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**Practical Application of Thermodynamics to Plutonium
Process Reactions at High Temperature**

by

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INTRODUCTION

The important high temperature reactions for processing plutonium involve equilibria between the liquid metal and a fused salt system. In almost all of these processes, the kinetics are rapid, and equilibria are of overwhelming importance. The attainment of equilibrium is usually faster by many orders of magnitude in liquid phases than in solid phases. For example the self diffusion coefficient of Pb in solid lead is $5.5 \times 10^{-10} \text{ cm}^2/\text{sec}$ at 597°K [1]. In liquid lead at 616°K the self diffusion coefficient is $2.6 \times 10^{-5} \text{ cm}^2/\text{sec}$ [2]. Therefore, the application of appropriate thermodynamic data and estimates are of major importance in selecting the proper reaction system.

Examples of high temperature plutonium processes where thermodynamic considerations are of principal importance are (1) bomb reduction of plutonium halides by an active metal such as calcium, (2) electrorefining of liquid plutonium in fused salt media, and (3) extraction of impurities such as radionuclides from molten plutonium into fused salt media. These three processes represent varying degrees of the equilibrium reaction. Although they are superficially different, they are best understood by considering the individual metal-salt phase heterogeneous equilibria. The reaction of principal importance is represented by the generalized equation

where X is either a halogen or oxygen. If the process reaches equilibrium, the standard free energy change for equation (1) at temperature T, can be used to calculate the equilibrium ratio of the activities of reactants and products by the standard manner:

$$-\Delta F_T^\circ = RT \ln K \quad (2)$$

$$\text{where } K = \frac{a_{\text{MX}} a_{\text{Pu}}}{a_{\text{PuX}} a_{\text{M}}} = \frac{[x_{\text{MX}}][x_{\text{Pu}}]}{[x_{\text{PuX}}][x_{\text{M}}]} \frac{\gamma_{\text{MX}} \gamma_{\text{Pu}}}{\gamma_{\text{PuX}} \gamma_{\text{M}}} \quad (3)$$

$$\text{or } K = K_c K_\gamma$$

In almost all cases, the activity coefficients, γ_i , are not known and their experimental determination would indeed be a monumental if not impossible task. In spite of this, useful estimates of the concentrations at equilibrium can be made by assuming ideal or regular solution behavior or by estimating the activity coefficients from the phase diagrams, when available.

FUSED SALT EXTRACTION PROCESSES

Plutonium fused salt extraction processes can be represented by the generalized equation

Examples of this type process are the removal of impurities from plutonium metal or plutonium metallic fuels and the removal of plutonium metal from uranium. The liquid salt and metal phases are thoroughly mixed at constant temperature for a period of time that is sufficient to insure the attainment of equilibrium.

The purification of Pu-10 atom % Fe "fissium" fuel by fused salt extraction processes has been reported [3,4]. PuCl_3 dissolved in NaCl and MgCl_2 dissolved in either LiCl-KCl or NaCl-KCl were used to extract rare earth impurities from the metal fuel into the salt phase. The total rare earth concentrations were reduced from 3 wt. % to <0.05 wt. % in the liquid metal. The results were in agreement with qualitative predictions based on standard free energy data. The rare earths concentrated in the salt phase and the metals more noble than plutonium, i.e. Fe, Mo and Ru, concentrated in the metal phase. The removal of Ce by PuCl_3 can be written

In the case of MgCl_2 , the MgCl_2 reacted with the large excess of Pu to form PuCl_3 so that the ratio of Ce to Pu in the purified fuel was still dictated by equation (6). Although Ce was reduced to less than detectable amounts in the Pu-Fe alloy, estimates of K_0 can be made. The estimated value is $>1 \times 10^4$. A consideration of the free energy values* given in ref. [5] predicts that the equilibrium constant, K, for reaction (6) at 973°K should be 5×10^4 .

Recent measurements[6] of K_e for the reaction

* The free energy values discussed in this text are the standard Gibbs free energy values.

at 1423°K resulted in a value of 0.7×10^4 . The calculated value of K is again 5×10^4 . For the removal of La from a Pu-Fe fissium alloy an equation similar to (6) can be written. The estimated value of K_c at 973°K is $>.04 \times 10^5$ [4]. The calculated value of K at 973°K is 1.8×10^5 .

In all of the above cases the values of K_c and K are significantly different. However, from the practical viewpoint of predicting process feasibility the calculated values of K afford excellent estimates of K_c . In other cases however, the estimates must be used with extreme caution. For example, studies of the assumed equilibrium

yielded a value of K_c at 1000°K of 227 in a 2.10 mole % PuCl_3 solution [7]. The calculated value of K for reaction (8) at this temperature is 2×10^5 . This large difference between K_c and K would occur if either equation (8) did not represent the true equilibrium or if K_y varied over a wide range. Recent experimental data [8] indicate that the reaction actually is

ELECTROREFINING

A "near equilibrium" process, the LAMEX electrorefining process [8-15], has been developed for producing high purity Pu metal from impure Pu or alloys of Pu-Fe and Pu-Ga on the multikilogram scale. A schematic drawing of the LAMEX cell is given in Fig. 1. During operation, Pu is oxidized at the anode, enters the molten salt electrolyte and is reduced to metal at the cathode. The molten product drains continuously into the annular product collection zone. The theory of operation of the cell is discussed in ref. [7].

Table I, [7], presents data derived from many electrorefining runs. The behavior of impurity elements is compared qualitatively with the behavior predicted on the basis of standard free energy of formation data. In every case qualitative agreement of experiment with prediction was obtained. Metals less noble (more electropositive) than Pu concentrated

Fig. 1. LAMEX electrorefining cell, schematic drawing.

TABLE I
BEHAVIOR OF IMPURITY ELEMENTS IN ELECTROREFINING

<u>Element</u>	<u>$-\Delta F^\circ$, ^a kcal./g. atom Cl</u>	<u>Concentration, p.p.m.</u>		<u>Element Concentrated in</u>
		<u>Feed</u>	<u>Product</u>	
Ni	18	750	10	Anode
Cu	21	100	2	Anode
Ta	22	5,000	80	Anode
Fe	27	25,000	20	Anode
Cr	32	280	<10	Anode
Ga	32	10,000	<25	Anode
Mn	41	70	< 2	Anode
Al	46	2,700	< 5	Anode
U	54	275	<20	Anode
Th	59	365	<10	Anode
Pu	59	-	-	-
Ce	66	527	<25	Salt
Am	67	850	82	Salt

^a $-\Delta F^\circ$ at 1000°K is tabulated. For elements having a multiplicity of oxidation states, the $-\Delta F^\circ$ for the most stable form of the chloride is given.

in the salt phase and the more noble metals concentrated in the anode. Unfortunately the data of Table I permit quantitative comparisons for only a few elements since most of the elements are below the limits of detectability. The Am data however, can be compared with the fused salt extraction data reported above. A value of K_c for reaction (8) of 190, (± 20), was obtained in electrefining experiments at 1000°K in a 2.10 mole % PuCl_3 solution. This value of K_c approaches the value 227 which was obtained at 2.10 mole % PuCl_3 in the fused salt extraction described above [7].

The electrefining of the Pu-Fe fuels irradiated to 0.1% burnup gave K_c values of 1×10^4 for Ce and 1×10^3 for Nd at 1000°K. The calculated values of K are 4×10^4 and 4×10^5 for Ce and Nd, respectively.

The LAMEX process for electrefining Pu-Fe and Pu-Ga alloys affords an interesting example of the use of phase diagrams for optimizing the yield of a process and affording a means for control of product purity. To illustrate these points consider the case of electrefining a Pu-10 atom % Fe alloy. Since only Pu will be dissolved at the anode, the Fe concentration will increase continuously during the electrefining. From the Pu-Fe phase diagram [16], this increase will result in phase changes in the anode at all temperatures lower than 1809°K. For example, at 1013°K, the anode will be a single phase liquid up to ~25 atom % Fe, liquid plus solid PuFe_2 up to 66.7 atom % Fe and completely solid at 66.7 atom % Fe. As long as the Fe concentration is less than 25 atom %, there should be essentially no significant polarization of a well-stirred anode. At this stage of the electrefining process the net reaction is

and the free energy change is

$$\Delta F = -RT \ln (a_{\text{Pu anode}}) \quad (11)$$

Since the initial plutonium anode atom fraction is 0.9, the free energy change is small.

When the Fe concentration reaches 25 a/o, the PuFe_2 solid phase appears. Unless the anode is stirred well, this solid phase will float in the anode surface, thereby producing a polarized anode. However, polarization can be minimized by stirring as long as some liquid phase remains. As the limit of this two phase region is approached, it becomes less possible to maintain a well-stirred anode, and serious anode polarization

occurs. When the anode is seriously polarized, the net electrorefining reaction is

which corresponds to a potential

$$E = 0.0291 \ln (a_{\text{Pu}})_{\text{solid anode surface}} \quad (13)$$

Generally the activity of Pu in the polarized anode surface will be considerably less than unity, which results in a measurable e.m.f. for the cell. For example, when

$(a_{\text{Pu}})_{\text{solid anode surface}}$ is 10^{-3} , E is -0.20 volt.

During the initial stages of electrorefining, while there is a stirred liquid Pu anode, the cell can be operated at high anode current densities that are required for reasonable processing times. However, after the anode solidifies, the same high anode current densities can be maintained only by dissolving Fe at the anode. (The diffusion of Pu in the solid anode is much too slow to meet the high current density requirements.) Therefore, the electrorefining must be terminated before a significant amount of Fe is dissolved anodically, if a pure Pu product is to be achieved. This condition is indicated by a rapid rise in the back e.m.f. of the cell, corresponding to equation (13).

The experimental control of product purity and anode depletion was in general agreement [15], with the theory. Theory predicts serious anode polarization at Fe concentration $\cong 66.7$ atom % Fe. The experiments gave an average value of 47%. Although this value is smaller than expected, the extremely slow rate of diffusion of plutonium in the anode at the end of a run and the physical appearance of the anode residue show that the anode is actually in a "paste-like" condition at the termination of the electrorefining. For the case of electrorefining Pu-Ga alloys at 1000°K , the phase diagram [17] predicts anode solidification at 24 atom % Ga. The experiments gave a value of 23 atom % Ga.

BOMB REDUCTION PROCESSES

Baker's process for producing Pu metal by the bomb reduction of PuF_4 by Ca [18] is the primary method used by all of the major plutonium laboratories in the United States. A recent literature survey by Conner [19] provides an excellent summary of the refinements which have been made to this process. In the bomb reduction, PuF_4 and Ca are mixed in a refractory lined metal container and heated until the reduction reaction is initiated. To obtain good yields the metal must separate cleanly from the salt. To realize the latter condition both metal and salt phases must be in the liquid state. The attainment of equilibrium in this process is doubtful. Although the temperature attained in the bomb reduction is very high, $\sim 1900^\circ\text{K}$ [20] the components are in the liquid state for only a brief period of time [20]. Nevertheless thermodynamic considerations can be applied to bomb reduction processes and indeed such calculations are useful in estimating both the extent of a proposed reaction and the heat requirements necessary to yield a liquid metal-salt system.

Table II lists some thermodynamic properties of reactions which have been studied by various investigators. The maximum temperature rise was estimated by assuming adiabatic conditions in the reduction process [21].

Table II illustrates several interesting points. Although the free energy change for all of the reactions listed predict favorable production of Pu metal, only reactions (1), (2), (3), (6) and (8) yield sufficient heat to produce metal and molten slag without the application of additional heat. PuF_4 has been reduced successfully to metal by Li [28], Ca [18] and Ba [28]. PuF_3 has been reduced successfully to metal by Li [29]. Successful reductions of PuF_3 by Ca required either an I_2 booster [18] or additional external heating [34]. Quantitative reduction of PuCl_3 by Ca required an iodine booster [18, 31]. It has been reported that PuBr_3 and PuI_3 can be reduced by Ca [29], but details of the procedure are not available. Reductions of CaPuF_6 by Li and Ca resulted in high reduction efficiencies but poor separation of metal globules from the slag [29]. Reduction of Cs_2PuCl_6 resulted in metal powders [29]. Attempts to prepare coalesced Pu metal from PuO_2 have been unsuccessful, but small spherical particles of Pu were produced by the heating of PuO_2 with Ca chips for 15 min. at 1273°K [30]. Metal powders have been produced by the reduction of PuO_2 with Ca in a CaCl_2 flux and with Li in a LiCl flux [29]. The results of these studies are in good agreement with the thermodynamic estimates.

TABLE II

Bomb Reduction Reactions

Reaction	$-\Delta F^\circ$ 1000°K kcal	$-\Delta H^\circ$ 298°K kcal	Max. Temp. Rise °K	Slag M. P. (a) °K
(1) $\text{PuF}_4 + 4 \text{ Li} = \text{Pu} + 4 \text{ LiF}$	136	158.4	2200	1123
(2) $\text{PuF}_4 + 2 \text{ Ca} = \text{Pu} + 2 \text{ CaF}_2$	148	156.6	2450	1691
(3) $\text{PuF}_4 + 2 \text{ Ba} = \text{Pu} + 2 \text{ BaF}_2$	140	148	2450	1866
(4) $\text{PuF}_3 + 3/2 \text{ Ca} = \text{Pu} + 3/2 \text{ CaF}_2$	56	60.8	1160	1691
(5) $\text{PuF}_3 + 3 \text{ Li} = \text{Pu} + 3 \text{ LiF}$	47	62	844	1120
(6) $\text{PuCl}_3 + 3/2 \text{ Ca} = \text{Pu} + 3/2 \text{ CaCl}_2$	57	56.3	1100	1055
(7) $\text{PuBr}_3 + 3/2 \text{ Ca} = \text{Pu} + 3/2 \text{ CaBr}_2$	--	42.8	835	1033
(8) $\text{PuI}_3 + 3/2 \text{ Ca} = \text{Pu} + 3/2 \text{ CaI}_2$	--	60	1250	1013
(9) $\text{CaPuF}_6 + 4 \text{ Li} = \text{Pu} + 4 \text{ LiF} + \text{CaF}_2$	--	--	--	1040
(10) $\text{CaPuF}_6 + 2 \text{ Ca} = \text{Pu} + 3 \text{ CaF}_2$	--	--	--	1691
(11) $\text{Cs}_2\text{PuF}_6 + 4 \text{ Li} = \text{Pu} + 4 \text{ LiF} + 2 \text{ CsF}$	--	--	--	970
(12) $\text{Cs}_2 \text{ PuF}_6 + 2 \text{ Ca} = \text{Pu} + 2 \text{ CaF}_2 + 2 \text{ CsF}$	--	--	--	--
(13) $\text{PuO}_2 + 4 \text{ Li} = \text{Pu} + 2 \text{ Li}_2\text{O}$	18	39.1	185	2000
(14) $\text{PuO}_2 + 2 \text{ Ca} = \text{Pu} + 2 \text{ CaO}$	54	57.4	500	2873
(15) $\text{PuO}_2 + \text{Mg} = \text{Pu} + 2 \text{ MgO}$	34	41.7	55	3075

(a) Melting Point

Sources of Data

Thermodynamic and thermochemical properties of the elements, oxides, chlorides and fluorides [5].

Thermodynamic and thermochemical properties of the bromides and iodides [22]

CaF_2 - LiF melting points [23].

CsF - LiF melting points [24].

Heats of transition and heat capacity of Pu [25].

The heat required to melt the slag may be decreased by reducing the melting point of the slag. Additional heat may be provided either by external heating or by a booster reaction such as

The heat loss will obviously be greater in small scale reductions than in large ones. If a booster reaction is used to supply additional heat, the amount of booster used will depend on the scale and geometry of the system. For example, the reduction of PuF_4 on the 2 kg scale can be done successfully without a booster [27]. Reductions on the 160 g scale are made with a booster [18].

If equilibrium conditions existed during the bomb reduction of PuF_4 by excess Ca, little or no separation of plutonium from impurities could be expected by virtue of metal salt reactions discussed above. Metals which are more soluble in Ca than in Pu could be expected to concentrate in the Ca metal phase if an excess of Ca is used.

The degree of purification obtained during the bomb reduction of PuF_4 by Ca is a matter of controversy. Separation to some degree of Na, Cu, Ag, B, Sn, Pb, Bi [32] and of Mg, Al, Si, Ni, Fe [33] from Pu has been reported. Other data show no separation for Mg, Al, Ni, Fe [34]. Reduction of PuF_3 by Ca results in little or no separation of Al, Cr and Ni [35]. These conflicting results are probably due to the fact that equilibrium conditions are not achieved in bomb reductions. Kinetic effects are extremely important and a direct comparison of data would require exact duplication of experimental conditions.

OXIDE DROSSING OF LIQUID PLUTONIUM FUELS

The remaining processes to be considered are characterized by reactions between a liquid metal phase and a solid phase. Reactions proceed quite slowly and generally the processes do not reach equilibrium. Kinetic considerations in the oxide are most important and indeed much of the development work on these processes has been concerned with studying solid phase kinetics.

Oxide drossing methods have been studied extensively with uranium fuel [36-39]. The method consists of holding the impure molten metal in a refractory oxide crucible for several hours to accomplish selective oxidation of impurities. For the removal of Ce from Pu-rich fuels by MgO at 1700°K the idealized reactions can be written as

Small scale experiments with MgO have shown that temperatures of ~1700°K were required to achieve reasonable rates of removal of Ce and La from liquid Pu-Fe and Pu-Co fuels [41,3]. Similar results were obtained with ZrO₂, Table III [41]. A comparison of ZrO₂ and MgO as reaction crucibles is given in Table IV [41]. ZrO₂ removed La more rapidly from Pu-Fe fissium fuel than did MgO. However, removal of Ce was very slow in both media. Essentially complete removal of Ce was achieved in MgO in 8 hrs. at the expense of high losses (28%) of plutonium to the crucible as shown in Table V. The behavior of the "noble" elements Fe, Zr, Mo, and Ru in all cases was in agreement with standard free energy estimates.

TABLE III

Effect of Drossing Temperature on Purification of Pu-10 atom % Fe Fissium Alloy
by Melting in ZrO_2 Crucibles

Temp., °K	Time, Hr.	C/C_o^a					
		Fe	Zr	Mo	Ru	Ce	La
1273	4	1.01	1.00	1.04	1.01	0.99	0.97
1473	4	0.99	0.99	0.96	1.00	0.79	0.46
1673	4	1.02	0.98	1.09	0.99	0.39	0.03

$^a C$ = grams of element per gram of plutonium after reaction.

C_o = grams of element per gram of plutonium before reaction.

TABLE IV

Effect of Drossing Time at 1673°K on Purification of Pu-10 atom % Fe Fissium Alloy and Recovery of Plutonium

Time Hr.	Crucible	C/C _o						Pu Recovery, %
		Fe	Zr	Mo	Ru	Ce	La	
2	MgO	0.90	0.93	0.95	1.01	0.57	0.40	>91
2	ZrO ₂	1.00	0.98	0.95	1.03	0.63	0.16	93
4	ZrO ₂	1.02	0.98	1.09	0.99	0.39	0.03	91
5	MgO	1.02	0.98	0.98	1.07	0.40	0.13	93
8.3	MgO	1.02	0.81	0.85	1.00	<0.006	<0.01	72

REFRACTORY OXIDES AND FLUORIDES AS CONTAINER MATERIALS FOR PLUTONIUM

An examination of standard free energy of formation data for oxides at 1000°K suggests the use of MgO, ThO₂ and CaO as container materials for molten Pu [5]. The reaction of MgO with Pu in an inert atmosphere, 1 atmosphere pressure, at 1000°K can be represented as

It is assumed that Pu₂O₃ (s) is immiscible with MgO (s) and the activity of Pu(ℓ) is ~1, the equilibrium activity of Mg in Pu is 6.6 x 10⁻³. From the Pu-Mg phase diagram [42] and the assumption that Mg behaves ideally in the Mg-rich liquid, the activity coefficient of Mg in Pu-rich liquid is estimated to be ~20. The equilibrium concentration of Mg in Pu would therefore be ~33 parts of Mg per million parts of Pu, wt. basis. The corresponding amount of oxide formed, would be 22 parts of O per million parts Pu. These estimates can be compared with results obtained in the electrorefining process where MgO is contacted for several days with Pu(ℓ). The Mg concentration in the product metal is equal to or less than 5 p.p.m. and the O concentration is ~20 p.p.m.

Similar estimates for CaO and CaF₂ as container materials for Pu show that the equilibrium activity of Ca in Pu for both cases will be ~1 x 10⁻⁴ at 1000°K and 1 atm pressure. Similarly, the estimated equilibrium activity of Th in Pu is ~2 x 10⁻⁷.

Glossary of Symbols and Terms

ΔF_T° Gibbs free energy change, standard state conditions for reactants and products, at temperature T

ΔF_T Gibbs free energy change, at temperature T

ΔH_T° Heat of reaction, standard state conditions for reactants and products, at temperature T

a_i activity of component i

γ_i activity coefficient of component i

x_i mole fraction of component i

$$a_i = \gamma_i x_i$$

REFERENCES

- [1] Hevesy, G. von, Seith, W., Keil, A., Z Physik. 79, 197 (1932).
- [2] Groh, J., Hevesy, G. von, Ann. Physik (4) 63, 85 (1926).
- [3] Leary, J. A., et al., 2nd International Conference on Peaceful Uses of Atomic Energy, United Nations, Vol. 17, 376-382, Geneva (1958).
- [4] Mullins, L. J., Leary, J. A., and Maraman, W. J., Industrial and Engineering Chemistry 52, 227 (1960).
- [5] Glassner, A., The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500 K, ANL-5750 (1957).
- [6] Bennett, G. A., Burris, L. Jr., Vogel, R. C., ANL-6918 (1964).
- [7] Mullins, L. J., and Leary, J. A., "Fused Salt Electrorefining of Molten Plutonium and Its Alloys", Ind. Eng. Chem. Process Design Develop. (in press).
- [8] Mullins, L. J., Beaumont, A. J., Leary, J. A., LA Report, (in press).
- [9] Mullins, L. J., Leary, J. A., and Bjorklund, C. W., LAMS-2441 (1960).
- [10] Mullins L. J., Leary, J. A., Morgan, A. N., and Maraman, W. J., LA-2666 (1962).
- [11] Mullins, L. J., Leary, J. A., Morgan, A. N., and Maraman, W. J., Ind. Eng. Chem. Process Design Develop., 2, 20 (1963).
- [12] Mullins, L. J., and Leary, J. A., Proceedings First Australian Conference Electrochemistry, Pergamon Press, Oxford, England, 923 (1964).
- [13] Mullins, L. J., Leary, J. A., and Morgan, A. N., LA-3029 (1963).
- [14] Mullins, L. J., Leary, J. A., and Morgan, A. N., LA-2758 (1962).
- [15] Mullins, L. J., Leary, J. A., and Morgan, A. N., LA-2981 (1963).
- [16] Schonfeld, F. W., Cramer, E. M., Miner, W. N., Ellinger, F. H., Coffinberry, A. S., Progr. Nucl. Energy, Ser. V, Vol. 2, 585 (1959),
- [17] Ellinger, F. H., Land, C. C., Struebing, V. O., J. Nuclear Materials 12, 226 (1964).
- [18] Baker, R. D., LA-473 (1946).
- [19] Conner, W. V., RFP 356 (1964).
- [20] Weidenbaum, B., Plutonium 1960, ed. E. Grison, W. B. H. Lord, and R. D. Fowler, Cleaver-Hume Press Ltd., 195, London (1961).
- [21] Rand, M. H., and Kubaschewski, O., The Thermochemical Properties of Uranium Compounds, Interscience Publishers, 81 (1963).
- [22] Kubaschewski, O., Evans, E., Metallurgical Thermochemistry, Pergammon Press Ltd. (1956).

- [23] Roake, W. E., J. Electrochem. Soc. 104, 661 (1957).
- [24] Barton, C. J., Bratcher, L. M., McVay, T. N. Grimes, W. R., ORNL 2548, 17 (1959).
- [25] Hultgren, Orr, Anderson, Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys, John Wiley and Sons, Inc. (1963).
- [26] McCreary, W. J., J. Am. Chem. Soc., 77, 2214 (1955).
- [27] Orth, D. A., Ind. Eng. Chem., 2, No. 2, 121-127 (1963).
- [28] Grison, E., Progress in Nuclear Energy, Series V, Vol. 2, Pergammon Press 91-97 (1959).
- [29] Jenkins, I. L., Keen, N. J., Wain, A. C., Extractive and Physical Metallurgy of Plutonium and Its Alloys, ed. W. D. Wilkinson, Interscience 25-42, (1960).
- [30] Runnals, O. J. C., Progress in Nuclear Energy, Series V, Vol. 2, Pergammon Press, 98-118 (1959).
- [31] Rasmussen, M. J., Hopkins, H. H. Jr., Ind. Eng. Chem. 53, No. 6, 453-471 (1961).
- [32] Maraman, W. J., Baker, R. D., Plutonium 1960, ed. E. Grison, W. B. H. Lord, R. D. Fowler, Cleaver-Hume Press Ltd. 214 (1961).
- [33] Johnson, K. W. R., J. Inorg. Nucl. Chem. 9, 200 (1959).
- [34] Anselin, F., Extractive and Physical Metallurgy of Plutonium and Its Alloys, ed. W. D. Wilkinson, Interscience 61-74 (1960).
- [35] Cleveland, J. M., I & EC Process Design Develop., 4, No. 2, 230 (1965).
- [36] Motta, E. E., Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva 1955, p. 542, Vol. 9, 596 United Nations, New York (1956).
- [37] Feder, H. M., Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva 1955, p. 544, Vol. 9, 586, United Nations, New York (1956).
- [38] Feder, H. M., Symposium on the Reprocessing of Irradiated Fuels held at Brussels, Belgium, Book 2, Session IV, TID-7534, 667-718, (1957).
- [39] Burris, L., et. al., 2nd International Conference on the Peaceful Uses of Atomic Energy, United Nations, Vol. 17, Geneva, (1958).
- [40] Leary, J. A., LA-2132 (1957).
- [41] Mullins, L. J., Leary, J. A., and Maraman, W. J., Ind. Eng. Chem. 52, 227 (1960).
- [42] Schonfeld, F. W., The Metal Plutonium, ed. A. S. Coffinberry, W. N. Miner, Univ. of Chicago Press 244, (1961).