCl_6$, and $CO_2$, as shown in reaction (2), and no $UCl_4$ forms. This assumption is supported by the calculations and discussion in Sec 6. The assumed products of reaction (2), then, are starting materials for the problem considered in this report. Thus, a small increase in the rate of reaction (2), which has been observed when chlorine is introduced, in no way affects the calculations.

2. Neither $CCl_4$ nor $CO_2$ react with $UCl_6$, $UCl_5$, $PuCl_4$, $PuCl_3$, or $Cl_2$.

3. Chlorine does not react to any appreciable extent with $U_3O_8$ or $PuO_2$.

4. Carbon tetrachloride does not thermally decompose.

5. Plutonium oxide chlorinates as rapidly as it becomes exposed at the reaction surface. This assumption is necessary because the maximum

wt % $PuO_2$ in $UO_2$ which can be converted to volatile $PuCl_4$, using a given quantity of $Cl_2$, is back-calculated from the capacity of this amount of chlorine for transporting plutonium (Sec 3.2). Obviously, such a calculation is valid only if the $PuO_2$ reacts with $CCl_4$ [reaction (3)] as rapidly as it becomes exposed at the surface where reaction (2) is occurring. The particle size of the $PuO_2$ produced by neutron irradiation of $UO_2$ is probably very small, and therefore reaction (2) should occur rapidly, as assumed. However, this assumption still needs to be tested experimentally.

6. Equilibrium is achieved rapidly in reaction (4); this is to say, very little $PuCl_3$ forms at the reaction surface. A simplification in the calculations is made possible by this assumption (see last paragraph in Sec 5).

## 3. THE CAPACITY OF CHLORINE FOR TRANSPORTING PLUTONIUM TETRACHLORIDE VAPOR

The equilibrium constants for reactions (4) and (5) (Sec 2) were calculated as a function of temperature from the standard free energy changes (see Sec 4). The amount of each gaseous product at equilibrium was calculated from the equilibrium constants as a function of temperature and amounts of $Cl_2$ and inert gas by the usual thermodynamic methods (Sec 5). The equilibrium amount of $PuCl_4$ formed was taken to be the equilibrium capacity of $Cl_2$ for transporting $PuCl_4$.

Both reactions (4) and (5) are affected by inert gas, since the number of molecules of gaseous reagents differs from that of the products. Therefore, in the calculations below it was necessary to introduce a term to account for the number of moles of inert gas present at equilibrium. Unreacted $CCl_4$ and $CO_2$ product, as well as any inert diluent gas such as nitrogen, were grouped together under the classification of "inert gas". Since some unreacted $CCl_4$ and $CO_4$ product will always be present at equilibrium, the introduction of this term cannot be avoided.

All calculations were made for 1 atm pressure. The calculations could be easily modified so that the effect of increased or decreased pressure could be determined. It was assumed that the equilibrium constants

remained constant at each temperature under all conditions investigated, that is, that the gases involved behaved ideally and that their partial pressures were equal to their fugacities.

In addition to presenting the results of the equilibrium calculations, the results of additional calculations of interest for practical process application are presented in Sec 3.2. A complete table of the data used in preparing the figures in this section is included in the Appendix.

### 3.1 Equilibrium Calculations

In the first series of calculations, it was assumed that 1 mole of $Cl_2$ and zero or 10 moles of inert gas were introduced for each mole of $U_3O_8$ chlorinated according to reaction (2) (Fig. 1). As the temperature increased from 500 to 1050°K, with no inert gas (IG) present, the amount of $UCl_6$ formed at equilibrium decreased from 3 moles to 0.01 mole, while $UCl_5$ increased correspondingly. This behavior reflects the increase in stability of $UCl_5$ as temperature increases. Due to the liberation of chlorine when $UCl_6$ converts to $UCl_5$ [reaction (5), Sec 2], the equilibrium amount of chlorine increased from 0.02 mole to 1.494 moles over this temperature range. Therefore, at 1050°K, there was 0.49 mole more chlorine, which originally came from the $CCl_4$, at equilibrium than was originally introduced. When 10 moles of inert gas were introduced, the amount of $UCl_6$ converted to $UCl_5$ increased. Therefore, the amount of $Cl_2$ at equilibrium was further increased by the presence of inert gas to 0.04 mole at 500°K and to 1.496 moles at 1050°K. As the equilibrium amounts of $Cl_2$ increased with increasing temperature or increasing amounts of inert gas, the amounts of $PuCl_4$ formed also increased. With no inert gas present, $2 \times 10^{-4}$ and 0.05 mole of $PuCl_4$ could be formed at 800 and 1050°K, respectively. When 10 moles of inert gas were present, these respective values increased to $3.5 \times 10^{-4}$ and 0.09 mole of $PuCl_4$, or 75 and 80%.

In practice, more than 1 mole of $Cl_2$ would ordinarily be introduced per mole of $U_3O_8$ chlorinated. When 10 moles of $Cl_2$ were introduced (Fig. 2), more $UCl_6$, 0.02 mole vs 0.01 mole above, remained when the

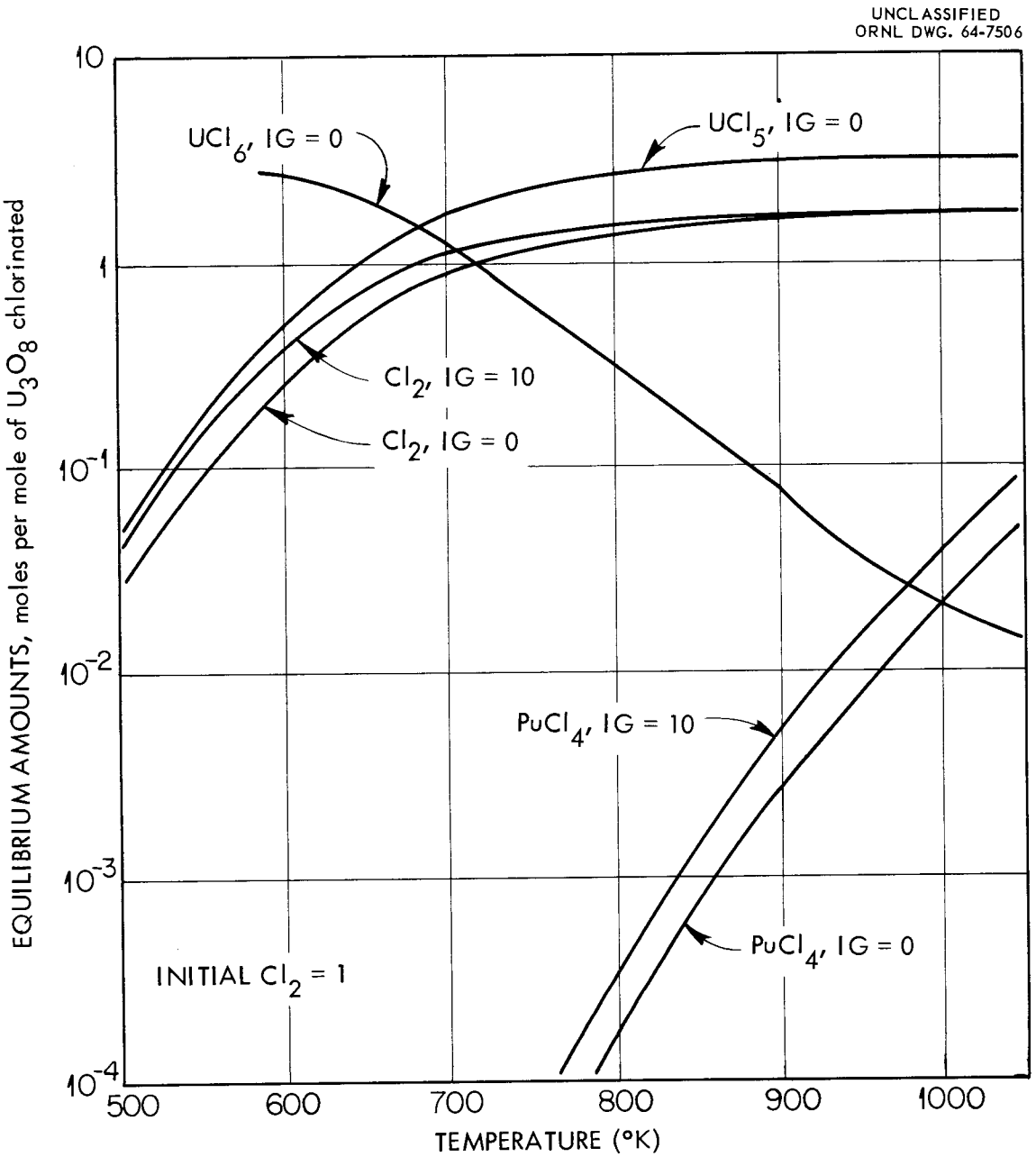


Fig. 1. Equilibrium Amounts of Gaseous Products from the Reaction of $CCl_4$ with $U_3O_8$-$PuO_2$, Assuming 1 mole of $Cl_2$ Introduced Per mole of $U_3O_8$ Chlorinated. Inert gas (IG) is moles of unreacted $CCl_4$ plus $CO_2$ and diluent gases.

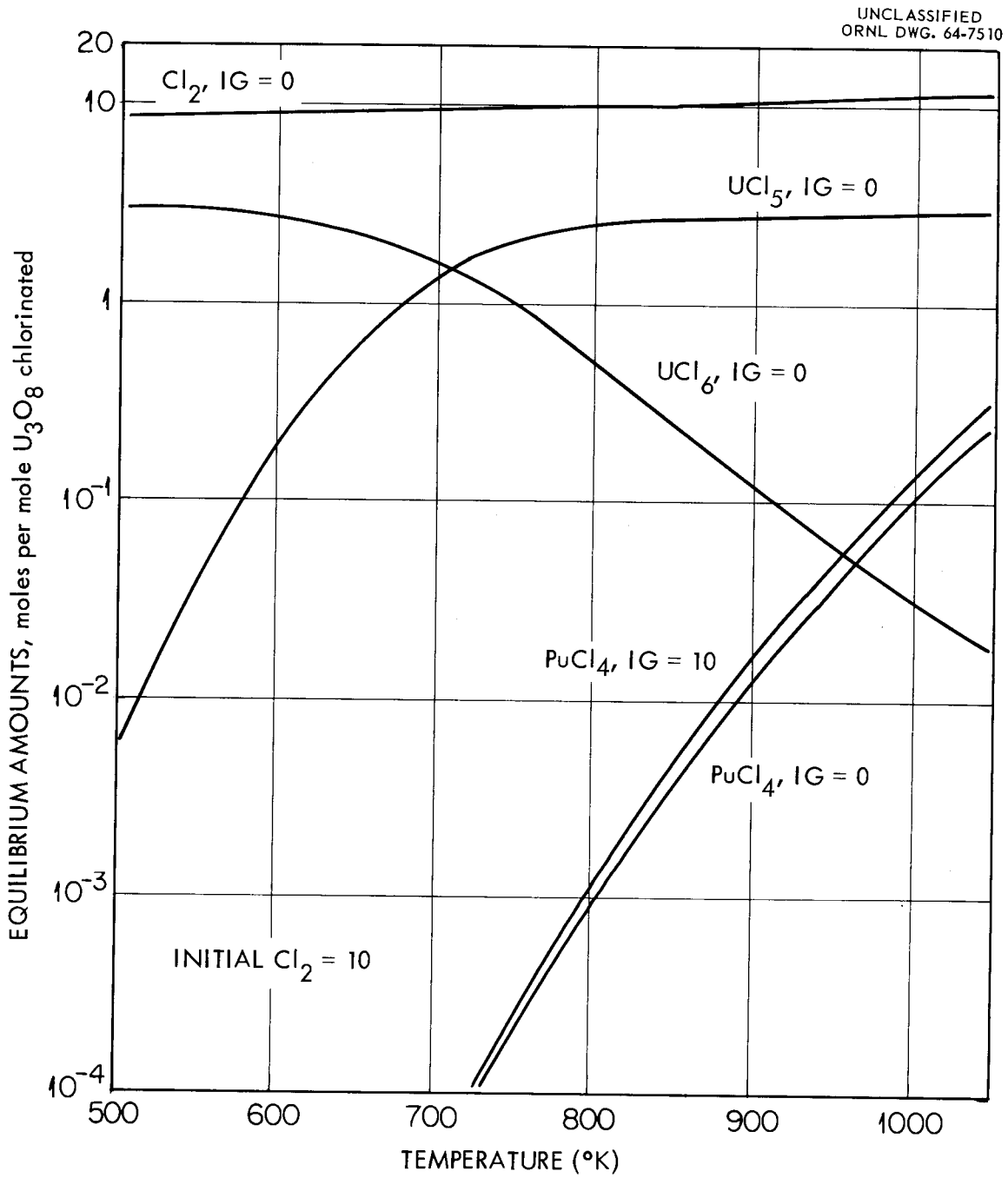


Fig. 2. Equilibrium Amounts of Gaseous Products from the Reaction of $CCl_4$ with $U_3O_8$-$PuO_2$, Assuming 10 moles of $Cl_2$ Introduced per mole of $U_3O_8$ Chlorinated.

temperature had been increased to 1050°K, and, correspondingly, a slightly smaller amount of $UCl_5$, 2.98 vs 2.99 moles above, was present at equilibrium. Because slightly less $UCl_6$ converted to $UCl_5$ when 10 moles rather than 1 mole of $Cl_2$ were introduced initially, the equilibrium amounts of chlorine are slightly less than 10 times greater than in the former case. Therefore the amount of $PuCl_4$ that can be formed must also increase by less than tenfold. For example, while the introduction of 1 mole of $Cl_2$ yielded an equilibrium capacity of 0.052 mole of $PuCl_4$ at 1050°K, the introduction of 10 moles of $Cl_2$ yielded a capacity of 0.24 mole, only 4.6 times greater. Since the ratio of the equilibrium amounts of chlorine in these two cases was greater than the ratio of capacities for $PuCl_4$ (7.0 vs 4.6), it is also apparent that the capacity does not increase linearly with the amount of $Cl_2$ at equilibrium. In this system, as in the one considered above where only 1 mole of $Cl_2$ was used, the introduction of 10 moles of inert gas slightly increases the equilibrium amounts of $Cl_2$. The capacity for transporting $PuCl_4$ increased by about a third.

From the results described above, it is apparent that calculations to determine the changes in capacity for transporting $PuCl_4$ as various amounts of $Cl_2$ are introduced would be useful. The results of such calculations, using up to 100 moles of $Cl_2$ per mole of $U_3O_8$ chlorinated at 500, 750, and 1000°K, are shown in Fig. 3. In these calculations, 10 moles of inert gas per mole of $U_3O_8$ were also introduced, because in practical operation it is probable that about this amount of inert gas will be present. By increasing the amount of $Cl_2$ introduced initially from 1 to 100 moles per mole of $U_3O_8$ chlorinated, the capacity for transporting $PuCl_4$ is actually increased over 100 times at 500°K but only about 25 times at 750 and 1000°K. The lowest temperature considered, 500°K, yields an impractically small capacity for transporting $PuCl_4$. This capacity increases about a million times upon increasing the temperature to 750°K, and a further increase of about 550 times occurs upon increasing the temperature from 750 to 1000°K. Therefore, in the useful temperature range, that is, above 750°K, increasing the amount of $Cl_2$ can be said, very approximately, to increase the capacity for transporting

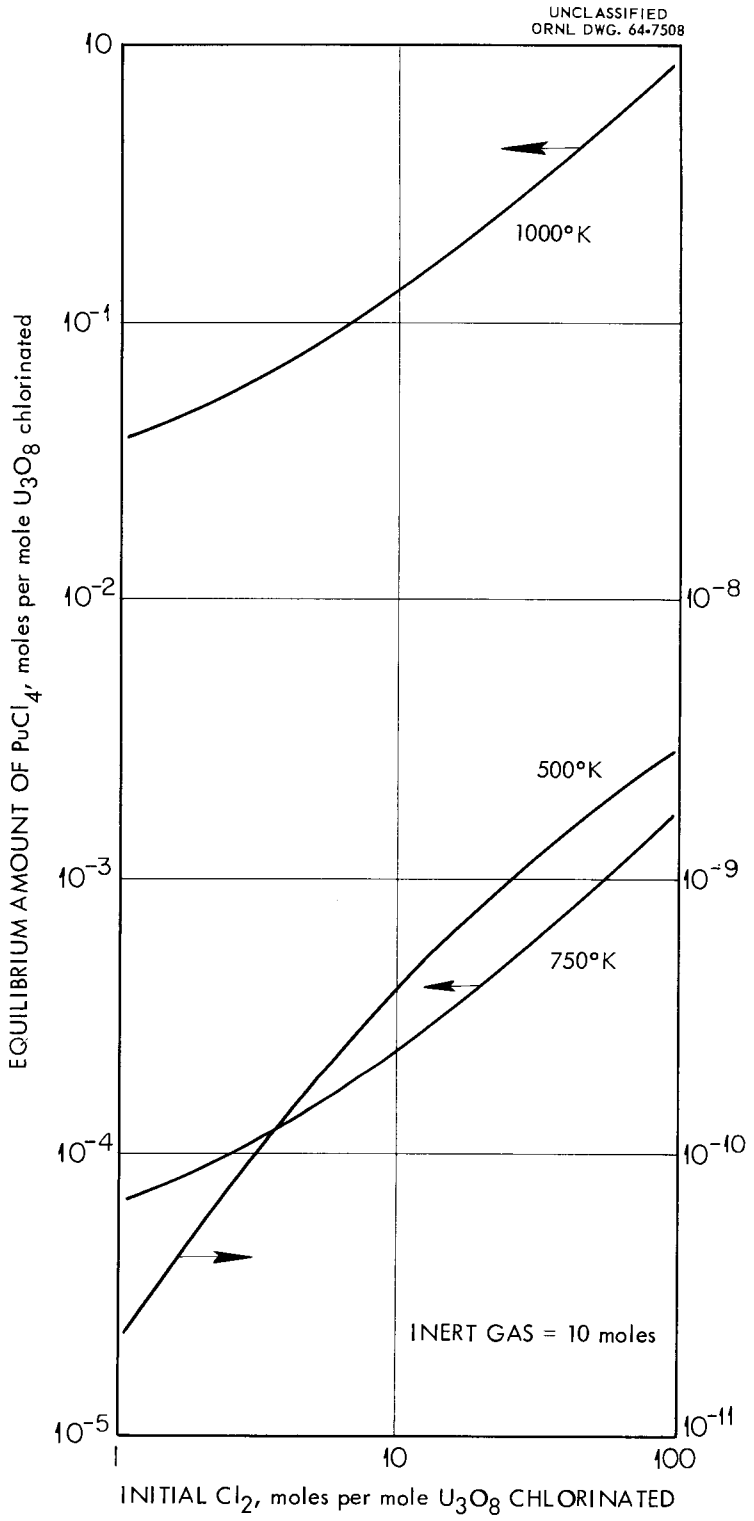


Fig. 3. Increasing the Amount of Chlorine Introduced During Chlorination of $U_3O_8$-$PuO_2$ with Carbon Tetrachloride Increases Greatly the Amount of $PuCl_4$ Formed at Equilibrium.

$PuCl_4$ by a factor of one-fourth of the ratio of $Cl_2$ introduced in the second case to that introduced in the first case.

Increasing the amount of inert gas present has an appreciable effect on the capacity for transporting $PuCl_4$, although the effect is much less than is the effect of increasing the amount of $Cl_2$. Calculations to illustrate the effect of up to 100 moles of inert gas per mole of $U_3O_8$ chlorinated were made at 500, 750, and 1000°K for the particular case in which 10 moles of $Cl_2$ were used per mole of $U_3O_8$ chlorinated (Fig. 4). At all three temperatures, increasing the amount of inert gas from 1 to 100 moles resulted in approximately a threefold increase in the amount of $PuCl_4$ that could be transported.

It was already apparent from the data in Fig. 3 that temperature is the variable that has the greatest effect on the amount of $PuCl_4$ that can be formed. This effect is illustrated in Fig. 5 for the cases in which 1, 10, and 100 moles of $Cl_2$, with no inert gases, were introduced per mole of $U_3O_8$ chlorinated. Over the temperature range 700 to 1000°K, the capacities increase by a factor of $10^4$, from about $5 \times 10^{-6}$ to $5 \times 10^{-2}$ mole of $PuCl_4$ per mole of $Cl_2$ introduced. Since no inert gases were present, the equilibrium capacity per mole of $Cl_2$ under process conditions, where "inert" gases will be present, will be slightly higher than shown here.

For comparison, the capacity per mole of $Cl_2$ in the system $PuCl_3$-$Cl_2$ is also shown. The latter results were calculated from the equilibrium constants[9] for reaction (4). The effect of the chlorine supplied by decomposition of $UCl_6$ [reverse of reaction (5)] is evident from Fig. 5. When only 1 mole of $Cl_2$ is introduced per mole of $U_3O_8$ chlorinated, the decomposition of $UCl_6$ is not suppressed appreciably, and the amount of $PuCl_4$ that is formed per mole of $Cl_2$ introduced is greater than in cases where more $Cl_2$ is introduced. As more chlorine is introduced, the capacity per mole approaches that in the $PuCl_3$-$Cl_2$ system, since the chlorine liberated from $UCl_6$ decomposition becomes a relatively small fraction of the total chlorine.

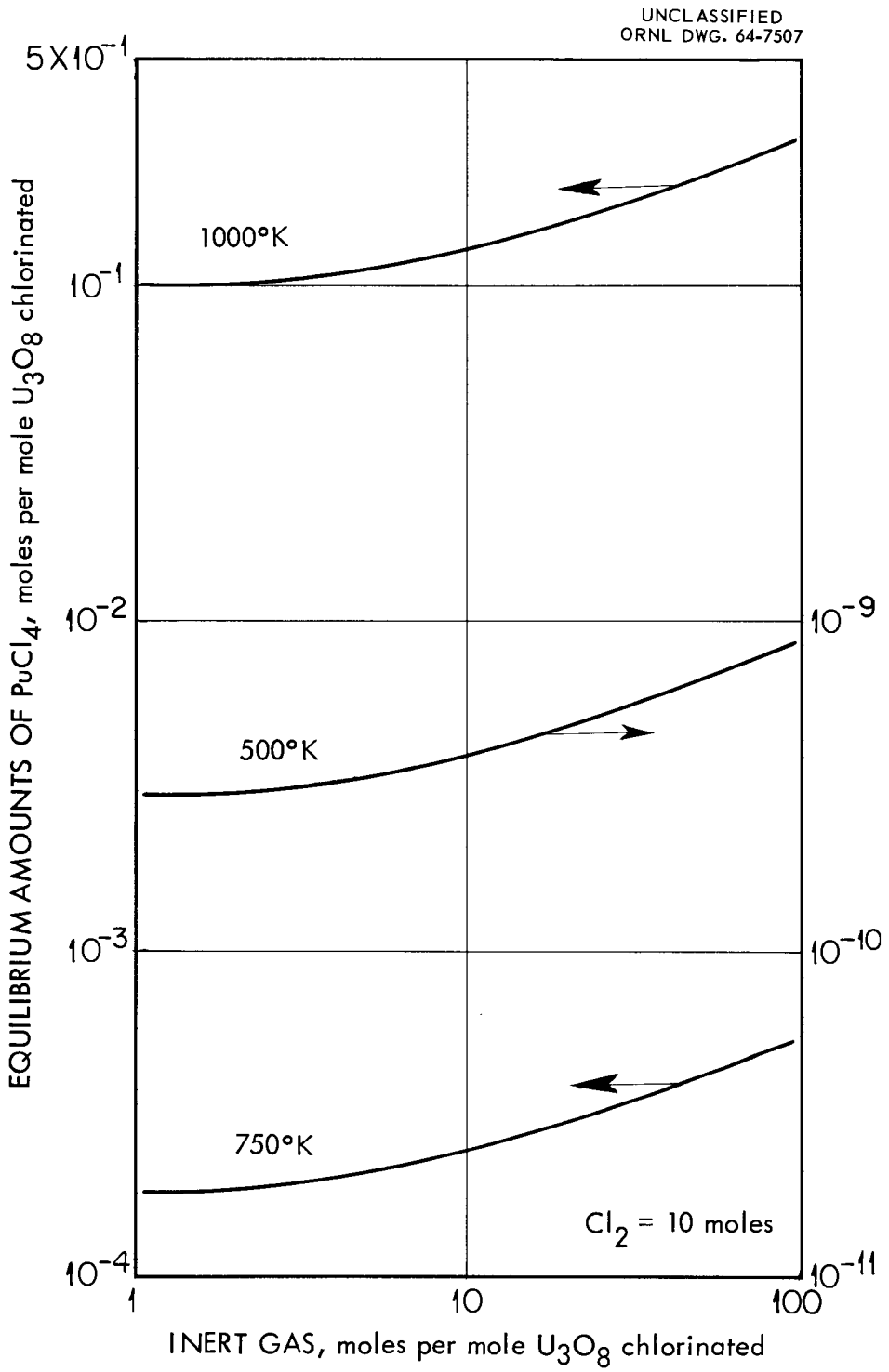


Fig. 4. Increasing the Amount of Inert Gas Introduced During Chlorination of $U_3O_8$-$PuO_2$ with Carbon Tetrachloride Increases Slightly the Amount of $PuCl_4$ Formed at Equilibrium.

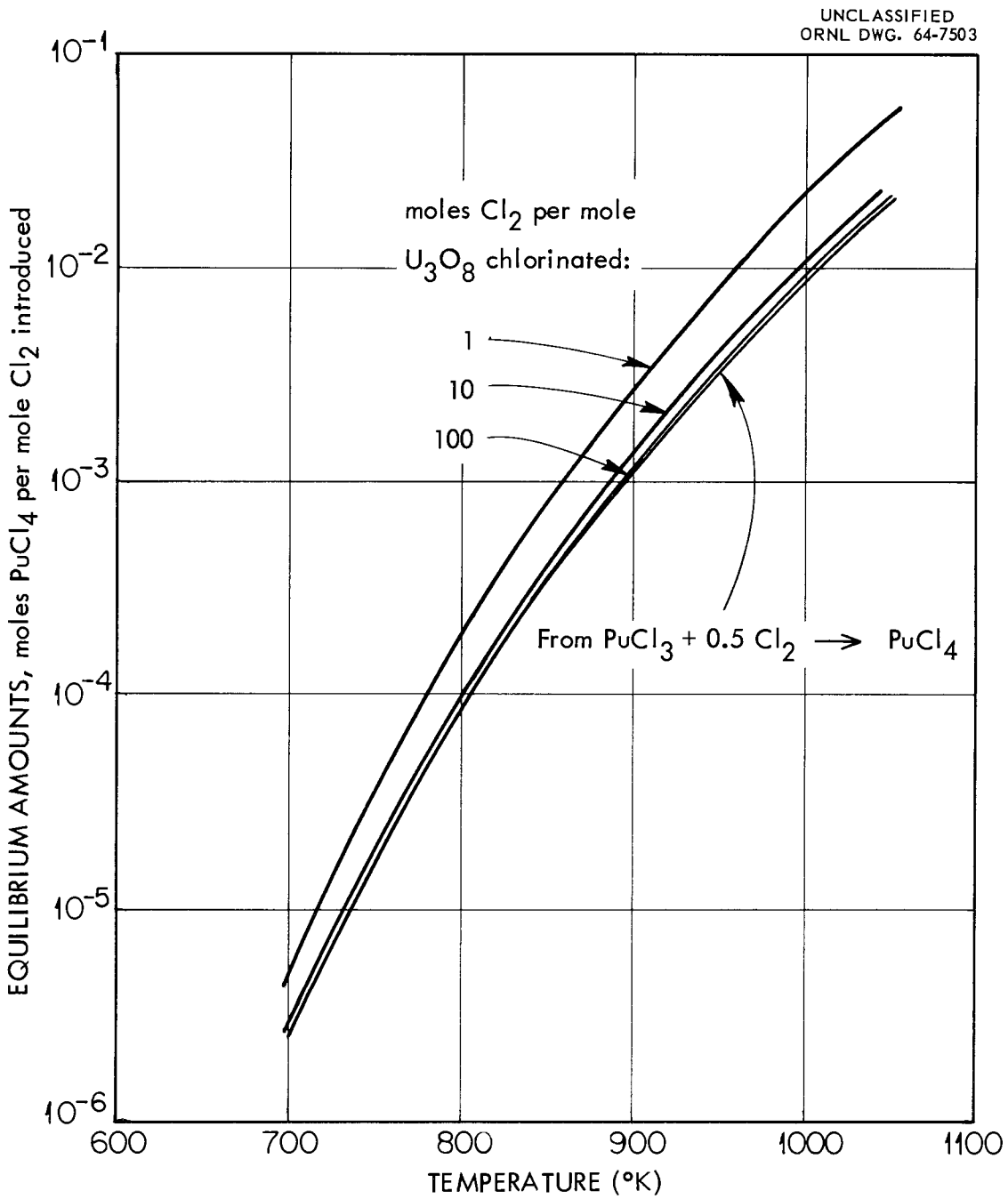


Fig. 5. The Equilibrium Capacity of Chlorine, per mole of Chlorine Introduced, for Transporting $PuCl_4$ Vapor is Greater During Reaction of $U_3O_8$-$PuO_2$ with Carbon Tetrachloride than During Chlorination of $PuCl_3$.

The optimum processing condition would not necessarily correspond to the maximum capacity per mole of chlorine, since the capacity does not decrease rapidly with increasing amounts of chlorine, and a reagent of high chlorine content is simple to prepare (see Sec 3.2).

### 3.2 The Volume Percent of Chlorine Required in $Cl_2$-$CCl_4$ Mixtures as a Function of Plutonium Oxide Content of the Fuel

In actual operation of a process in which $U_3O_8$-$PuO_2$ is chlorinated with $CCl_4$, the problem of supplying enough $Cl_2$ to volatilize all the plutonium as rapidly as the oxide is chlorinated reduces to the problem of determining the minimum vol % $Cl_2$ which can be used in the mixed $Cl_2$-$CCl_4$ reagent. This was done by using the results of the equilibrium calculations described in Sec 3.1 (tabulated in the Appendix), at temperatures between 700 and 1000°K and for $UO_2$ fuels containing up to 1.7 wt % $PuO_2$ (Fig. 6 and Table 1). The case in which only 1 mole of $Cl_2$ was introduced per mole of $U_3O_8$ converted to chlorides was used to determine the minimum vol % of $Cl_2$ required, because, as was discussed in connection with Fig. 5, the capacity per mole of $Cl_2$ to transport $PuCl_4$ increases slightly as the amount of $Cl_2$ introduced decreases. In these calculations, the small amount of $CCl_4$ consumed in chlorinating $PuO_2$ was neglected. The effect of "inert" gases was neglected, although product $CO_2$ and unreacted $CCl_4$ would certainly be present. These inert gases serve to decrease slightly the amount of chlorine needed (see Fig. 4), and the magnitude of this decrease can be calculated by using the results tabulated in the Appendix.

An efficiency of about 20% in the use of $CCl_4$ during chlorination (with $CCl_4$) of $U_3O_8$ has been observed in several large, laboratory-scale experiments. The remaining 80% of the $CCl_4$ passed through without reacting. Therefore, the minimum values of vol % $Cl_2$ shown in Fig. 6 were calculated on the basis of 20% efficiency in use of the $CCl_4$. The results of calculations at both 100% and 20% efficiency are compared in Table 1. In the latter case, a smaller vol % $Cl_2$ is needed because a larger volume of the mixed reagent is used. Although the efficiency will vary with process conditions, it is likely that the process conditions will resemble

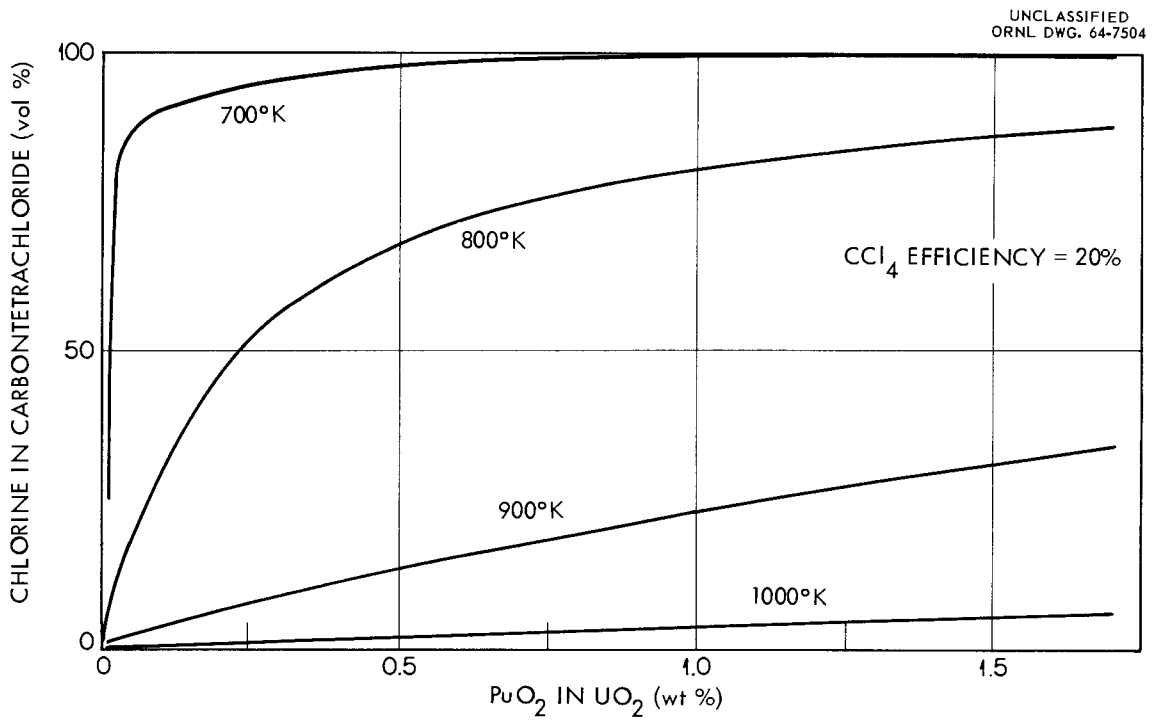


Fig. 6. The Volume % Chlorine Needed in $Cl_2$-$CCl_4$ Gaseous Mixtures to Volatilize $PuCl_4$ Decreases Rapidly with Temperature and Increases with Wt % $PuO_2$ in Mixed $UO_2$-$PuO_2$ Fuel.

Table 1. Minimum Amounts of Chlorine in Mixed Chlorine-Carbontetrachloride Required to Volatilize Plutonium from Mixed $PuO_2$-$UO_2$ Fuel. The small effect of inert gas is neglected

| $PuO_2$ (wt %) | $Cl_2$ (vol %) 700°K | 800°K | 900°K | 1000°K |
|---|---|---|---|---|
| | | Efficiency of $CCl_4$, 100% | | |
| 0.033 | 96.31 | 41.72 | 4.79 | 0.63 |
| 0.33 | 99.62 | 87.74 | 33.47 | 6.00 |
| 0.67 | 99.81 | 93.47 | 50.15 | 11.31 |
| 1.00 | 99.87 | 95.55 | 60.14 | 16.06 |
| 1.33 | 99.90 | 96.63 | 66.80 | 20.33 |
| 1.67 | 99.92 | 97.28 | 71.55 | 24.18 |
| | | Efficiency of $CCl_4$, 20% | | |
| 0.033 | 83.92 | 12.52 | 1.00 | 0.13 |
| 0.33 | 96.12 | 58.87 | 9.14 | 1.26 |
| 0.67 | 99.05 | 74.11 | 16.75 | 2.49 |
| 1.00 | 99.37 | 81.11 | 23.18 | 3.69 |
| 1.33 | 99.52 | 85.13 | 28.69 | 4.85 |
| 1.67 | 99.62 | 87.74 | 33.47 | 6.00 |

those used in the large, laboratory-scale work closely enough so that an assumption of 20% efficiency is a satisfactory approximation.

The rapid increase with temperature in the capacity of chlorine for transporting $PuCl_4$ vapor is evident in Fig. 6. For example, for a fuel containing 0.5 wt % $PuO_2$, the amount of $Cl_2$ required at 700°K, about 98 vol %, is impractically high, since only 2 vol % $CCl_4$ would be available for chlorinating the uranium and plutonium oxides. However, at 800, 900, and 1000°K, less than 70, 14, and 2 vol % $Cl_2$, respectively, are required. Therefore, it would not be feasible to operate a chlorination process involving volatilization of $PuCl_4$ with fuels containing a few tenths percent $PuO_2$ at temperatures much below 800°K, even if the equilibrium in reaction (4) could be closely approached. A maximum $PuO_2$ content of about 0.8 wt % is expected in existing $UO_2$ fuels, after neutron-irradiation.[14] As discussed in Sec 2 and ref 13, it should be possible to closely approach the stoichiometry of reaction (2) at temperatures over 700°K.

A reagent-gas mixture containing about 85 vol % $Cl_2$ and 15 vol % $CCl_4$ can be prepared very simply by saturating $Cl_2$ vapor with $CCl_4$ vapor at room temperature. The calculations show that this mixture should contain enough chlorine at equilibrium to volatilize all the plutonium during the chlorination of fuels which contain up to 1 wt % $PuO_2$ if the temperature of the reactor is 550°C or higher (Fig. 6).

Calculations such as those illustrated by Fig. 6 could also be made for fuels of higher $PuO_2$ content. The amount of $CCl_4$ consumed in chlorinating $PuO_2$ must be considered in calculations involving fuels containing larger amounts of $PuO_2$.

## 4. STANDARD FREE ENERGY CHANGES AND EQUILIBRIUM CONSTANTS

In the calculations presented here, the equilibrium constants for reactions (4), (5), and (8),

$$UCl_{6(gas)} \longrightarrow UCl_{4(solid)} + Cl_2 , \qquad (8)$$

are needed. These equilibrium constants ($K_{eq}$) were calculated from the standard free energy changes from the relation:

$$\Delta F^\circ = -RT \ln K_{eq} . \qquad (9)$$

The standard free energies of formation (literature values) of uranium chlorides needed in calculating the free energy changes in reaction (5) and (8) were presented as a function of temperature in written and graphical form in a previous report.[15] The free energies of formation of $UCl_5$ and $UCl_6$ are estimations, and, therefore, the calculations involving the equilibrium constants of reactions (5) and (8) yield only approximate results. An examination of Fig. 5 shows that these reactions have only a minor effect, compared with the effect of reaction (4), on the capacity of chlorine for transporting $PuCl_4$, and therefore the approximate results are adequate for use in this report. If more valid values for the free energies of formation of $UCl_5$ and $UCl_6$ become available, the calculations can be repeated with new values for the equilibrium constants.

The standard free energy change in reaction (4) was taken from the literature.[9] This expression, as a function of temperature, is:

$$\Delta F^\circ = 44{,}360 + 8T \ln T - 90.13T \ . \tag{10}$$

The values of this expression are shown graphically in Fig. 7 over the temperature range 500 to 1000°K, along with the values obtained for reactions (5) and (8).

The large, positive, free energy change in reaction (4) exerts a major influence on the calculations in this report. The increasing stability of $UCl_5$ and the decreasing stability of $UCl_6$ (lower curve, Fig. 7) affect the results of these calculations to a relatively small extent. The free energy change in reaction (8) was used in calculating the minimum amount of $Cl_2$ required to prevent $UCl_4$ formation (Sec 6).

## 5. DERIVING AND SOLVING THE EQUATION

The equilibrium constants for reactions (4) and (5) can be expressed in terms of the equilibrium partial pressures of the gaseous reactants and products by:

$$K_4 = \frac{P_{PuCl_4}}{(P_{Cl_2})^{1/2}} \ , \tag{11}$$

$$K_5 = \frac{P_{UCl_6}}{P_{UCl_5}(P_{Cl_2})^{1/2}} \ . \tag{12}$$

Considering that the partial pressure is the product of the mole fraction of a particular gas times the total pressure, when the total pressure is 1 atm, Eqs. (11) and (12) can be rewritten as:

$$K_4 = \frac{N_{PuCl_4}}{(N_{Cl_2})^{1/2}(N_T)^{1/2}} \ , \tag{13}$$

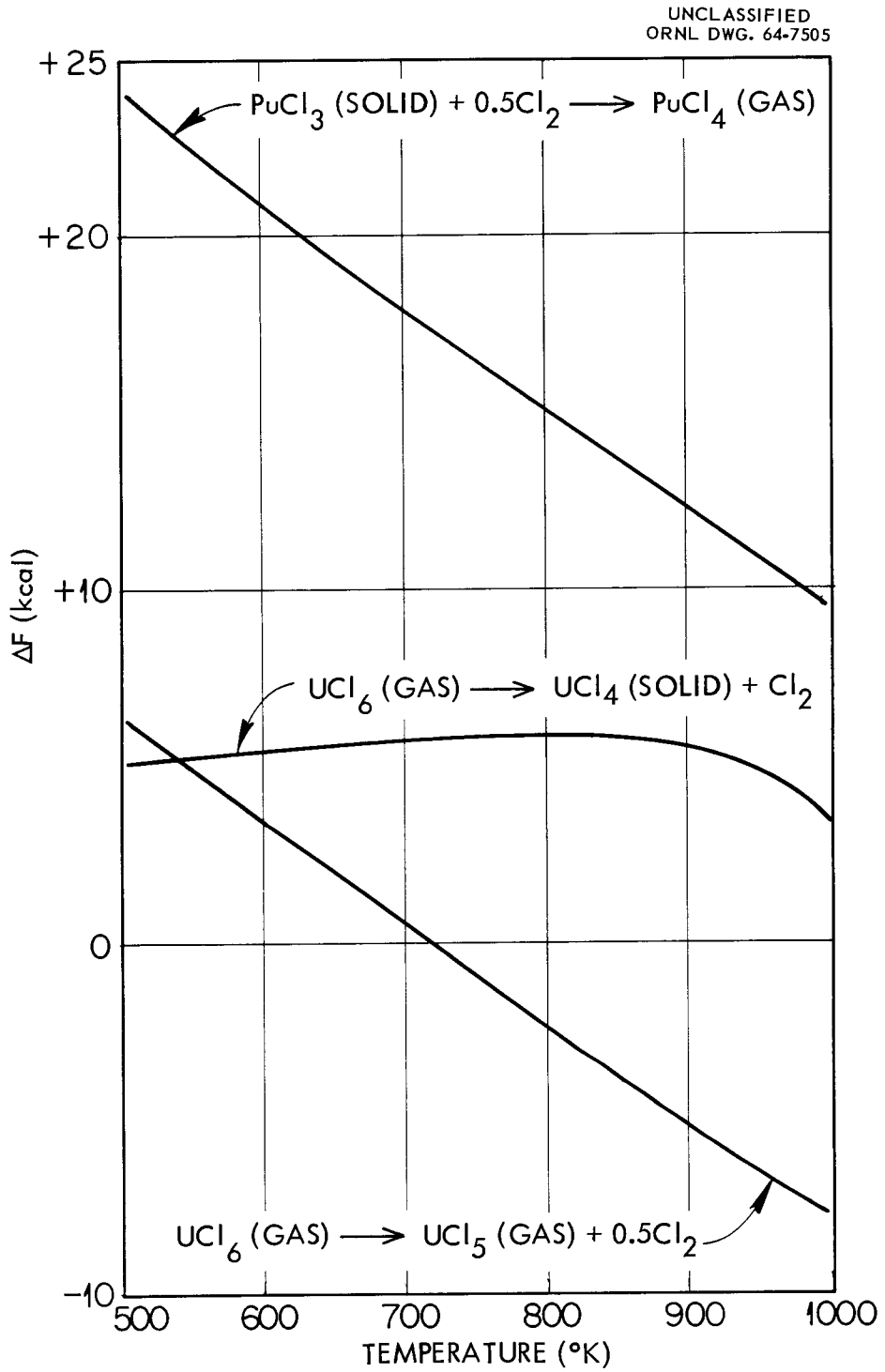


Fig. 7. Standard Free Energy Changes.

$$K_5 = \frac{N_{UCl_6}(N_T)^{1/2}}{N_{UCl_5}(N_{Cl_2})^{1/2}} , \tag{14}$$

where N denotes number of moles, and $N_T$ denotes the total number of moles of gas at equilibrium.

From the stoichiometry of reaction (2), 2 moles of $UCl_5$ and 1 mole of $UCl_6$ are produced for each mole of $U_3O_8$ chlorinated if the reaction proceeds to completion. Therefore, the number of moles of $Cl_2$ at equilibrium will be the amount introduced, either decreased by the amount taken up by conversion of $UCl_5$ to $UCl_6$, or increased by the amount liberated by the reverse reaction. Thus,

$$N_{Cl_2} = N_{Cl_{2,i}} - 1/2(N_{UCl_6} - N_{UCl_{6,i}}) , \tag{15}$$

where "i" denotes quantities introduced, as contrasted to amounts present at equilibrium. Equation (14) can be rearranged to:

$$N_{UCl_6} = K_5 N_{UCl_5}(N_{Cl_2})^{1/2}/(N_T)^{1/2} . \tag{16}$$

The amount of $UCl_5$ present at equilibrium equals the number of moles of uranium chloride gas minus the number of moles of $UCl_6$ present at equilibrium. Thus,

$$N_{UCl_5} = N_{UCl_{6,i}} + N_{UCl_{5,i}} - N_{UCl_6} . \tag{17}$$

Only values of $N_{Cl_{2,i}}$ large enough to prevent any significant formation of $UCl_4$ at equilibrium (see Sec 6) were considered in this work. As mentioned above, chlorination of $U_3O_8$ with $CCl_4$ produces 2 moles of $UCl_6$ for each mole of $UCl_5$. Therefore,

$$N_{UCl_5} = 3N_{UCl_{6,i}} - N_{UCl_6} , \tag{18}$$

or,

$$3N_{UCl_{6,i}} = N_{UCl_5} + N_{UCl_6} . \tag{19}$$

The moles of gas present at equilibrium can be summed up:

$$N_T = N_{1G} + N_{Cl_2} + 3N_{UCl_{6,i}} + N_{PuCl_4} , \tag{20}$$

where $N_{1G}$ is the number of moles of inert gas, that is, gas not involved in reactions (4) or (5).

Substituting Eqs. (18) and (20) in Eq. (16) and rearranging, one gets:

$$N_{UCl_6} = \frac{3K_5(N_{Cl_2})^{1/2}N_{UCl_{6,i}}}{(N_{1G} + N_{Cl_2} + 3N_{UCl_{6,i}} + N_{PuCl_4})^{1/2} + K_5(N_{Cl_2})^{1/2}} . \tag{21}$$

Substituting Eq. (21) in Eq. (15), one gets:

$$N_{Cl_2} = N_{Cl_{2,i}} - \frac{3K_5(N_{Cl_2})^{1/2}N_{UCl_{6,i}}}{2(N_{1G} + N_{Cl_2} + 3N_{UCl_{6,i}} + N_{PuCl_4})^{1/2} + 2K_5(N_{Cl_2})^{1/2}} + \frac{N_{UCl_{6,i}}}{2} . \tag{22}$$

Substituting Eq. (20) in Eq. (13) and rearranging, one gets:

$$N_{PuCl_4} = \frac{K_4^2N_{Cl_2} + \sqrt{K_4^4(N_{Cl_2})^2 + 4K_4^2N_{Cl_2}(N_{1G} + N_{Cl_2} + 3N_{UCl_{6,i}})}}{2} . \tag{23}$$

Therefore, for any given values of temperature (from which $K_4$ and $K_5$ can be calculated, as shown in Sec 4), and moles of inert gas, chlorine, and $UCl_5$ and $UCl_6$ introduced, $N_{Cl_2}$ can be calculated by using Eqs. (22) and (23). Because those two equations are complicated, an iterative method must be used to solve for $N_{Cl_2}$. The method used was the same as described in a previous report.[15] From $N_{Cl_2}$, $N_{PuCl_4}$ can be calculated by use of Eq. (23), and $N_{UCl_6}$ and $N_{UCl_5}$ can be calculated by use of Eqs. (15) and (18). The summary of the results of these calculations, made with the ORNL 1604 CDC computer, is included in the Appendix.

A clear understanding of the meaning of Eq. (23) and the way it is used is necessary before the results of the calculations based on Eqs. (22) and (23) can be applied. Equation (23) yields values of $N_{PuCl_4}$ which represent the maximum that can be transported by $N_{Cl_2}$ moles of $Cl_2$. These values are valid only when $N_{Cl_2}$ is large enough to transport the plutonium as rapidly as it becomes exposed at the reaction surface. Therefore, the results of the calculations based on Eqs. (22) and (23) are used to further calculate, in a reverse manner (as was done to obtain the data in Fig. 6), the wt % of $PuO_2$ which can be present in the original fuel without exceeding the capacity for transporting plutonium under the particular conditions ($T°K$, $N_{lG}$, $N_{Cl_{2,i}}$, $N_{UCl_{6,i}}$) specified. By use of this approach, complications that would arise from an additional term in Eq. (22) are avoided. An additional term would be required to account for 0.5 mole of $Cl_2$ for each mole of $PuCl_3$ present at equilibrium, if the equilibrium amount of chlorine were insufficient to transport all plutonium as $PuCl_4$ as rapidly as the $PuO_2$ became exposed and reacted with $CCl_4$. The method described here could also be applied to the mixed $PuO_2$-$UO_2$ fuels, in which the plutonium content is higher than in the fuels under consideration in the present report. The maximum $PuO_2$ content for which the assumption is valid that the $PuO_2$ chlorinates as rapidly as it becomes exposed at the reaction surface remains to be determined experimentally.

## 6. CALCULATIONS OF MINIMUM AMOUNTS OF CHLORINE NEEDED TO PREVENT FORMATION OF SOLID URANIUM TETRACHLORIDE

The calculations described in Sec 5 involve only reactions (4) and (5) and would be more complicated if, in addition to these reactions, the formation of $UCl_4$ (reaction 6) had to be considered. In practice, it is desirable to introduce enough $Cl_2$ to prevent the formation of solid $UCl_4$ because (1) the process can then be carried out below temperatures at which $UCl_4$ has appreciable vapor pressure (the vapor pressure of $UCl_4$ = 1 atm at 792°C) and (2) under conditions which permit the formation of $UCl_4$, very little $PuCl_4$ could be volatilized. Therefore, it was necessary to determine, as a function of temperature, the minimum amount of $Cl_2$ required at equilibrium per mole of $U_3O_8$ chlorinated,

to ensure that no significant amount of solid $UCl_4$ could form. Since some solid $UCl_4$ can form under any conditions, calculations were made to determine the minimum amount of $Cl_2$ needed to ensure that not more than 1% of the uranium chlorides formed during chlorination could decompose to solid $UCl_4$.

The decomposition reactions which must be considered are:

$$UCl_{6(gas)} \xrightarrow{K_5} UCl_{5(gas)} + 1/2Cl_2 \ , \tag{5}$$

$$UCl_{5(gas)} \xrightarrow{K_6} UCl_{4(solid)} + Cl_2 \ , \tag{6}$$

$$UCl_{6(gas)} \xrightarrow{K_8} UCl_{4(solid)} + Cl_2 \ . \tag{8}$$

These reactions have been discussed previously, as written, except that reaction (5) was reversed in Secs 2 and 4. It is apparent that only two independent reactions are involved; adding reactions (5) and (6) yields (8). Therefore, only reactions (5) and (8) are used in the calculations below. The method used to determine the equilibrium constants, $K_5$ and $K_8$, is described in Sec 5. From considerations analogous to those developed in Sec 5,

$$K_5 = \frac{N_{UCl_5}(N_{Cl_2})^{1/2}}{N_{UCl_6}(N_T)^{1/2}} \ , \tag{24}$$

$$K_8 = \frac{N_{Cl_2}}{N_{UCl_6}} \ . \tag{25}$$

The number of moles of $UCl_5$ present at equilibrium is the moles of uranium chloride introduced, $N_{U,i}$, minus the moles of $UCl_4$ and $UCl_6$ present. Thus,

$$N_{UCl_5} = N_{U,i} - N_{UCl_4} - N_{UCl_6} \ . \tag{26}$$

When 1 mole of $U_3O_8$ has been chlorinated, $N_{U,i}$ is 3. From Eqs. (18) and (19),

$$N_{U,i} = 3N_{UCl_6,i} \quad . \tag{27}$$

Rearranging Eq. (25), one gets:

$$N_{UCl_6} = N_{Cl_2}/K_8 \quad . \tag{28}$$

The total number of moles of gas present at equilibrium is:

$$N_T = N_{U,i} - N_{UCl_4} + N_{Cl_2} + N_{1G} \quad . \tag{29}$$

The amount of $Cl_2$ present at equilibrium is the amount introduced plus the amount of $UCl_6$ and one-half the amount of $UCl_5$ that has decomposed to $UCl_4$. Thus,

$$N_{Cl_2} = N_{Cl_{2,i}} + (N_{UCl_{6,i}} - N_{UCl_6}) + 1/2(N_{UCl_{5,i}} - N_{UCl_5}) \quad . \tag{30}$$

Substituting Eqs. (26), (27), and (28) in Eq. (30) and rearranging, one gets:

$$N_{Cl_2} = \frac{1 + 2N_{Cl_{2,i}} + N_{UCl_4}}{2 + (1/K_8)} \tag{31}$$

for the case where $N_{U,i} = 3$.

Substituting Eqs. (26), (28), (29), and (31) in Eq. (24) and rearranging, one gets:

$$K_5 = \frac{\left(3 - N_{UCl_4} - \dfrac{1 + 2\,N_{Cl_{2,i}} + N_{UCl_4}}{2K_8 + 1}\right)\left(\dfrac{1 + 2N_{Cl_{2,i}} + N_{UCl_4}}{2 + (1/K_8)}\right)^{1/2}}{\left(\dfrac{1 + 2N_{Cl_{2,i}} + N_{UCl_4}}{2K_8 + 1}\right)\left(3 - N_{UCl_4} + N_{1G} + \dfrac{1 + 2N_{Cl_{2,i}} + N_{UCl_4}}{2 + (1/K_8)}\right)} \quad , \tag{32}$$

where $N_{U,i} = 3$.

The only unknown is $N_{UCl_4}$. Equation (32) was solved for $N_{UCl_4}$ by the same iterative method used with Eq. (22), substituting increasing values of $N_{Cl_{2,i}}$, at selected temperatures and values of $N_{1G}$ until a value of $N_{Cl_{2,i}}$ was found which caused $N_{UCl_4}$ to be less than 0.03, that is, less than 1% of the 3 moles of uranium chlorides introduced. These minimum amounts of $Cl_2$, with zero, 1, 10, and 100 moles of inert gas present, are shown graphically in Fig. 8. The results are also tabulated in Table A.2 in the Appendix.

The results of these equilibrium calculations show that only below 630°K is it necessary to add $Cl_2$ to prevent significant formation of $UCl_4$ during chlorination of $U_3O_8$ with $CCl_4$. When 1, 10, or 100 moles of inert gas are introduced per mole of $U_3O_8$ chlorinated, the respective temperatures are lowered to about 625, 600, and 565°K. In all calculations in Sec 5, enough $Cl_2$ was introduced so that the amount of $UCl_4$ formed at equilibrium was insignificantly small.

As discussed in ref 13, the results shown in this section are in good agreement with experimental observations only at temperatures over 800°K. Apparently, below this temperature, some $UCl_4$ forms because slow, interfering reactions cause the stoichiometry of the chlorination reaction to differ from that shown in reaction (2).

## 7. CONCLUSIONS

During chlorination of mixed $U_3O_8$-$PuO_2$ with $CCl_4$, the equilibrium capacity of $Cl_2$ for forming and transporting volatile $PuCl_4$ by the reaction, $PuCl_3 + 0.5Cl_2 \longrightarrow PuCl_4$, can be closely estimated from the equilibrium constants for this reaction. This capacity increases from about $3 \times 10^{-6}$ to $10^{-2}$ mole of $PuCl_4$ per mole of $Cl_2$ as the temperature increases from 700 to 1000°K. The uranium chlorides formed by the reaction of $CCl_4$ and $U_3O_8$ do not interact with the chlorine to prevent its participation in the above equilibrium; rather, the uranium chlorides so formed actually contribute additional chlorine through the decomposition of $UCl_6$ to the relatively stable $UCl_5$. The capacity of this small amount of additional chlorine, then, contributes to the capacity of any

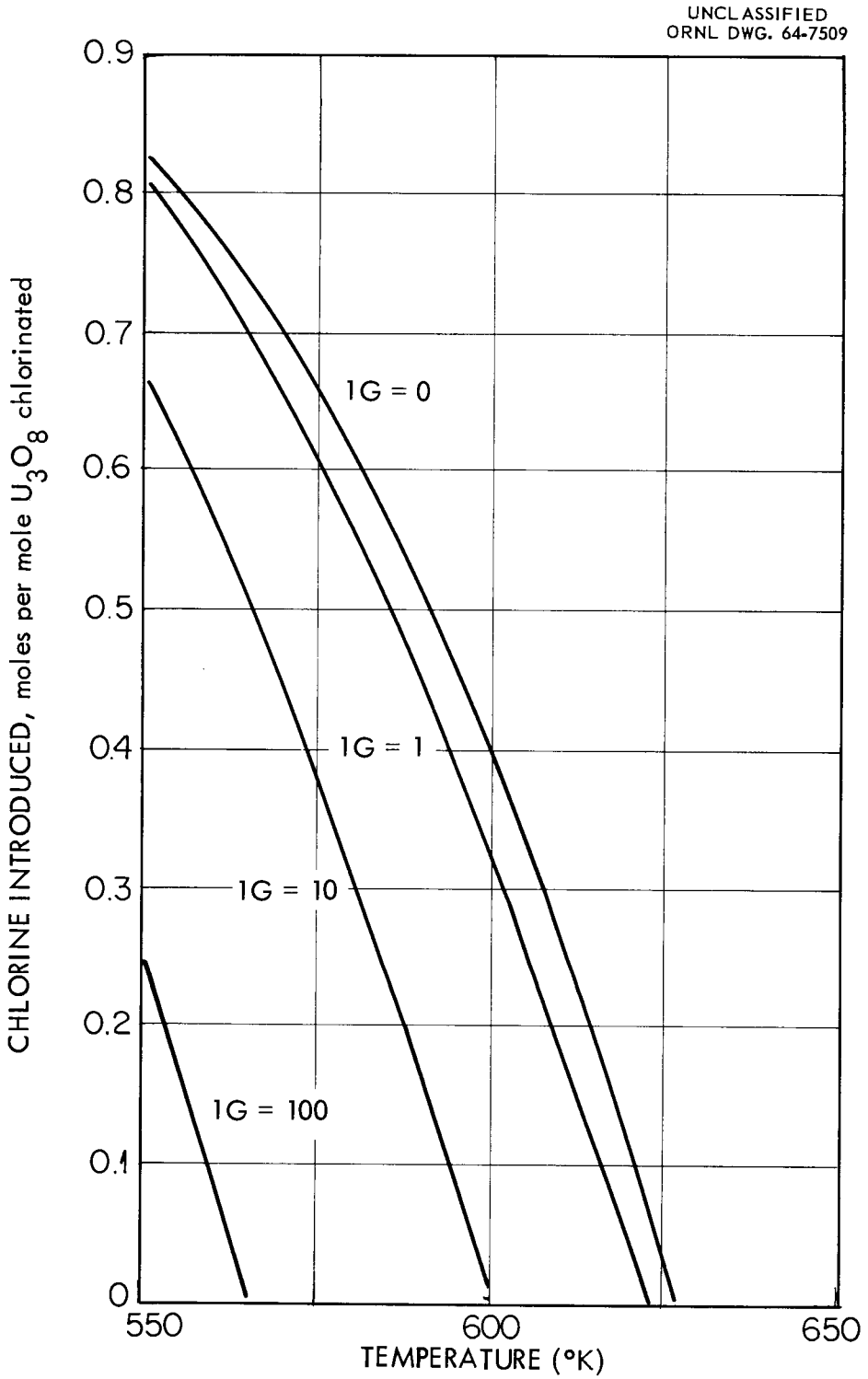


Fig. 8. Minimum Amounts of Chlorine Required to Prevent the Conversion of More than 1% of $U_3O_8$ to Uranium Tetrachloride.

chlorine introduced initially. In addition, any inert gases present serve to increase the capacity slightly. The equilibrium capacity is great enough to indicate the feasibility of a separations process involving the volatilization of $PuCl_4$ during chlorination of neutron irradiated $UO_2$ fuels at practical operating temperatures of 500 to 600°C.

Additional work is needed to extend the calculations in this report to mixed $UO_2$-$PuO_2$ fuels, to determine experimentally if the equilibrium conditions are approached closely in practice, and to determine the effect, at equilibrium, of carbon monoxide (a by-product of the reaction with $CCl_4$) on $PuCl_4$ vapor. From a practical viewpoint, it will also be necessary to determine if the rates of reaction of $CCl_4$ with plutonium oxide compare favorably with the rates for $U_3O_8$.

## 8. ACKNOWLEDGEMENTS

The services of G. Atta and A. Jenkins of the Mathematics Division in programming equations for the CDC-1604 A computer are gratefully acknowledged.

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## 10. Appendix - Results of Computer Calculations

Table A.1. The Capacity of Chlorine for Transporting Plutonium Tetrachloride Vapor (Eq. 22).

| T(°K) | $\Delta F_5$ | $\Delta F_4$ | $K_5$ | $K_4$ | $N_{Cl_2\,i}$ | $N_{1G}$ | $N_{Cl_2}$ | $N_{PuCl_4}$ | $N_{UCl_6}$ | $N_{UCl_5}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 500 | -6.4316.+003 | 2.4153.+004 | 6.4894.+002 | 2.7480.+011 | | | | | | |
| | | | | | 1 | | 2.4961.-002 | 7.5509.-012 | 2.9501.+000 | 4.9922.-002 |
| | | | | | 1 | 1 | 2.7436.-002 | 9.1346.-012 | 2.9451.+000 | 5.4873.-002 |
| | | | | | 1 | 10 | 4.0386.-002 | 1.9942.-011 | 2.9192.+000 | 8.0773.-002 |
| | | | | | 10 | | 9.0027.+000 | 2.8565.-010 | 2.9947.+000 | 5.3190.-003 |
| | | | | | 10 | 1 | 9.0028.+000 | 2.9731.-010 | 2.9945.+000 | 5.5337.-003 |
| | | | | | 10 | 10 | 9.0036.+000 | 3.8678.-010 | 2.9928.+000 | 7.1820.-003 |
| | | | | | 10 | 100 | 9.0081.+000 | 8.7287.-010 | 2.9839.+000 | 1.6126.-002 |
| | | | | | 100 | | 9.9002.+001 | 2.7615.-009 | 2.9953.+000 | 4.6851.-003 |
| | | | | | 100 | 1 | 9.9002.+001 | 2.7750.-009 | 2.9953.+000 | 4.7080.-003 |
| | | | | | 100 | 10 | 9.9002.+001 | 2.8937.-009 | 2.9951.+000 | 4.9090.-003 |
| | | | | | 100 | 100 | 9.9003.+001 | 3.8861.-009 | 2.9934.+000 | 6.5887.-003 |
| | | | | | 100 | 1000 | 9.9008.+001 | 9.0769.-009 | 2.9847.+000 | 1.5343.-002 |
| 550 | -4.9365.+003 | 2.2552.+004 | 9.1669.+001 | 1.0854.-009 | | | | | | |
| | | | | | 1 | | 8.9492.-002 | 5.7075.-010 | 2.8210.+000 | 1.7898.-001 |
| | | | | | 1 | 1 | 9.8038.-002 | 6.8801.-010 | 2.8039.+000 | 1.9608.-001 |
| | | | | | 1 | 10 | 1.4204.-001 | 1.4830.-009 | 2.7159.+000 | 2.8409.-001 |
| | | | | | 10 | | 9.0186.+000 | 1.1301.-008 | 2.9628.+000 | 3.7247.-002 |
| | | | | | 10 | 1 | 9.0194.+000 | 1.1762.-008 | 2.9613.+000 | 3.8731.-002 |
| | | | | | 10 | 10 | 9.0250.+000 | 1.5304.-008 | 2.9499.+000 | 5.0086.-002 |
| | | | | | 10 | 100 | 9.0552.+000 | 3.4576.-008 | 2.8897.+000 | 1.1034.-001 |
| | | | | | 100 | | 9.9016.+001 | 1.0909.-007 | 2.9671.+000 | 3.2855.-002 |
| | | | | | 100 | 1 | 9.9017.+001 | 1.0963.-007 | 2.9670.+000 | 3.3013.-002 |
| | | | | | 100 | 10 | 9.9017.+001 | 1.1432.-007 | 2.9656.+000 | 3.4409.-002 |
| | | | | | 100 | 100 | 9.9023.+001 | 1.5352.-007 | 2.9540.+000 | 4.6026.-002 |
| | | | | | 100 | 1000 | 9.9053.+001 | 3.5863.-007 | 2.8947.+000 | 1.0532.-001 |
| 600 | -3.4548.+003 | 2.0987.+004 | 1.8149.+001 | 2.2534.-008 | | | | | | |
| | | | | | 1 | | 2.4897.-001 | 2.0267.-008 | 2.5021.+000 | 4.9794.-001 |
| | | | | | 1 | 1 | 2.6970.-001 | 2.4181.-008 | 2.4606.+000 | 5.3939.-001 |
| | | | | | 1 | 10 | 3.7235.-001 | 5.0283.-008 | 2.2553.+000 | 7.4470.-001 |
| | | | | | 10 | | 9.0895.+000 | 2.3622.-007 | 2.8210.+000 | 1.7900.-001 |
| | | | | | 10 | 1 | 9.0929.+000 | 2.4587.-007 | 2.8143.+000 | 1.8574.-001 |
| | | | | | 10 | 10 | 9.1182.+000 | 3.2001.-007 | 2.7636.+000 | 2.3643.-001 |
| | | | | | 10 | 100 | 9.2410.+000 | 7.2573.-007 | 2.5180.+000 | 4.8197.-001 |
| | | | | | 100 | | 9.9079.+001 | 2.2662.-006 | 2.8411.+000 | 1.5890.-001 |
| | | | | | 100 | 1 | 9.9080.+001 | 2.2773.-006 | 2.8404.+000 | 1.5963.-001 |
| | | | | | 100 | 10 | 9.9083.+001 | 2.3747.-006 | 2.8339.+000 | 1.6608.-001 |
| | | | | | 100 | 100 | 9.9109.+001 | 3.1893.-006 | 2.7812.+000 | 2.1883.-001 |
| | | | | | 100 | 1000 | 9.9233.+001 | 7.4525.-006 | 2.5346.+000 | 4.6543.-001 |
| 650 | -1.9845.+003 | 1.9456.+004 | 4.6500.+000 | 2.8589.-007 | | | | | | |
| | | | | | 1 | | 5.3369.-001 | 3.9260.-007 | 1.9326.+000 | 1.0674.+000 |
| | | | | | 1 | 1 | 5.6780.-001 | 4.6041.-007 | 1.8644.+000 | 1.1356.+000 |
| | | | | | 1 | 10 | 7.2500.-001 | 9.0181.-007 | 1.5500.+000 | 1.4500.+000 |
| | | | | | 10 | | 9.2972.+000 | 3.0568.-006 | 2.4056.+000 | 5.9439.-001 |
| | | | | | 10 | 1 | 9.3065.+000 | 3.1814.-006 | 2.3869.+000 | 6.1308.-001 |
| | | | | | 10 | 10 | 9.3736.+000 | 4.1401.-006 | 2.2528.+000 | 7.4720.-001 |
| | | | | | 10 | 100 | 9.6352.+000 | 9.4180.-006 | 1.7296.+000 | 1.2704.+000 |
| | | | | | 100 | | 9.9269.+001 | 2.8805.-005 | 2.4625.+000 | 5.3751.-001 |
| | | | | | 100 | 1 | 9.9270.+001 | 2.8946.-005 | 2.4603.+000 | 5.3966.-001 |
| | | | | | 100 | 10 | 9.9279.+001 | 3.0184.-005 | 2.4416.+000 | 5.5839.-001 |
| | | | | | 100 | 100 | 9.9352.+001 | 4.0536.-005 | 2.2955.+000 | 7.0450.-001 |
| | | | | | 100 | 1000 | 9.9626.+001 | 9.4753.-005 | 1.7488.+000 | 1.2512.+000 |

Table A.1. The Capacity of Chlorine for Transporting Plutonium Tetrachloride Vapor (Eq. 22). (Continued)

| T(°K) | $\Delta F_5$ | $\Delta F_4$ | $K_5$ | $K_4$ | $N_{Cl_2\,i}$ | $N_{1G}$ | $N_{Cl_2}$ | $N_{PuCl_4}$ | $N_{UCl_6}$ | $N_{UCl_5}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 700 | -5.2338E+002 | 1.7955E+004 | 1.4570E+000 | 2.4678E-006 | | | | | | |
| | | | | | | | 1.4368E-001 | 1.6585E-006 | 7.1264E-001 | 2.2874E+000 |
| | | | | | | 1 | 1.6372E-001 | 2.0375E-006 | 6.7257E-001 | 2.3274E+000 |
| | | | | | 1 | | 8.8477E-001 | 4.5751E-006 | 1.2305E+000 | 1.7695E+000 |
| | | | | | 1 | 1 | 9.2019E-001 | 5.2509E-006 | 1.1596E+000 | 1.8404E+000 |
| | | | | | 1 | 10 | 1.0700E+000 | 9.5754E-006 | 8.5990E-001 | 2.1401E+000 |
| | | | | | 10 | | 9.6599E+000 | 2.7290E-005 | 1.6803E+000 | 1.3197E+000 |
| | | | | | 10 | 1 | 9.6739E+000 | 2.8383E-005 | 1.6523E+000 | 1.3477E+000 |
| | | | | | 10 | 10 | 9.7674E+000 | 3.6800E-005 | 1.4653E+000 | 1.5347E+000 |
| | | | | | 10 | 100 | 1.0046E+001 | 8.3162E-005 | 9.0849E-001 | 2.0915E+000 |
| | | | | | 100 | | 9.9616E+001 | 2.4950E-004 | 1.7682E+000 | 1.2318E+000 |
| | | | | | 100 | 1 | 9.9618E+001 | 2.5072E-004 | 1.7647E+000 | 1.2353E+000 |
| | | | | | 100 | 10 | 9.9633E+001 | 2.6142E-004 | 1.7344E+000 | 1.2656E+000 |
| | | | | | 100 | 100 | 9.9742E+001 | 3.5093E-004 | 1.5163E+000 | 1.4837E+000 |
| | | | | | 100 | 1000 | 1.0004E+002 | 8.1977E-004 | 9.1492E-001 | 2.0851E+000 |
| 750 | 9.3002E+002 | 1.6483E+004 | 5.3568E-001 | 1.5677E-005 | | | | | | |
| | | | | | | | 2.9326E-001 | 1.5407E-005 | 4.1348E-001 | 2.5865E+000 |
| | | | | | | 1 | 3.1126E-001 | 1.8161E-005 | 3.7748E-001 | 2.6225E+000 |
| | | | | | 1 | | 1.1684E+000 | 3.4597E-005 | 6.6327E-001 | 2.3367E+000 |
| | | | | | 1 | 1 | 1.1934E+000 | 3.9030E-005 | 6.1316E-001 | 2.3868E+000 |
| | | | | | 1 | 10 | 1.2919E+000 | 6.7364E-005 | 4.1621E-001 | 2.5838E+000 |
| | | | | | 10 | | 1.0020E+001 | 1.7907E-004 | 9.5911E-001 | 2.0409E+000 |
| | | | | | 10 | 1 | 1.0032E+001 | 1.8601E-004 | 9.3525E-001 | 2.0648E+000 |
| | | | | | 10 | 10 | 1.0108E+001 | 2.3959E-004 | 7.8482E-001 | 2.2152E+000 |
| | | | | | 10 | 100 | 1.0291E+001 | 5.3531E-004 | 4.1703E-001 | 2.5830E+000 |
| | | | | | 100 | | 9.9982E+001 | 1.5908E-003 | 1.0364E+000 | 1.9636E+000 |
| | | | | | 100 | 1 | 9.9983E+001 | 1.5985E-003 | 1.0331E+000 | 1.9669E+000 |
| | | | | | 100 | 10 | 9.9997E+001 | 1.6665E-003 | 1.0052E+000 | 1.9948E+000 |
| | | | | | 100 | 100 | 1.0009E+002 | 2.2352E-003 | 8.1985E-001 | 2.1801E+000 |
| | | | | | 100 | 1000 | 1.0029E+002 | 5.2149E-003 | 4.1715E-001 | 2.5829E+000 |
| 800 | 2.3772E+003 | 1.5038E+004 | 2.2406E-001 | 7.7726E-005 | | | | | | |
| | | | | | | | 3.9365E-001 | 8.9838E-005 | 2.1270E-001 | 2.7873E+000 |
| | | | | | | 1 | 4.0373E-001 | 1.0364E-004 | 1.9253E-001 | 2.8075E+000 |
| | | | | | 1 | | 1.3340E+000 | 1.8690E-004 | 3.3192E-001 | 2.6681E+000 |
| | | | | | 1 | 1 | 1.3482E+000 | 2.0871E-004 | 3.0364E-001 | 2.6964E+000 |
| | | | | | 1 | 10 | 1.4018E+000 | 3.4924E-004 | 1.9639E-001 | 2.8036E+000 |
| | | | | | 10 | | 1.0253E+001 | 9.0608E-004 | 4.9388E-001 | 2.5061E+000 |
| | | | | | 10 | 1 | 1.0260E+001 | 9.4023E-004 | 4.7910E-001 | 2.5209E+000 |
| | | | | | 10 | 10 | 1.0305E+001 | 1.2046E-003 | 3.8902E-001 | 2.6110E+000 |
| | | | | | 10 | 100 | 1.0405E+001 | 2.6699E-003 | 1.9067E-001 | 2.8093E+000 |
| | | | | | 100 | | 1.0023E+002 | 7.9064E-003 | 5.4254E-001 | 2.4575E+000 |
| | | | | | 100 | 1 | 1.0023E+002 | 7.9447E-003 | 5.4041E-001 | 2.4596E+000 |
| | | | | | 100 | 10 | 1.0024E+002 | 8.2813E-003 | 5.2230E-001 | 2.4777E+000 |
| | | | | | 100 | 100 | 1.0030E+002 | 1.1099E-002 | 4.0793E-001 | 2.5921E+000 |
| | | | | | 100 | 1000 | 1.0041E+002 | 2.5871E-002 | 1.8993E-001 | 2.8101E+000 |
| 850 | 3.8193E+003 | 1.3617E+004 | 1.0415E-001 | 3.1451E-004 | | | | | | |
| | | | | | | | 4.4562E-001 | 3.8974E-004 | 1.0877E-001 | 2.8912E+000 |
| | | | | | | 1 | 4.5168E-001 | 4.4600E-004 | 9.6640E-002 | 2.9034E+000 |
| | | | | | 1 | | 1.4162E+000 | 7.8663E-004 | 1.6750E-001 | 2.8325E+000 |
| | | | | | 1 | 1 | 1.4238E+000 | 8.7407E-004 | 1.5239E-001 | 2.8476E+000 |
| | | | | | 1 | 10 | 1.4519E+000 | 1.4407E-003 | 9.6183E-002 | 2.9038E+000 |
| | | | | | 10 | | 1.0374E+001 | 3.7051E-003 | 2.5204E-001 | 2.7480E+000 |
| | | | | | 10 | 1 | 1.0378E+001 | 3.8424E-003 | 2.4385E-001 | 2.7561E+000 |
| | | | | | 10 | 10 | 1.0403E+001 | 4.9077E-003 | 1.9478E-001 | 2.8052E+000 |
| | | | | | 10 | 100 | 1.0454E+001 | 1.0832E-002 | 9.1940E-002 | 2.9081E+000 |
| | | | | | 100 | | 1.0036E+002 | 3.2037E-002 | 2.7919E-001 | 2.7208E+000 |
| | | | | | 100 | 1 | 1.0036E+002 | 3.2192E-002 | 2.7797E-001 | 2.7220E+000 |
| | | | | | 100 | 10 | 1.0037E+002 | 3.3553E-002 | 2.6772E-001 | 2.7323E+000 |
| | | | | | 100 | 100 | 1.0040E+002 | 4.4949E-002 | 2.0453E-001 | 2.7955E+000 |
| | | | | | 100 | 1000 | 1.0045E+002 | 1.0472E-001 | 9.1397E-002 | 2.9086E+000 |

Table A.1. The Capacity of Chlorine for Transporting Plutonium Tetrachloride Vapor (Eq. 22).
(Continued)

| T(°K) | $\Delta F_5$ | $\Delta F_4$ | $K_5$ | $K_4$ | $N_{Cl_2\,i}$ | $N_{1G}$ | $N_{Cl_2}$ | $N_{PuCl_4}$ | $N_{UCl_6}$ | $N_{UCl_5}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 900 | 5.2575E+003 | 1.2220E+004 | 5.2830E-002 | 1.0753E-003 | | | | | | |
| | | | | | | | 4.7132E-001 | 1.3757E-003 | 5.7352E-002 | 2.9426E+000 |
| | | | | | | 1 | 4.7461E-001 | 1.5673E-003 | 5.0786E-002 | 2.9492E+000 |
| | | | | | 1 | | 1.4559E+000 | 2.7396E-003 | 8.8255E-002 | 2.9117E+000 |
| | | | | | 1 | 1 | 1.4600E+000 | 3.0368E-003 | 8.0073E-002 | 2.9199E+000 |
| | | | | | 1 | 10 | 1.4750E+000 | 4.9695E-003 | 4.9946E-002 | 2.9501E+000 |
| | | | | | 10 | | 1.0433E+001 | 1.2736E-002 | 1.3341E-001 | 2.8666E+000 |
| | | | | | 10 | 1 | 1.0436E+001 | 1.3204E-002 | 1.2891E-001 | 2.8711E+000 |
| | | | | | 10 | 10 | 1.0449E+001 | 1.6838E-002 | 1.0216E-001 | 2.8978E+000 |
| | | | | | 10 | 100 | 1.0476E+001 | 3.7081E-002 | 4.7391E-002 | 2.9526E+000 |
| | | | | | 100 | | 1.0043E+002 | 1.0965E-001 | 1.4837E-001 | 2.8516E+000 |
| | | | | | 100 | 1 | 1.0043E+002 | 1.1018E-001 | 1.4769E-001 | 2.8523E+000 |
| | | | | | 100 | 10 | 1.0043E+002 | 1.1483E-001 | 1.4200E-001 | 2.8580E+000 |
| | | | | | 100 | 100 | 1.0045E+002 | 1.5377E-001 | 1.0734E-001 | 2.8927E+000 |
| | | | | | 100 | 1000 | 1.0048E+002 | 3.5811E-001 | 4.7067E-002 | 2.9529E+000 |
| 950 | 7.2989E+003 | 1.0846E+004 | 2.0907E-002 | 3.1923E-003 | | | | | | |
| | | | | | | | 4.8836E-001 | 4.1691E-003 | 2.3278E-002 | 2.9767E+000 |
| | | | | | | 1 | 4.8972E-001 | 4.7361E-003 | 2.0566E-002 | 2.9794E+000 |
| | | | | | 1 | | 1.4821E+000 | 8.2354E-003 | 3.5781E-002 | 2.9642E+000 |
| | | | | | 1 | 1 | 1.4838E+000 | 9.1137E-003 | 3.2406E-002 | 2.9676E+000 |
| | | | | | 1 | 10 | 1.4900E+000 | 1.4841E-002 | 2.0059E-002 | 2.9799E+000 |
| | | | | | 10 | | 1.0473E+001 | 3.7973E-002 | 5.4226E-002 | 2.9458E+000 |
| | | | | | 10 | 1 | 1.0474E+001 | 3.9359E-002 | 5.2356E-002 | 2.9476E+000 |
| | | | | | 10 | 10 | 1.0479E+001 | 5.0128E-002 | 4.1285E-002 | 2.9587E+000 |
| | | | | | 10 | 100 | 1.0491E+001 | 1.1020E-001 | 1.8941E-002 | 2.9811E+000 |
| | | | | | 100 | | 1.0047E+002 | 3.2600E-001 | 6.0465E-002 | 2.9395E+000 |
| | | | | | 100 | 1 | 1.0047E+002 | 3.2757E-001 | 6.0181E-002 | 2.9398E+000 |
| | | | | | 100 | 10 | 1.0047E+002 | 3.4137E-001 | 5.7796E-002 | 2.9422E+000 |
| | | | | | 100 | 100 | 1.0048E+002 | 4.5697E-001 | 4.3389E-002 | 2.9566E+000 |
| | | | | | 100 | 1000 | 1.0049E+002 | 1.0636E+000 | 1.8800E-002 | 2.9812E+000 |
| 1000 | 8.7666E+003 | 9.4920E+003 | 1.2118E-002 | 8.4105E-003 | | | | | | |
| | | | | | | | 4.9321E-001 | 1.1057E-002 | 1.3578E-002 | 2.9864E+000 |
| | | | | | | 1 | 4.9401E-001 | 1.2549E-002 | 1.1989E-002 | 2.9880E+000 |
| | | | | | 1 | | 1.4896E+000 | 2.1803E-002 | 2.0853E-002 | 2.9791E+000 |
| | | | | | 1 | 1 | 1.4906E+000 | 2.4113E-002 | 1.8879E-002 | 2.9811E+000 |
| | | | | | 1 | 10 | 1.4942E+000 | 3.9193E-002 | 1.1665E-002 | 2.9883E+000 |
| | | | | | 10 | | 1.0484E+001 | 1.0037E-001 | 3.1602E-002 | 2.9684E+000 |
| | | | | | 10 | 1 | 1.0485E+001 | 1.0402E-001 | 3.0507E-002 | 2.9695E+000 |
| | | | | | 10 | 10 | 1.0488E+001 | 1.3238E-001 | 2.4032E-002 | 2.9760E+000 |
| | | | | | 10 | 100 | 1.0494E+001 | 2.9063E-001 | 1.1001E-002 | 2.9890E+000 |
| | | | | | 100 | | 1.0048E+002 | 8.6119E-001 | 3.5255E-002 | 2.9647E+000 |
| | | | | | 100 | 1 | 1.0048E+002 | 8.6533E-001 | 3.5089E-002 | 2.9649E+000 |
| | | | | | 100 | 10 | 1.0048E+002 | 9.0168E-001 | 3.3690E-002 | 2.9663E+000 |
| | | | | | 100 | 100 | 1.0049E+002 | 1.2062E+000 | 2.5257E-002 | 2.9747E+000 |
| | | | | | 100 | 1000 | 1.0049E+002 | 2.8043E+000 | 1.0917E-002 | 2.9891E+000 |
| 1050 | 1.0233E+004 | 8.1585E+003 | 7.4028E-003 | 2.0013E-002 | | | | | | |
| | | | | | | | 4.9585E-001 | 2.6448E-002 | 8.3097E-003 | 2.9917E+000 |
| | | | | | | 1 | 4.9633E-001 | 2.9996E-002 | 7.3363E-003 | 2.9927E+000 |
| | | | | | 1 | | 1.4936E+000 | 5.2147E-002 | 1.2744E-002 | 2.9873E+000 |
| | | | | | 1 | 1 | 1.4942E+000 | 5.7641E-002 | 1.1538E-002 | 2.9885E+000 |
| | | | | | 1 | 10 | 1.4964E+000 | 9.3510E-002 | 7.1292E-003 | 2.9929E+000 |
| | | | | | 10 | | 1.0490E+001 | 2.4018E-001 | 1.9288E-002 | 2.9807E+000 |
| | | | | | 10 | 1 | 1.0491E+001 | 2.4886E-001 | 1.8621E-002 | 2.9814E+000 |
| | | | | | 10 | 10 | 1.0493E+001 | 3.1631E-001 | 1.4672E-002 | 2.9853E+000 |
| | | | | | 10 | 100 | 1.0497E+001 | 6.9285E-001 | 6.7188E-003 | 2.9933E+000 |
| | | | | | 100 | | 1.0049E+002 | 2.0611E+000 | 2.1514E-002 | 2.9785E+000 |
| | | | | | 100 | 1 | 1.0049E+002 | 2.0709E+000 | 2.1413E-002 | 2.9786E+000 |
| | | | | | 100 | 10 | 1.0049E+002 | 2.1574E+000 | 2.0560E-002 | 2.9794E+000 |
| | | | | | 100 | 100 | 1.0049E+002 | 2.8820E+000 | 1.5418E-002 | 2.9846E+000 |
| | | | | | 100 | 1000 | 1.0050E+002 | 6.6846E+000 | 6.6670E-003 | 2.9933E+000 |

Table A.2. The Minimum Amounts of Chlorine Required to Prevent the Conversion of More Than 1% of $U_3O_8$ to $UCl_4$ (Eq. 32).

| T(°K) | $\Delta F_5$ | $\Delta F_8$ | $K_5$ | $K_8$ | $N_{1G}$ | $N_{Cl_2}$ |
|---|---|---|---|---|---|---|
| 550 | 4.93646E+003 | 5.21116E+003 | 1.09088E-002 | 8.48370E-003 | | .83 |
| 550 | 4.93646E+003 | 5.21116E+003 | 1.09088E-002 | 8.48370E-003 | 1 | .81 |
| 550 | 4.93646E+003 | 5.21116E+003 | 1.09088E-002 | 8.48370E-003 | 10 | .67 |
| 550 | 4.93646E+003 | 5.21116E+003 | 1.09088E-002 | 8.48370E-003 | 100 | .25 |
| 560 | 4.63913E+003 | 5.25144E+003 | 1.54487E-002 | 8.90938E-003 | | .77 |
| 560 | 4.63913E+003 | 5.25144E+003 | 1.54487E-002 | 8.90938E-003 | 1 | .74 |
| 560 | 4.63913E+003 | 5.25144E+003 | 1.54487E-002 | 8.90938E-003 | 10 | .57 |
| 560 | 4.63913E+003 | 5.25144E+003 | 1.54487E-002 | 8.90938E-003 | 100 | .09 |
| 570 | 4.34232E+003 | 5.29032E+003 | 2.16027E-002 | 9.35200E-003 | | .70 |
| 570 | 4.34232E+003 | 5.29032E+003 | 2.16027E-002 | 9.35200E-003 | 1 | .66 |
| 570 | 4.34232E+003 | 5.29032E+003 | 2.16027E-002 | 9.35200E-003 | 10 | .44 |
| 570 | 4.34232E+003 | 5.29032E+003 | 2.16027E-002 | 9.35200E-003 | 100 | .00 |
| 580 | 4.04601E+003 | 5.32780E+003 | 2.98477E-002 | 9.81209E-003 | | .61 |
| 580 | 4.04601E+003 | 5.32780E+003 | 2.98477E-002 | 9.81209E-003 | 1 | .56 |
| 580 | 4.04601E+003 | 5.32780E+003 | 2.98477E-002 | 9.81209E-003 | 10 | .30 |
| 580 | 4.04601E+003 | 5.32780E+003 | 2.98477E-002 | 9.81209E-003 | 100 | .00 |
| 590 | 3.75019E+003 | 5.36389E+003 | 4.07734E-002 | 1.02902E-002 | | .51 |
| 590 | 3.75019E+003 | 5.36389E+003 | 4.07734E-002 | 1.02902E-002 | 1 | .45 |
| 590 | 3.75019E+003 | 5.36389E+003 | 4.07734E-002 | 1.02902E-002 | 10 | .16 |
| 590 | 3.75019E+003 | 5.36389E+003 | 4.07734E-002 | 1.02902E-002 | 100 | .00 |
| 600 | 3.45483E+003 | 5.39863E+003 | 5.51007E-002 | 1.07868E-002 | | .39 |
| 600 | 3.45483E+003 | 5.39863E+003 | 5.51007E-002 | 1.07868E-002 | 1 | .32 |
| 600 | 3.45483E+003 | 5.39863E+003 | 5.51007E-002 | 1.07868E-002 | 10 | .02 |
| 600 | 3.45483E+003 | 5.39863E+003 | 5.51007E-002 | 1.07868E-002 | 100 | .00 |
| 610 | 3.15992E+003 | 5.43200E+003 | 7.37036E-002 | 1.13026E-002 | | .26 |
| 610 | 3.15992E+003 | 5.43200E+003 | 7.37036E-002 | 1.13026E-002 | 1 | .18 |
| 610 | 3.15992E+003 | 5.43200E+003 | 7.37036E-002 | 1.13026E-002 | 10 | .00 |
| 610 | 3.15992E+003 | 5.43200E+003 | 7.37036E-002 | 1.13026E-002 | 100 | .00 |
| 620 | 2.86545E+003 | 5.46404E+003 | 9.76322E-002 | 1.18381E-002 | | .13 |
| 620 | 2.86545E+003 | 5.46404E+003 | 9.76322E-002 | 1.18381E-002 | 1 | .05 |
| 620 | 2.86545E+003 | 5.46404E+003 | 9.76322E-002 | 1.18381E-002 | 10 | .00 |
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