A THERMODYNAMIC STUDY
OF THE URANIUM OXYCARBIDE
SYSTEM

A thesis

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ABSTRACT

The maximum solubility of oxygen in the UC lattice and the thermodynamic properties of the resulting U(C,O) phase have been studied using both isothermal and isopiestic techniques in the temperature range of 1473°K to 1648°K. These techniques enabled the U(C,O) to be equilibrated with uranium activities in the range of $1 - 10^{-3}$, and oxygen partial pressures of $4 \times 10^{-26} - 4.4 \times 10^{-35}$ atm. The results indicate that the maximum solubility of oxygen corresponds to the formula $U(C_{0.68},O_{0.32})$. With increasing oxygen content the lattice parameter usually decreases and the lowest lattice parameter value is given by the oxygen saturated UC, and is in the range of 4.951 - 4.952 Å. The maximum solubility of oxygen in the UC lattice is also found to be almost independent of temperature within the range of 1473°K to 1648°K.

Assuming, that the U (C,O) phase is a pseudobinary solid solution of UC and UO; a modified Gibbs-Duhem relationship has been derived in order to calculate the activity coefficients of UC, at various compositions of the pseudobinary solid solutions. The results indicate a negative deviation from Raoult's law.

The activities of carbon were also calculated and employed to calculate the standard free energy of formation values of the U(C,O) phase, and the associated equilibrium partial pressures of carbon monoxide for various compositions and at different temperatures.

Equilibration experiments were also carried out at 1573°K, in which either UC_2 or U_2C_3, were equilibrated with UC, at fixed activities of uranium and oxygen. The results indicated that UC_2 containing oxygen could be more stable than U_2C_3 phase. U_2C_3 was not found to contain any measurable oxygen in its lattice.

A tentative phase relationship for the U - C - O, system at 1573°K is also proposed.

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CHAPTER 1

Introduction

The continuous trend of nuclear power reactors towards higher operating temperature, higher ratings and higher fuel burn up ensures the importance of ceramic materials as fuels for future systems. The carbides and oxides of uranium are being carefully evaluated for use as potential nuclear fuels. Uranium monocarbide in particular has several attractive features. It has a density 24% higher than that of uranium dioxide (which is already used as a satisfactory fuel for many of the reactors), and an appreciable thermal conductivity at higher temperatures. Dimensional stability under irradiation is also encouraging (1,2). All these properties are important from a nuclear viewpoint.

Although, uranium monocarbide has got some useful properties which offer advantages over uranium dioxide (UO_2) as a nuclear fuel, certain problems remain:

(i) Corrosion resistance is inferior to UO_2.

(ii) Commercial preparation is costly.

(iii) The carbide is easily contaminated by oxygen and nitrogen from the atmosphere.

It has recently been found that uranium monocarbide (UC), is attacked by hot water and in fact cannot be stored for any appreciable length of time in ordinary moist air. However organic coolant moderators, i.e. the di- and terphenyls appear to be fairly inert to UC, (2.A.). Similarly corrosion by sodium-potassium alloy (NaK) is caused by residual oxygen in the NaK and not by the liquid metal alloy itself.

The principal problem in the projected use of uranium-monocarbide as a nuclear fuel is, in establishing a method for cheap commercial preparation. The two main methods of preparation are:

(a) Reaction of uranium metal at high temperature with carbon in some form, e.g. graphite, carbon black and methane.

(b) Reaction of uranium dioxide with carbon at high temperature.

The reduction of the uranium dioxide with carbon appears to be economically attractive. However it is expensive to eliminate impurities such as oxygen and nitrogen introduced during this preparation and subsequent processing. Accurate thermodynamic data are needed to know the effect of such impurities. It is obviously important, therefore, to study the uranium-carbon-oxygen system.

The earlier studies on U - C - O systems revealed the existence of a single uranium oxycarbide phase. Vaughan, et al[3]., and Namba, et al[4], reported a uranium oxycarbide (UCO) phase, when they reacted uranium monocarbide (UC), with uranium-dioxide (UO_2) in a temperature range of 1600 - 1800°C. The former investigators reported that nearly fifty per cent of the carbon atoms of UC had been replaced by oxygen, while the latter investigators suggested that nearly eighty per cent of the carbon in UC was replaced by oxygen. The existence of this U(CO) phase was later confirmed by Magnier, et al[5], Stoops and Hamme[6], Brett, et al[7], and Russell[8].

The existence of a substituted solid solution between uranium monocarbide and oxygen is thus well established and most of the investigators agree that in this $U(C_{1-x}O_x)^*$ phase, the maximum value of x lies between 0.25 - 0.35, i.e. approximately 2 wt.% oxygen. The lattice parameter of this phase has been found to be in the range of 4.948 - 4.952 A°, and slightly dependent upon temperature.

However, the available data about the stability and phase boundaries of the uranium oxycarbide phase are very limited. The existence of the U(CO) phase has only been reported in the presence of other phases such as uranium and uranium dioxide and it is not possible to specify at present the appropriate conditions to prepare the single oxycarbide phase.

* The uranium to carbon + oxygen ratio remains very close to unity, hence one may write the formula as $U\,C_{1-x}\,O_x$.

It was therefore, the purpose of the present investigation to study the thermodynamics of the pseudobinary UC and UO system and to determine the following:

(i) The limit of oxygen solubility in the UC lattice by examining the quenched samples equilibrated at 1200 - 1375°C.

(ii) The relationships between the oxygen chemical potentials, activities of uranium and carbon and the condensed phases at 1300°C.

(iii) The relationships between the oxygen chemical potentials and the solubility of oxygen at a fixed activity of uranium at 1200 - 1375°C.

In addition to controlling the activities of the three components, U, C, O, as a function of temperature; the equilibrated samples were subjected to chemical analysis, X-ray diffraction analysis, and metallographic and microprobe examinations to accomplish the above objectives.

CHAPTER 2

Review of Literature

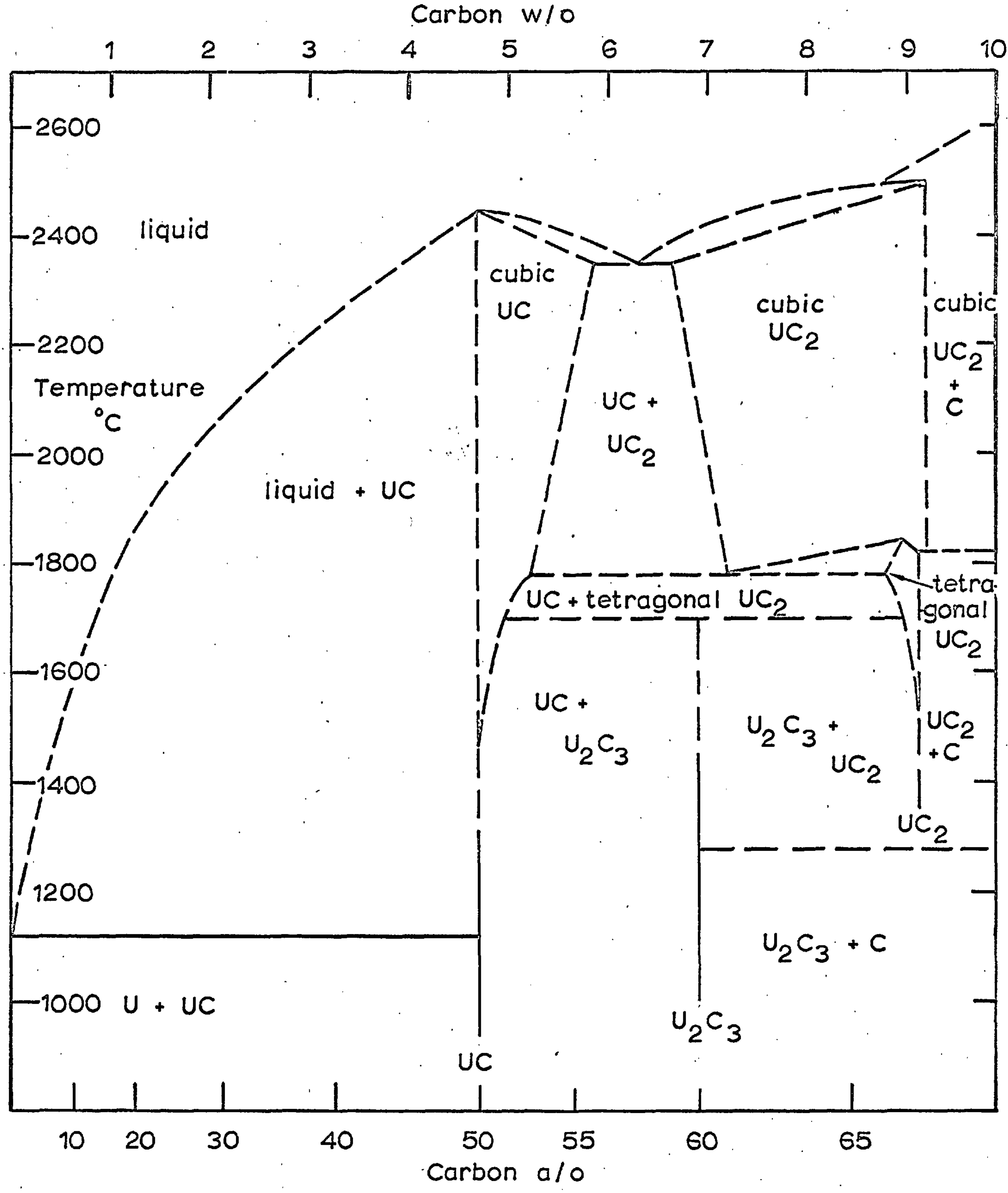
2.A The U-C System.

The U-C system has been the subject of considerable research effort and much literature is available for this binary system. However, the discussion here will be limited primarily to those aspects of the U-C system that are of direct concern in this investigation.

2.A.1 Phase Diagram and Structure.

Chubb and Phillips[11], presented the results of their work in the form of a constitutional diagram which is shown in figure 1. It is seen that they found approximately 2-5 atomic per cent carbon solubility in uranium from 1200 - 1375°C (temperature range in this investigation). For the UC phase at 1300°C they found a range of homogeneity upto nearly fifty atomic per cent. To the right of this region is the U_2C_3 phase, which is not stable above 1700°C, the UC_2 exists at higher temperatures, They reported the melting point of UC as 2450 $\pm$-70°C and the structure as cubic sodium chloride type, with no transformations between the melting point and room temperature. The cubic UC_2 phase was given as the CaF_2 type having a melting point of 2500 $\pm$ 50°C.

However Magnier and Accary[12], while investigating the solubility of uranium in uranium monocarbide found out that uranium-carbon



IG.1 URANIUM - CARBON CONSTITUTIONAL DIAGRAM AFTER CHUBB & PHILLIPS[11]

alloys can exist as a single phase UC, for carbon contents between 48 - 50 atomic per cent. They found out that the maximum solubility of uranium occurs at 1700 ± 30°C, the composition of UC in equilibrium with metallic uranium being $UC_{0.96}$. The proposed phase diagram by these workers is reproduced in figure 2. Bowman,[13] reported that the miscibility gap between UC and UC_2 closes at 1900°C and above this temperature there is a complete miscibility between UC and cubic UC_2. The transition temperature of cubic UC_2 to tetragmal UC_2 he reported 1750 to 1765°C. He also found that UC_2 had a composition range of $UC_{1.87}$ to $UC_{1.93}$.

Buckley[14], presented a revised uranium carbon phase equilibrium diagram. He found that the structure of UC is a defect-lattice with carbon atoms missing from the normal positions in the NaCl type structure. He found that the maximum value of the solubility of uranium in UC is about 1½ atomic per cent at about 2000°C and approaches zero at the eutectic temperature 1116.6°C. During the latter stages of cooling excess uranium is either retained in metastable solution, yielding a carbide with a diminished unit-cell dimension, or if the cooling rate is slow, precipitated as cubic particles about $^{1}/2\,\mu$ in size in the carbide grains. The retrograde solubility curves for UC, as drawn by Buckley, is shown in figure 3.

In general Chubb and Bowman, agree reasonably well on the general aspects of the phase diagram of the U-C system with the exception of the closure of the miscibility gap between UC and UC_2.

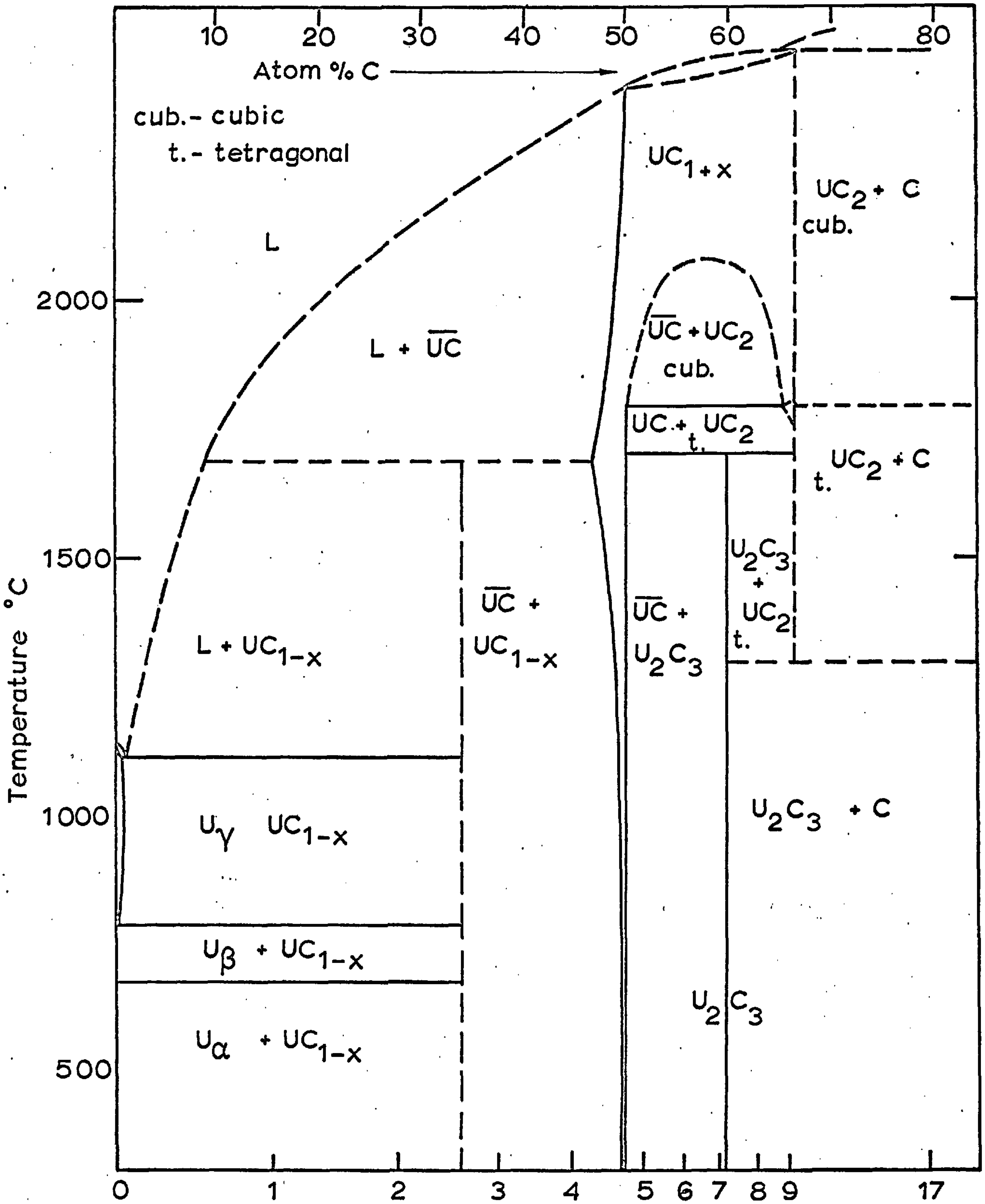


FIG. 2 URANIUM - CARBON CONSTITUTIONAL DIAGRAM AFTER P. MAGNIER & A. ACCARY 12

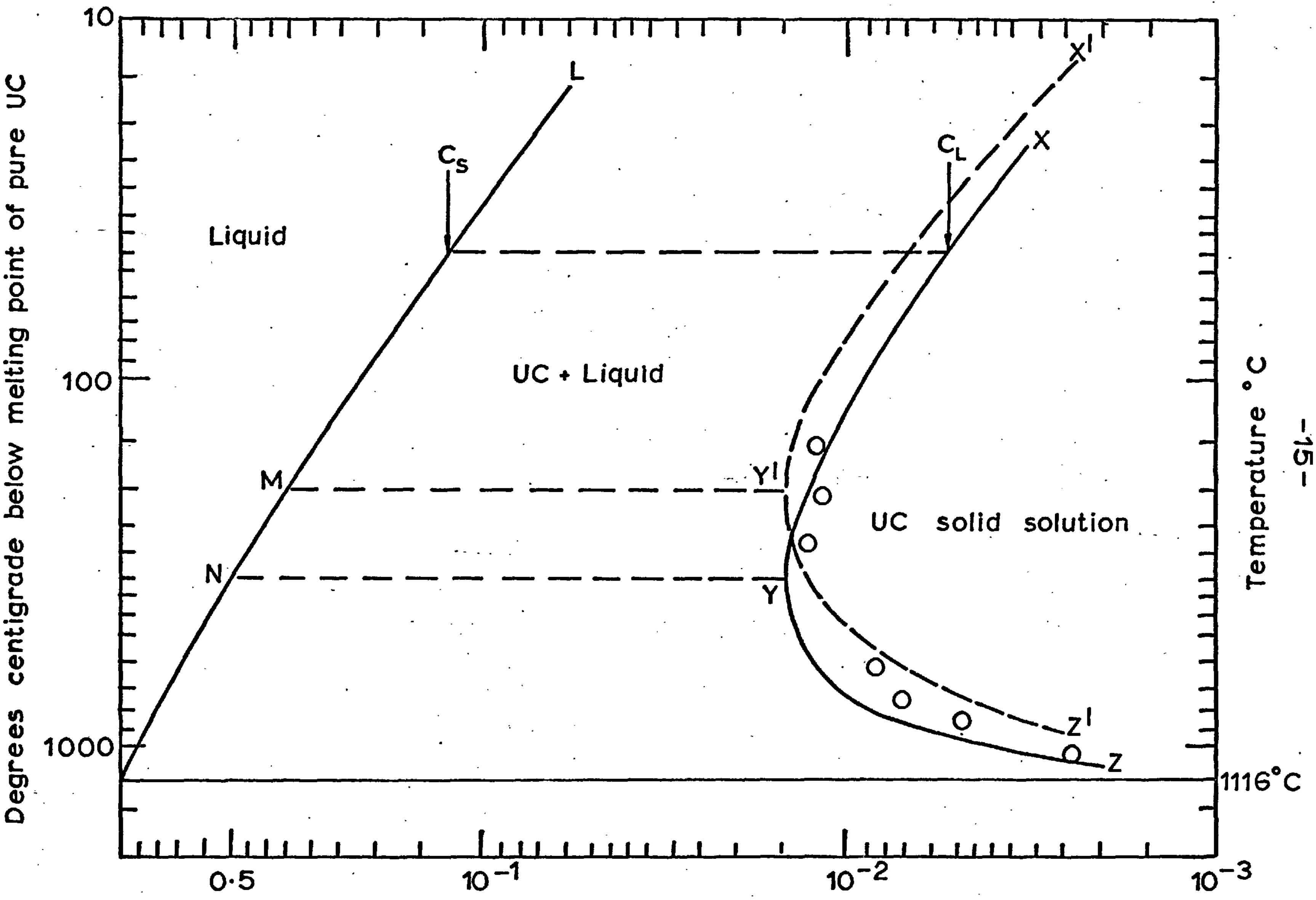


FIG.3 RETROGRADE SOLUBILITY CURVES FOR UC, AFTER BUCKLEY[14].

Since most of the differences in the data occur at a temperature above that of interest in this investigation, no further comments need be made regarding the discrepancy.

It is generally agreed that the uranium sesquicarbide (U_2C_3) phase forms in a sluggish manner and will not appear in the U-C system without special heat treatment or stress. Leitnaker and Witteman[15], reported that U_2C_3 decomposed into UC and UC_2 above 1780°C. These investigators found a region of complete solubility between UC and UC_2. Their determination of the lattice parameter for UC was 4.959 ± 0.001 °A. In the temperature range of 2000-2550°K Leitnaker and Witteman[15], showed that $UC_{1.86}$ lost carbon preferentially by vaporization. They found that $UC_{1.07}$ vaporized congruently and that UC richer in uranium than $UC_{1.07}$, yielded sublimates rich in uranium. Their studies were made in a vacuum of the order of 10^{-7} mm Hg.

Chubb and Dickerson[16], in their work with uranium carbides reported that uranium sesquicarbide (U_2C_3) did not occur in as cast carbide even with 7.0 wt.% carbon. They reported that it is stable below 1800°C and will form when a 7.0 wt.% carbon alloy was annealed at 1100 to 1400°C. Uranium dicarbide (UC_2) was found to be stable from its melting point down to 1500°C, below which temperature it decomposed slowly into U_2C_3 and carbon.

Alcock and Grieveson[17], during their equilibration studies of uranium-gold liquid solution with uranium-carbon alloys (in vacuum in beryllia crucibles fitted with molybdenum lids, at 1500 - 1700°C)found that at **uranium activity**, $3.9 \pm 0.3 \times 10^{-2}$, UC and UC_2 exist in equilibrium. In their studies they did not find any U_2C_3. The free energy giagram established from their equilibration experiments is shown in figure 4. During the I.A.E.A. panel meeting[18] while discussing the results of these investigators, it was assumed that the carbide phase consisted of a mixture of UC and oxygen stabilized "UC_2", as the uranium chemical potentials obtained from these measurements were all -12000 ± 500 cals over the temperature range and no change in this mean value was observed in any of the alloys as a function of carbon content.

Henney and Livey[19], studied the effects of oxygen and nitrogen impurities on the thermodynamic stability of uranium carbides in the presence of carbon. They suggested that at temperatures below 1700°C the solution of oxygen in UC_2 could stabilize this phase, with respect to U_2C_3 and carbon. Recent work[20], however has shown that in the temperature range of 1400 - 1700°C the partial molar free energy of uranium in its monocarbide is quite close to that in the dicarbide and sesquicarbide; and solution of oxygen in UC_2 and UC and nitrogen in UC can lower their free energies sufficiently to cause the disappearance of U_2C_3.Henney[20], also found that U_2C_3 can be formed but only very slowly, by the reactions sintering of uranium-carbon powder compacts at 1500 - 1600°C in vacuum or in an inert gas atmosphere.

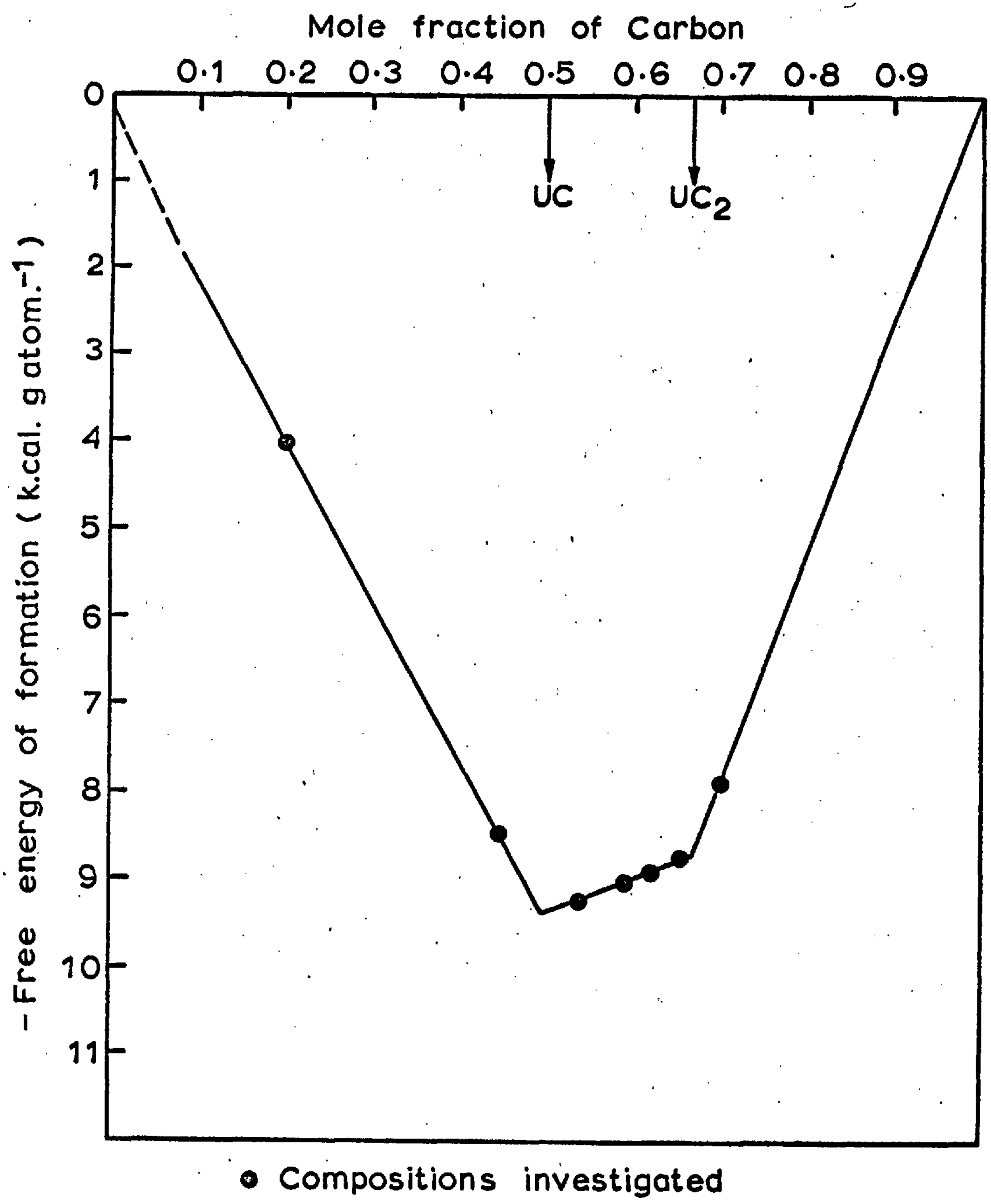


FIG. 4. INTEGRAL FREE ENERGY OF FORMATION CURVE FOR THE URANIUM - CARBON SYSTEM AT 1800°K, AFTER ALCOCK & GRIEVESON [17]

Austin and Gerds[21], have shown that in the absence of free carbon, U_2C_3 can exist in the presence of UO_2 at 1400°C.

Buredick, et al[22]., have found that the solubility of UC_2 in UC amounted to as much as 13.5 mole per cent at 1700°C, and that the solubility of UC in UC_2 was as much as 16 mole per cent at 1700°C.

The structure of uranium monocarbide is universally accepted as cubic with the NaCl structure as shown in figure 5. The most generally accepted lattice parameter for UC is 4.961 Å; however several investigators have reported lattice parameters considerably higher than 4.961 A. Kehl, et al[23]. found lattice parameters as high as 4.976 Å for UC inclusions in uranium metal. They believed that the lattice parameter of 4.961 Å, that is generally accepted, may be too low due to oxygen or nitrogen or both. Litz, et al[24]., and Stoops et al[6]. gave lattice parameters of 4.965 Å and 4.964 Å respectively for uranium monocarbide.

Uranium dicarbide has a body centred tetragonal structure between 1500 - 1800°C. The lattice parameters are

$a = 3.517$ Å $\qquad c = 5.987$ Å

Henney[20], maintains that the lattice parameters for stoichiometric UC_2 having oxygen 0.01 wt.% are $a = 3.525$ Å and $c = 6.000$ Å. At 1820°C the structure transforms to the fluorite (CaF_2) structure similar to UO_2. U_2C_3 has a body centred cubic structure with lattice parameter as 8.088 ± 0.001 Å. The constant value of the lattice parameter of U_2C_3, under various experimental conditions indicates

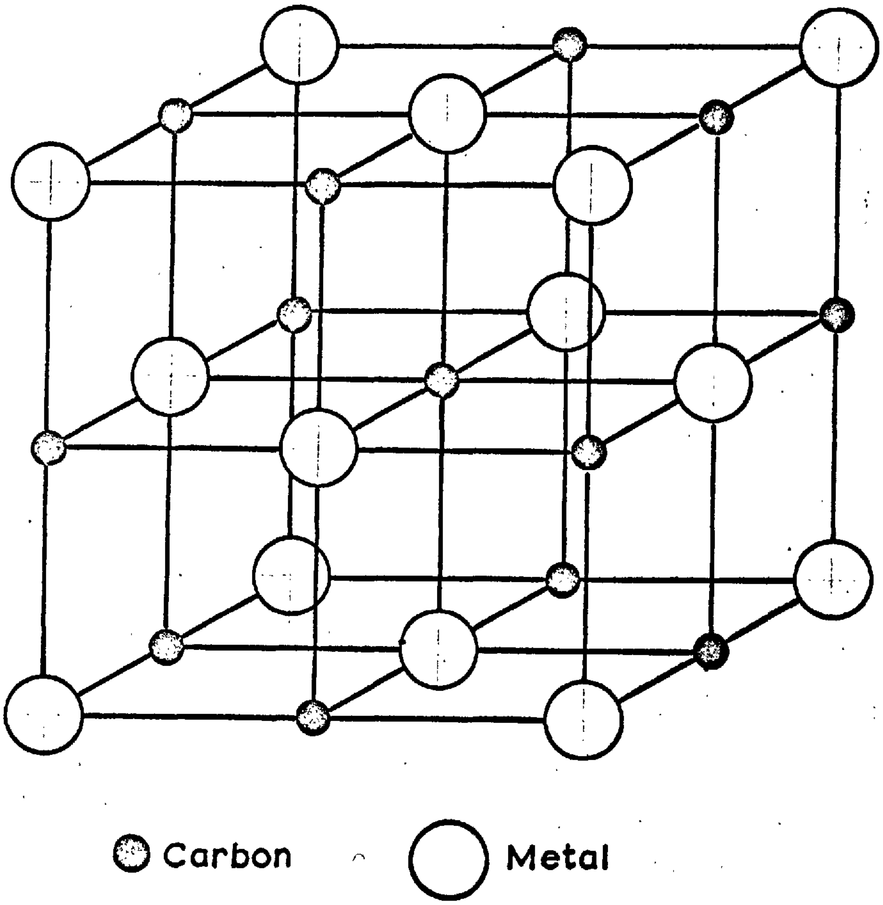


FIG. 5 STRUCTURE OF URANIUM MONOCARBIDE

that it has a very low solubility for oxygen, and an invariant carbon content.

2.A.2 Fabrication Processes

For use in nuclear fuel elements the carbides of uranium must be fabricated into pellets or rods of suitable size, shape, density, purity and grain size. The suitable fabrication techniques can be divided into :

(a) Melting and casting.

(b) Solid state compaction (sintering and hot pressing).

In the melting process the reaction to form the carbide may be allowed to occur in the arc, the common reactions being those between uranium metal and graphite, and between UO_2 and carbon in compacted form. The sintering and hot processing, on the otherhand, generally require a reacted carbide feed. The common methods for producing uranium-monocarbide or uranium-dicarbide powder are :

(i) Reaction between uranium and carbon powders between 1800 - 2600°C.

(ii) Reaction between UO_2 and carbon.

(iii) Reaction between uranium metal and hydrocarbon gas (usually methane).

Other processes have been investigated[25] (e.g. UF_6 + C and UF_6 + Ca + CaC_2) but have shown little promise.

In summarizing the above investigations in the U - C binary system, the following general statements which are particularly pertinent to this investigation may be made :

(a) Uranium will dissolve upto approximately 4-5 atomic per cent carbon at 1375°C.

(b) UC is not of a constant composition as generally believed, as it can accomodate excess uranium atoms. The maximum solubility of uranium takes place at 1700 ± 30°C and composition is $UC_{0.96}$. The solubility of uranium in UC at 1300°C is between 1 - 2 atomic per cent.

(c) Uranium monocarbide has the NaCl cubic structure. The lattice parameter most generally accepted for UC is 4.961 Å; however values as high as 4.976 Å and as low as 4.959 Å have been reported.

(d) Uranium dicarbide is metastable at room temperature. It will not decompose to form U_2C_3 and carbon without annealing or stressing and even then its formation is sluggish.

2.A.3 Thermodynamic Properties of Uranium Carbides

The stability of the various phases in temperature cycling, and for long times at different temperatures is an important technical consideration. However, the accurate thermodynamic data are not only desirable to establish the equilibrium phase diagrams but are also essential for the assessment of various compatability problems and the calculations of the composition of phases, prepared by different preparative routes.

A thermochemical assessment panel meeting was held in Vienna 1962, and they gave the following assessed values of the heats, Free energies and entropies of formation of the uranium-carbides from 298 - 2500°K.

Table 1

T K°	ΔH^{o} (Kcal/mole)	ΔS^{o} (cal $mole^{-1}$ K^{-1})	ΔG^{o} (Kcal/mole)
	$U + C_{(s)} = UC_{(s)}$		
298	- 21.7	+ 1.0	- 22.0
500	- 21.6	+ 1.4	- 22.3
1000	- 21.3	+ 1.8	- 23.1
1500	- 25.2	- 1.6	- 22.8
1750	- 25.1	- 1.5	- 22.5
2000	- 24.9	- 1.4	- 22.1
2500	- 24.6	- 1.2	- 21.6
	$2U + 3C_{(s)} = U_2C_3\,(s)$		
298	- 49.0	- 0.1	- 49.0
500	- 48.8	+ 0.3	- 49.0
1000	- 48.4	+ 0.9	- 49.3
1500	- 56.6	- 6.0	- 47.6
1750	- 56.6	- 5.9	- 46.3
2000	- 56.5	- 5.9	- 44.7
2500	- 56.3	- 5.9	- 41.7
	$U + 2C_{(s)} = UC2_{(s)}$		
298	- 23.0	+ 1.5	- 23.5
500	- 23.1	+ 1.5	- 23.9
1000	- 23.2	+ 1.1	- 24.3
1500	- 27.7	- 2.6	- 23.8
1750	- 27.7	- 2.6	- 23.2
2000	- 27.8	- 2.7	- 22.4
2500	- 24.5	- 1.0	- 22.0

The following values were finally suggested for the standard entropies and heats of formation of the uranium carbides.

Table 2

	UC	U_2C_3	UC_2	UC_xO_y
S_{298}(cal.mole^{-1} $^{\circ}$K)$^{-1}$	14.2±0.2	27.9±3.0	16.2±0.5	16.2±2.0
ΔH°_{298}(kcal/mole)	-21.7±1.0	-49.0±4.0	-23.0±2.0	-28.2±5.0

The heats of formation, standard entropies and high temperature heat capacities of UC and UC_2, may be combined to calculate the free energies of formation of these compounds upto 2500°K. For this calculation the following heat capacities and heats of transformation of uranium and carbon previously assessed have been used.

Table 3

T °K	Cp (cal mole^{-1} $^{\circ}$K^{-1}) Uranium	 Carbon	L_t, t_f (cal/mole) Uranium
298	6.6	2.1	
700	9.0	4.4	
1000			1800
1405			2500
1750	8.5	5.9	
2050	8.5	6.1	

It can be noticed that the two transformations of uranium at $941^{\circ}K$ and $1048^{\circ}K$ have been considered to be one transformation at $1000^{\circ}K$. An average value of ΔCp has been taken to apply over a temperature range which does not involve any phase change in the reactants and the products.

A plot showing the partial and integral free energies in the uranium carbon system derived from various equilibrium measurements is reproduced as figure 6.

Since the I.A.E.A. panel meeting in Vienna 1962, some more work has been done to study the thermodynamics of the U - C system. Behl, et al.[26], determined the free energy of formation of UC_2 and U_2C_3 using solid state galvanic cells. For the equation

$$U\ (\beta) + 2\ C\ (gr) = UC_2\ (S)$$

$$\Delta G^{\circ} = -15,820 - 8.2T \quad (Kcal)$$

$$U\ (\gamma) + 2\ C\ (gr) = UC_2\ (S)$$

$$\Delta G^{\circ} = -18,980 - 5.2T \quad (Kcal)$$

$$2\ U\ (\beta) + 3\ C\ (gr) = U_2C_3\ (S)$$

$$\Delta G^{\circ} = -43,860 - 7T \quad (Kcal)$$

These values are in quite close agreement with the assessed values by the I.A.E.A. panel.

Leitnaker and Godfrey[27], analysed the thermodynamic and phase-information relative to the uranium-carbon system. They also calculated the thermal functions (e.g. $(H^{\circ}_{T}-H^{\circ}_{298})$ and $(G^{\circ}_{T}-H^{\circ}_{298})/_{T}$ etc.

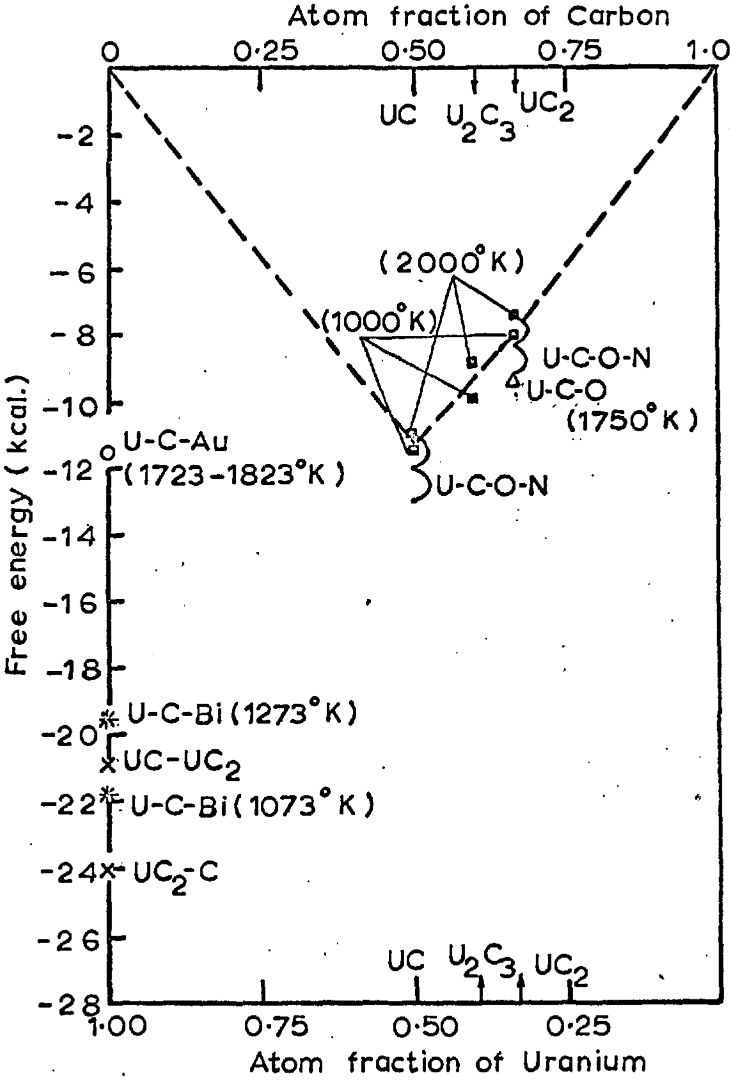


FIG.6 PARTIAL AND INTEGRAL FREE ENERGIES IN THE URANIUM CARBON SYSTEM DERIVED FROM VARIOUS EQUILIBRIUM MEASUREMENTS FROM REFERENCE[18]

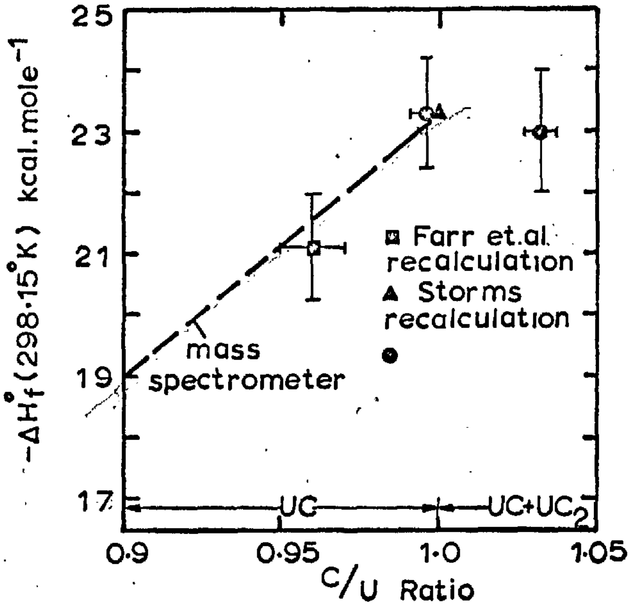


FIG.7 THE HEAT OF FORMATION OF UC AT 298·15°K AS A FUNCTION OF C/U RATIO AFTER STORMS & HUBER[28]

for UC and UC_2 using a non zero S^o_o (0.60 e.u.) for the dicarbide. The value for ΔH^o_{298}(vap.) was calculated as 123.7 ± 1.3 Kcal/mole.

Storms and Hubber[28], have recently determined the heat of combustion for $UC_{0.996\pm0.005}$ and $UC_{1.032\pm0.005}$. They calculated the heats of formation as -23.3±0.9 Kcal/mole and -23.0±1.0 Kcal/mole respectively at 298.15°K. By comparing the previous combustion and vapour pressure measurements, the change in the heat of formation as a function of composition was plotted by these authors; which is reproduced as in figure 7.

2.B The U - O System

Since uranium dioxide (UO_2) has been the principal nuclear fuel, considerable effort has been expended in studying the oxides of uranium. However, some of the earliest work on the higher oxides of uranium was that of Biltz and Müller[29]. Some of the more recent investigators have been Hering and Perio[30], Alberman and Anderson[31], Rauh and Thorn[32], Rundle[33] et al., Hoekstra and Siegel[34] Hockstra[35] et al., Ackermann[36], Perio[37], Wilson and Gerds[38], Lang[39] et al., Vaughan[40] et al., and Markin and Roberts[41].

The uranium - oxygen system is one of the most complex of metal oxide systems. Bright[42] et al; listed nine oxides of uranium including modifications; however the existence of at least four thermodynamically stable uranium oxides, UO_2, U_4O_9, U_3O_8 and UO_3 has been definitely proved. The system is further complicated by polymorphism solid solution and metastability phenomena.

However, those oxides having an oxygen content greater than UO_2 are not of interest in the present investigation, since UO_2 is the stable oxide in the presence of uranium metal or its alloys, carbides and carbon-monoxide at temperatures around 1300°C. Bright,[42] et al, used CO gas as the reducing agent for UO_{2+x} compositions in forming stoichiometric UO_2. Ackermann,[36] found that U_3O_8 decomposed in a vacuum of 10^{-3} mm. Hg at 1000°C. Several investigators including Perio,[37] have found a range of homogeneity for UO_2 extending to approximately $UO_{2.21}$. This range of homogeneity would not be expected to occur in an environment which is either reducing or having a very low oxygen partial pressure used in this investigation of the uranium-oxycarbide system.

2.B.1. Phase Diagram and Structure

The phase diagram of the uranium-uranium dioxide condensed system at elevated temperature has been studied by various investigators[38A-40A]. The phase diagram proposed by Edwards and Markin,[44] is shown in figure 8. A wide liquid miscibility gap at temperatures above 2470 ± 25°C is the most noticeable feature of this diagram. These investigators also established the hypostoichiometric boundary of urania and represented their data by the equation:

$$\log_{10} Xu = 1.404 - 5769/_T$$

where Xu is the mole fraction of uranium dissolved in stoichiometric uranium-dioxide and T is degrees Kelvin. From this equation they reported, the heat of solution of uranium in UO_2 as 26.5 Kcal/mole.

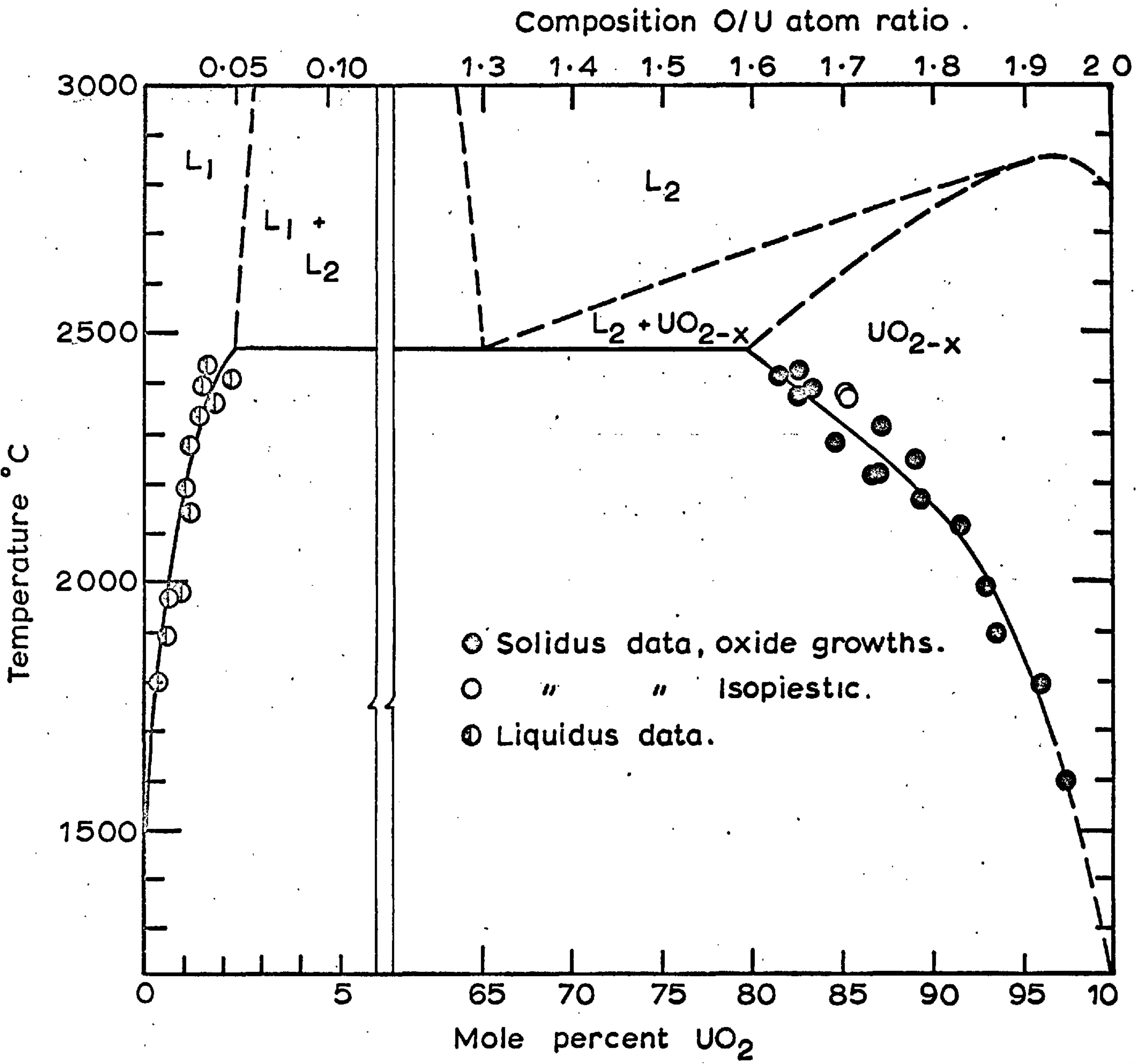


FIG. 8 PHASE DIAGRAM OF THE URANIUM - URANIUM DIOXIDE SYSTEM AT HIGH TEMPERATURES AFTER EDWARDS & MARTIN [44]

Using this equation the hypostoichiometry of urania at 1300°C comes out to be $\simeq UO_{1.9996}$ which is quite negligible. More recently a great deal of interest has developed in hypostoichiometric urania[45], with the observations that it can exist at higher temperatures but that uranium precipitates out readily, even on rapid cooling. Extension of the UO_2 fluorite structure to compositions below the stoichiometric 1:2 ratio has been reported on the basis of several X-ray diffraction studies[45]. The oxygen deficient phase was estimated to have the compositions $UO_{1.96}$ to $UO_{1.97}$ from an extrapolation of the data of Ackermann[36], for the cell dimensions of oxygen excess uranium dioxide. Aitken, et al.[46], recently presented further evidence of the existence, at high temperatures (2400°C) of a stable hypostoichiometric urania having oxygen to uranium ratio of 1.88.

The structure of uranium dioxide has been confirmed by many early workers in the field of X-ray diffraction, to be of fluorite type and various values of cubic spacing have been reported. The most generally accepted lattice parameter for the stoichiometric UO_2 is 5.4690 A . Vaughan, et al.[3], reported the lattice parameter for $UO_{2.00}$ as 5.472 Å and Rundle, et al.[33], found out the value of the lattice parameter as low as 5.4581 ± 0.0005 A°. However there is a general agreement that the lattice parameter decreases with the increase of oxygen atoms in $UO_{2.0}$ and would be expected to increase for the substoichiometric oxide.

Uranium monoxide was early reported by several investigators including Rundle, et al[33]., Katz and Rabinowitch[41A], Vaughan, et al[3]., and Dickerson, et al.[112], as an intermediate phase in the uranium-uranium dioxide system. Rundle, et al[33]. reported that UO has a face-centered-cubic sodium chloride structure with a lattice parameter of 4.92 Å. Katz and Rabinowitch[41 A], reported values of 4.91 to 4.93 Å for the value of the lattice parameter of UO. Although a phase identified as UO has been cited in the literature, bulk quantities have not been obtained in the pure form. Recently[3-5], it has been considered that pure UO is not thermodynamically a stable phase in the system when uncontaminated with carbon and nitrogen. This was also the opinion of Rundle, et al[33]. This will be explained in the following pages of this chapter. Ackermann[36], did not find solid UO, in his investigation of the vaporization of UO_2. He stated that if UO exists it probably does so at very high temperatures in a similar manner as does ThO. Perio[30], in his studies of the oxides of uranium could not confirm the existence of UO.

The solubility of oxygen in uranium is of the order of 0.05 atom per cent at the melting point of uranium (1133°C) according to Katz and Rabinowitch[41 A]. This amounts to 0.003 wt.% oxygen. Rundle, et al[33]. stated that uranium takes very little oxygen into solution.

In summarizing, the aspects of the uranium-oxygen binary system which are pertinent to this investigation, the following statements may be made:

(i) The solubility of oxygen in uranium is small at 1133°C, the melting point of uranium.

(ii) The existence of UO has been a controversial subjest, but the more recent investigations substantiate the opinion that the previously reported "UO" phases were probably phases consisting of U (CNO), U (CO), or U (CN).

(iii) Uranium dioxide becomes substoichiometric at very high temperatures. The solubility of uranium in UO_2 at 1300°C is extremely small (5.458×10^{-3} mole fraction).

(iv) Oxides of uranium higher than UO_2 are not stable at high temperatures.

2.B.2 Thermodynamic Properties

The thermodynamic properties of only those oxides of uranium are reported here which are of interest to this investigation. As reported earlier those oxides of uranium having an oxygen greater or less than UO_2 are not stable under the conditions of the present investigation, therefore the thermodynamic properties of UO (the controversial oxide of uranium) and those of stoichiometric UO_2 are reported here.

2.B.2 (i) Uranium Monoxide

As uranium monoxide (UO), has never been prepared in bulk quantities, there are no reliable thermodynamic data about this compound. The existence of UO is known as a gaseous species as demonstrated by Chupka[47], and DeMaria, et al.[48], with a dissociation energy of 7.9 ± 0.3 ev. Berkowitz, et al.[49], derive $\Delta H\ (0K^{o}) = 4.4 \pm 5$ Kcals, $\Delta H_{298} = 5 \pm 5$ Kcals for the heat of reaction

$$2\ (UO)_g = (U)_g + (UO_2)_g$$

from a mass spectrometric analysis of the vapour over $(UO_2)_s$, and DeMaria, et al.[48], has obtained

$$\Delta H\ (0\ ^{o}K) = 178.5 \pm 7 \text{ Kcals and}$$

$$\Delta H_{298} = 179.7 \text{ Kcals for}$$

$$(UO)_g = (U)_g + (O)_g$$

from a similar analysis of the vapour over $(U)_{liquid} + Al_2O_3$ from 1900 to 2300 °K.

Chiotti, et al.[51], while studying the thermodynamics of uranium-oxycarbides, calculated the standard free energy of formation of solid UO, for temperatures of 450 - 750°C using the relation:

$$\Delta G^o\ (UO_2) + \Delta G^o\ (UC) + \Delta \bar{G}\ (UC) = 2[\Delta G^o(UO) + \Delta \bar{G}(UO)]$$

by assuming that the UCO is a binary mixture of UO and UC. In their calculations at 750°C they employed the following quantities:

$$\Delta G^o\ (UO_2) = -217{,}280\ ;\ \Delta G^o\ (UC) = -24{,}735$$

$$\Delta \bar{G}\ (UC) = -20{,}210\ ;\ \Delta \bar{G}\ (UO) = -1490$$

and found $\Delta G^o\ (UO) = -129{,}650$ cals/mole

similarly for 450°C, these investigators employed the following quantities in the above equation to calculate the value of $\Delta G^o(UO)$.

ΔG^{o} (UO_2) = -229,100 ; ΔG^{o} (UC) = -24,385

$\Delta \bar{G}$ (UC) = -19600

and $\Delta \bar{G}$ (UO) = -1057

In this way the value of ΔG^{o} (UO) at 450° C = -135,485 cals/mole.

From this data these workers calculated an average value of -19.31 for ΔS^{o}, the standard entropy of formation of UO. Westrum and Grønvold[52], estimated that the entropy of UO at 298°K is 16.2 cal/(mole °K). This value, combined with the accepted values for the entropy of uranium and oxygen yields ΔS^{o}_{298} = -20.33 (e.s.u.). From this Chiotti, et al[51]., concluded that the monoxide is the stable phase in contact with uranium and not UO_2; as a much larger negative entropy change for the formation of UO is necessary if uranium monoxide is to become unstable relative to UO_2 and uranium metal at high temperatures.

In their study of the $UC_{1-x}O_x$ system Namba, et al[53]., measured the heat of formation of $UC_{1-x}O_x$ at a temperature of 640°K. by the DTA (differential thermal analysis) method, for various values of x. From their plot of the standard heat of formation versus x, the standard heat of formation of UO comes out to be $\Delta H_{298.16}$ = -130.2 Kcal/mole by extrapolation.

2.B.2. (ii) Uranium Dioxide

Mixter[54], determined the heats of formation of UO_2, U_3O_8 and UO_3 by two methods (combustion with molecular oxygen and reaction with sodium peroxide); the results are rather in poor agreement.

Jones, Gordon and Long[55], measured the heat capacity of uranium metal, UO_3, and UO_2 between 15°K and 300°K. The calculated entropy for uranium and UO_2 at 298.16°K was 12.03 and 23.57 cal. $degree^{-1}$ $mole^{-1}$ respectively. Huber, Holley and Meierkord[56], determined heats of formation of UO_2 and U_3O_8. Using these data, Brewer[57], arrived at the thermochemical properties given in table 4.

Table 4

Thermochemical properties of uranium oxides

Compound	$-\Delta H_{298}$ Kcal/g.atom uranium	$-\Delta G_{298}$ Kcal/g.atom uranium	$-\Delta S_{298}$ cals/g.atom uranium 8
UO_2	259.2	246.6	43.4
$UO_{2.25}$	270.0	256.6	
$UO_{2.62}$	285.6	269.9	
$UO_{2.67}$	284.5	268.6	55.4

Coughlin[58], calculated ΔH and ΔG values for the formation of UO_2 between 298°K and 1500°K which are given in table 5.

Table 5

Temperature °K	$-\Delta H(\pm 0.6)$ Kcal/g.atom uranium	$-\Delta \overset{o}{G}(\pm 5)$ Kcal/g.atom uranium
298.16	259.2	246.6
500	258.6	238.2

Table 5 (continued)

Temperature ^{o}K	$-\Delta H(\pm 0.6)$ Kcal/g.atom uranium	$-\Delta G(\pm 5)$ Kcal/g.atom uranium
800	257.8	226.1
1000	258.2	218.1
1100	259.1	214.1
1200	258.8	210.0
1300	258.4	206.0
1400	258.1	201.9
1500	261.1	197.7

Ackermann, Giles and Thorn[59], have measured the vapour pressure of uranium dioxide from 1600 - 2800°K. Their equation, which incorporates a ΔCp of -8.0 is

$$UO_{2(s)} \longrightarrow UO_{2(g)}$$

$$\Delta G = -151{,}500 \quad -104.5\,T + 18.4\,T \log T$$

$$\Delta H_{298} = 149{,}100 \text{ cals} \qquad \Delta S_{298} = 51.0$$

This heat of sublimation agrees excellently with the value obtained from the mass-spectrometric measurements of DeMaria et al[60]., from which the heat of dissociation of UO_2

$$(UO_2)_g \longrightarrow (U)_g + 2(O)_g$$

was derived as $\Delta H\ (0\ ^{o}K) = 340.4 \pm 7$ Kcals.

Rand and Kubaschewski[50], calculated the standard free energy expression from the existing data for the reaction:

$$U_{(l)} + O_2 \longrightarrow UO_{2\,(s)}$$

$$\Delta G = -269{,}700 + 97.0\,T - 15.4\,T \log T.$$

between (1405 - 2000°K)

2.C. The U-C-N and U-C-O-N Systems

Even though the present investigation has been concerned with the uranium oxycarbide (UCO) system, several aspects of the U-C-N system must be understood. Since air is composed of nearly eighty per cent of nitrogen, any adsorbed air on the specimens or nitrogen coming into the specimens preferentially from the materials used during equilibration at elevated temperatures, may cause nitrogen contamination.

2.C.1. The U-C-N System

According to Vaughan[62], and Rundle, et al.[33], there are three uranium nitrides, UN, U_2N_3 and UN_2. Katz and Rabinowitch[41 A], reported that the higher nitrides of uranium decomposed to UN at elevated temperatures, which is in agreement with the investigations by Williams and Sambell[63]. From 1200°c and above the latter investigators found that UC and UN form a continuous series of solid solutions. As reported by Keller[64], UN melts at 2885 ± 50°c under a nitrogen pressure of two atmospheres and decomposes at this temperature for lower nitrogen pressures. He also concluded that U_2N_3 and UN_2 form a solid solution.

In the ternary system of U-C-N, Austin and Gerds[65], found a complete solid solution range between UC and UN. They found no

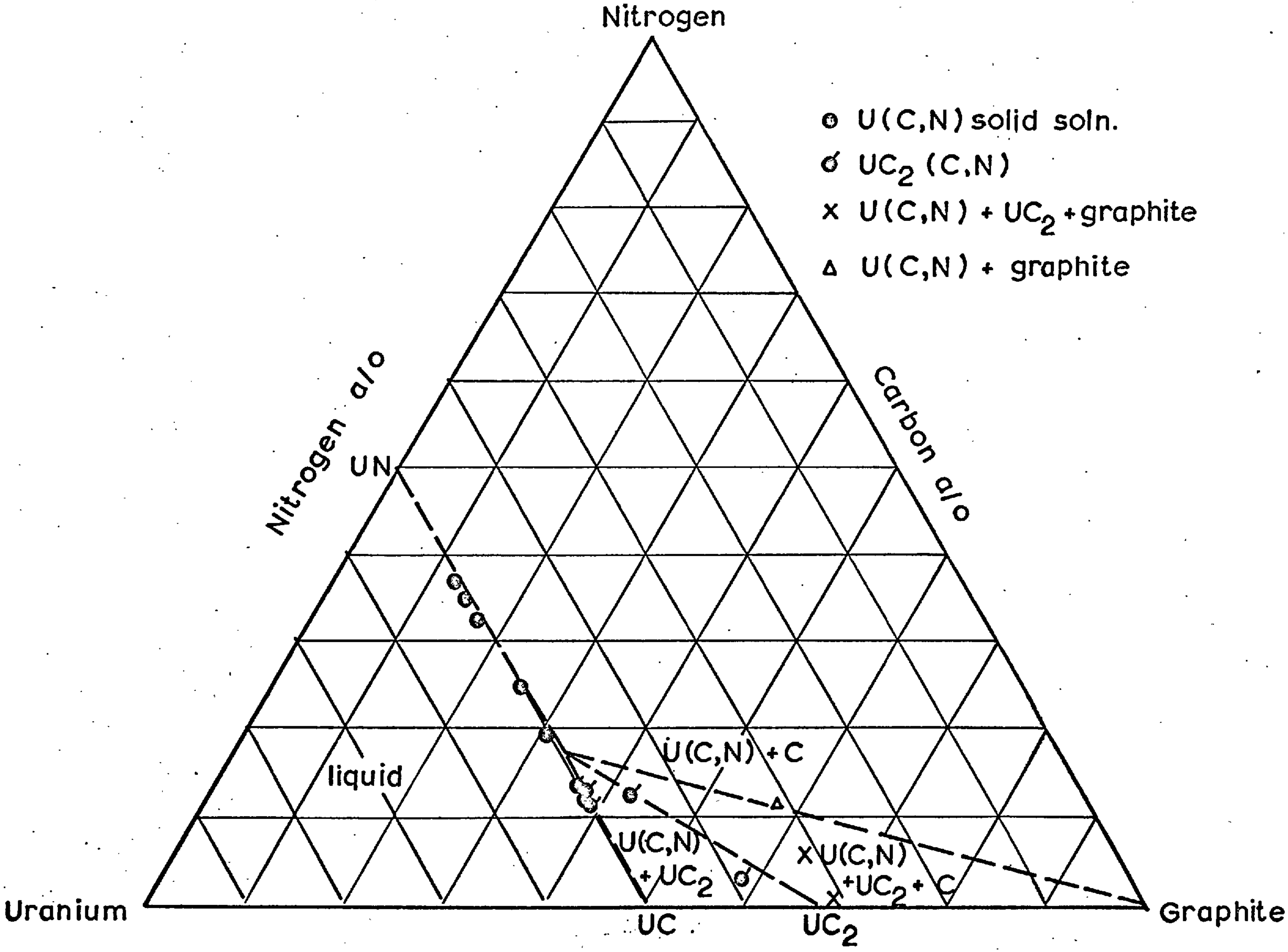


FIG.9 TERNARY SECTION OF URANIUM CARBON NITROGEN SYSTEM AT 1800°C IN ARGON ATMOSPHERE AFTER AUSTIN & GERDS.

solid solubility of nitrogen in either UC_2 or U_2C_3. Figure 9 is a ternary section of the U-C-N system as given by these investigators. For UC containing 95.3 wt.% U, 4.64 wt.% C, 0.04 wt.% N, and no detectable oxygen, they reported a lattice parameter of 4.9598 ± 0.0003 Å. For UN containing 94.8 wt.% U, 0.61 wt.% C, 5.3 wt.% N and no detectable oxygen, Austin and Gerds[65], reported a lattice parameter of 4.9889 ± 0.0003 Å. These investigators also found that nitrogen lowered the lattice parameter of UC but at a rate less than would be expected according to Vegard's Law, for UC contents greater than 0.65 ($UC_{6.65}N_{0.35}$). For higher nitrogen contents they found good agreement with Vegard's Law. However, Williams and Sambell[63], in their investigations of the uranium monocarbide-uranium mononitride system found that at 1200°C the alloys prepared by solid state diffusion obey Vegard's Law, but those prepared by fusion deviate from this law in a systematic fashion. The results of these investigators and those of Austin and Gerds[65], are shown in figure 10. Magnier and Accary[5], found that UC and UN form a continuous series of solid solutions and the variation of lattice parameter with composition showed a positive deviation from Vegard's Law.

2.C.2. The U-C-N-O System

As UC, UN and UO are isomorphous, they can form a phase of variable composition, U(CNO). However, Anselin, et al.[68], found that the solubility of UO in UN appeared to be very low or even

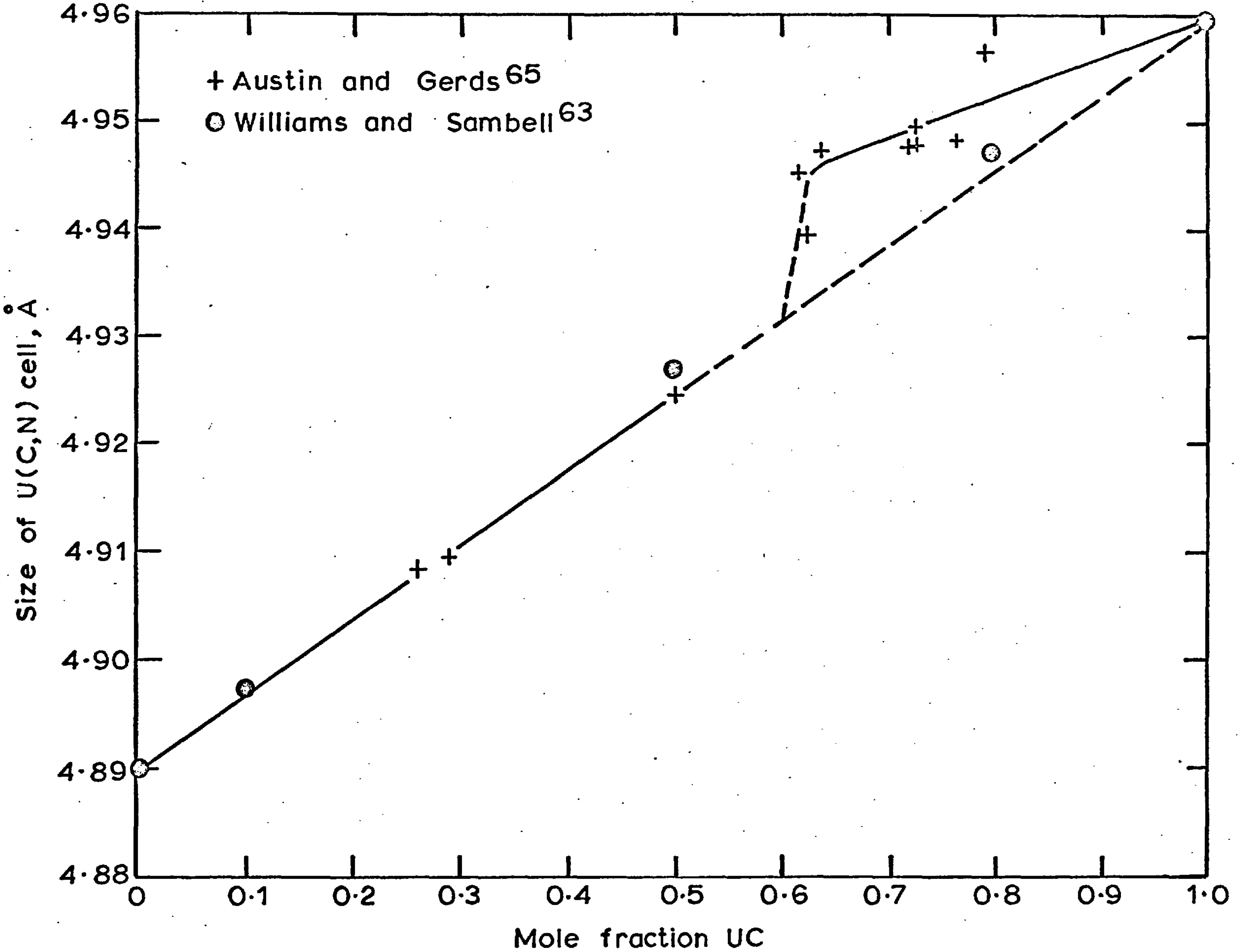


FIG.10 PLOT OF U(C,N) CELL SIZE vs. MOLE FRACTION OF UC IN SOLID SOLUTION

zero. On the other hand, it was found out by various investigators (referred to in the latter part of this chapter), that UO formed an extensive solid solution with UC. It appeared therefore that the phase U(CNO), was only formed as a solid solution of U (CN) and UO. The existence of the U(CNO) phase had been established by various investigators including Kehl and Mendell[23], Meredith and Waldron,[69] and Jepson, et al[70]. Very little quantitative data are available about this phase. Recently Imota and Stöcker,[71] did some theoretical calculations for the solid solution of the compositions $UN_{1-x-y}C_xO_y$, which shows the range of the one phase region as a function of temperature and partial pressures of carbon monoxide and nitrogen. These investigators also did some experiments to form U(CNO) under controlled nitrogen and CO partial pressures at 1900°C. For a compound of the composition $UN_{0.564}C_{0.43}O_{0.006}$ they determined the lattice parameter as 4.9205 ± 0.0005 Å.

However, there is a general agreement among the various investigators in this field, that the solid solution of UO in U (CN) is dependent upon the $^{C}/N$ ratio. It is higher when the $^{C}/N$ ratio is large.

To summarize the characteristics of the U-N, U-C-N and U-C-N-O systems it has been shown that the nitrogen is very reactive with uranium, and compounds of uranium nitride similar to the uranium carbides are formed. Furthermore, UC, UN and UO form extensive solid solutions having the cubic NaCl type structure.

In studying the uranium oxycarbide system it is obvious therefore, that precautions must be observed to avoid nitrogen contamination.

2.D. The U-C-O System

Interest in the uranium oxycarbide (UCO) system has increased recently as it has been recognised that oxycarbide phases are likely to occur in carbides prepared by the carbon reduction of $UO_{2.0}$, and in sintered pellets fabricated from the carbide powders which have become partially oxidised before sintering.

Work prior to 1953 has been summarized by Williams and Westmacott[72], who obtained small quantities of a composition $UC_{0.2}-O_{0.8}$ which had a lattice parameter of ≃ 4.953 Å, by heating uranium, or uranium-UO_2 mixtures in vacuum at 1100-1300°C in the presence of carbon.

Vaughan, Melton and Gerds[3], observed that when UC and UO_2 were reacted in vacuum at 1600-1800°C a phase of composition $UC_{1-x}-O_x$ was observed in which $x \simeq 0.5$. The lattice parameter reported for this U (CO) phase was 4.949 Å. Since there was no mention of nitrogen in this report by Vaughan et al[3]., there is the possibility that their results could have been influenced by nitrogen to some degree. They found that the value of x in the formula $UC_{1-x}O_x$ depended upon the ratio of UC to UO_2 when reacted in a vacuum in the temperature range of 1600 to 1800°C. The results of their reactions were evaluated by X-ray diffraction, metallography and carbon analysis. Metallic uranium was produced on the surface of all their specimens.

Sano, et al.[4], reported considerable replacement of carbon by oxygen in UC and quoted value of x as high as 0.84. From their thermodynamical study they inferred that $UC_{1-x}O_x$ would be in equilibrium with CO gas of $\simeq 10^{-4}$ mm.Hg partial pressure at 1600 °C. Their starting materials were mixtures of UO_2 and UC in various ratios.

Accary, et al.[5], have found that oxygen can be substituted for carbon in UC up to a composition of $UC_{0.63}O_{0.37}$. They prepared their samples by having a mixture of uranium, graphite and UO_2 powders, blended in the right proportions to achieve the desired $UC_{1-x}O_x$ composition, and heat treated at 1800°C for four hours in vacuum. These investigators also found that the lattice parameter versus composition plot did not follow Vegard's Law, since a maximum in the curve was found at the composition $UC_{0.973}O_{0.027}$. Their plot of the variation of lattice parameter of $UC_{1-x}O_x$ with oxygen content is reproduced as shown in figure 11.

Russell,[8] studied the solubility of oxygen in the monocarbide to form $UC_{1-x}O_x$ phase, by heat treating U + C + UO_2 mixtures in vacuum. He found that the maximum solubility of oxygen corresponded to $0.25 < x < 0.35$, and the solid solution appeared to be unaffected by variations in the temperature between 1100 and 1600°C. He also reported that the lattice parameter corresponding to the

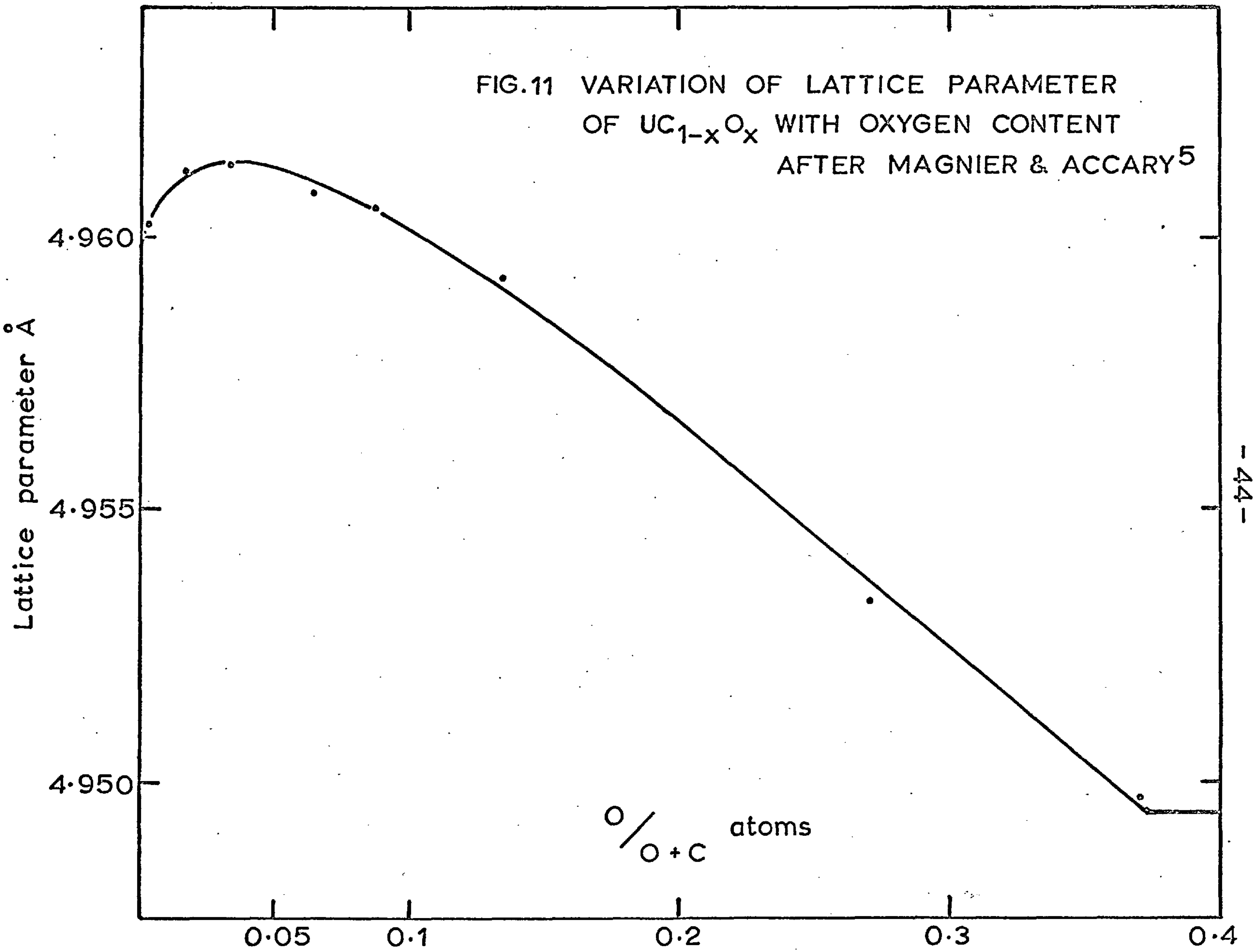


FIG. 11 VARIATION OF LATTICE PARAMETER OF $UC_{1-x}O_x$ WITH OXYGEN CONTENT AFTER MAGNIER & ACCARY[5]

maximum solubility of oxygen in $UC_{1-x}O_x$ is in the range of 4.948 - 4.949 Å. Brett, et al.[7], studied the formation of $UC_{1-x}O_x$ by using powdered uranium, uranium dioxide and graphite as the starting materials. They heated this mixture in vacuum to temperatures of 1100°C to 1500°C. They found that the limiting oxygen content under these conditions corresponded to approximately $UC_{0.7}O_{0.3}$, and the lattice parameter decreased from about 4.960 Å to 4.950 Å with the increase of oxygen content.

Anselin, et al[68]., found out that within broad limits, the UC lattice parameter is independent of oxygen content and that it has a range of values according to whether the UC is in equilibrium with uranium metal or U_2C_3. At 1200°C they found that the solubility of UO in UC in the presence of uranium, amounts to 35 mole per cent ($UC_{0.65}O_{0.35}$) compared with 5 mole per cent ($UC_{0.95}O_{0.05}$) when in equilibrium with U_2C_3.

Henry, et al.,[73] investigated the monocarbide region of the ternary system, U-C-O at 1700°C under an equilibrium partial - pressure of carbon monoxide. They established the solid solution boundaries and phase relations, and effects of the composition on the lattice parameter as well as the decomposition pressures have also been investigated. These investigators found that the solubility limit for oxygen is 17 atomic per cent for which the lattice parameter of stoichiometric UC was reduced from 4.961 Å to nearly 4.948 Å, by substitution of oxygen into the structure. Both free uranium and UO_2 coexisted with the uranium oxycarbide having the maximum oxygen content in it.

Henney[74], has studied the effect of oxygen on phase equilibria in the uranium-carbon system. He carried out series of experiments in which uranium, carbon and UO_2 powders were reacted to produce oxygen saturated carbides. His decomposition temperature of U_2C_3 to give UC and UC_2 was reduced from about 1800°C to 1625 ± 25°C when UO_2 was present and that UC_2 can contain upto $\simeq$ 2 wt.% oxygen at about 1550°C. Tentative isothermal sections of the U-C-O system proposed by Henney[74], are reproduced as in figure 12. In his experiments he also observed two types of 'UC' phases at 1420°C, 1530°C and 1650°C. He suggested that probably U(CO) solid solution decomposed into discrete U(CO) phases which were retained at room temperature by quenching; a situation found in the Zr - C - O system[75].

Besson, Blum and Morelvat[76], reported the existence of a eutectic involving UO_2 and uranium oxycarbide. Melts of U(CO) in UO_2 crucibles at temperatures below 2200°C were found to precipitate an oxycarbide with stoichiometry of $UC_{0.65}O_{0.35}$ and a lattice parameter of 4.947 ± 0.0005 Å. Samples quenched from higher temperatures gave an oxycarbide with larger lattice constant and these investigators suggested that the molefraction of UO in the oxycarbide decreases as the temperature increases above 2200°C.

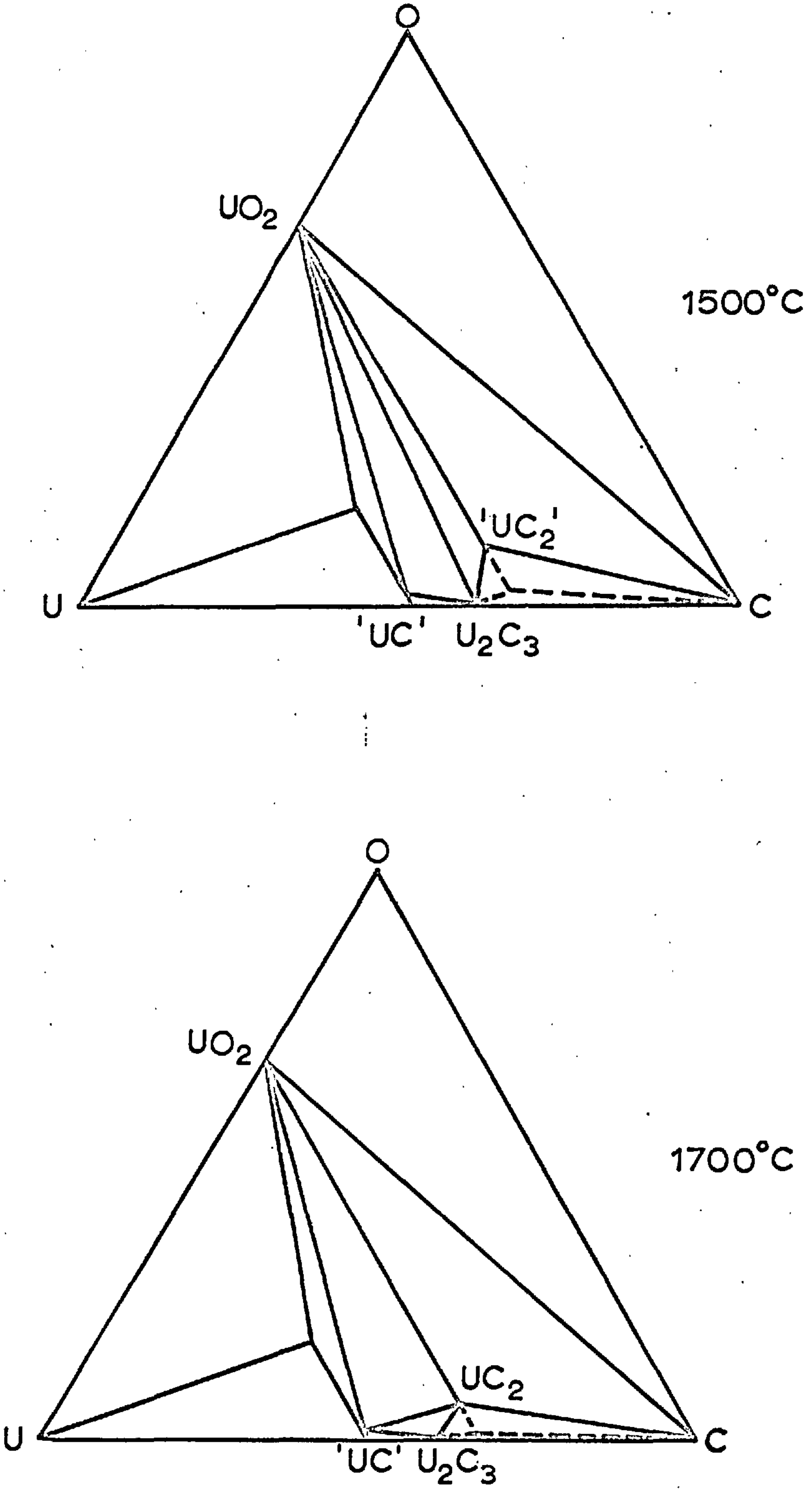


FIG.12 ISOTHERMAL SECTIONS FOR U-C-O SYSTEM AT 1500° & 1700°C AFTER HENNEY[20]

Phase relationship in the U-C-O system were studied by Stoops and Hamme[6], in vacuum and inert atmosphere over the temperature range 1705 - 1855° C. They found that the limit of oxygen solubility was 12.5 atomic per cent i.e. $x = 0.25$ ($UC_{0.75}O_{0.25}$). They also found that the lattice parameter for U(CO) decreases with increasing oxygen content varying from 4 .963 Å for pure UC to 4.952 Å for $U(C_{0.75}O_{0.25})$. These investigators also established the existence of U(CO) as a separate phase in the ternary diagram, which is reproduced as shown in figure 13. These investigators determined the CO partial pressures in equilibrium with the UCO phase between 1705°C and 1855°C, with uranium and UO_2 phases also present. From their pressure-temperature data they formulated the expression:

$$\log_{10} p_{CO} = 19.51 - 36{,}690/_{T}$$

where p_{CO} was measured in microns of mercury and T was the absolute temperature in K°.

This was the extent of knowledge when this work was commenced in 1964. This survey revealed that although some general feature of the phase boundaries of the U(CO) phase had been established, the solubility limit of oxygen in UC had not been determined with any degree of certainty. This latter statement was obvious from a comparison of the work of Vaughan, et al[3]., Namba, et al[4].,and that of Stoops and Hamme[6]. Moreover the previous investigators had in general not carried out their experiments

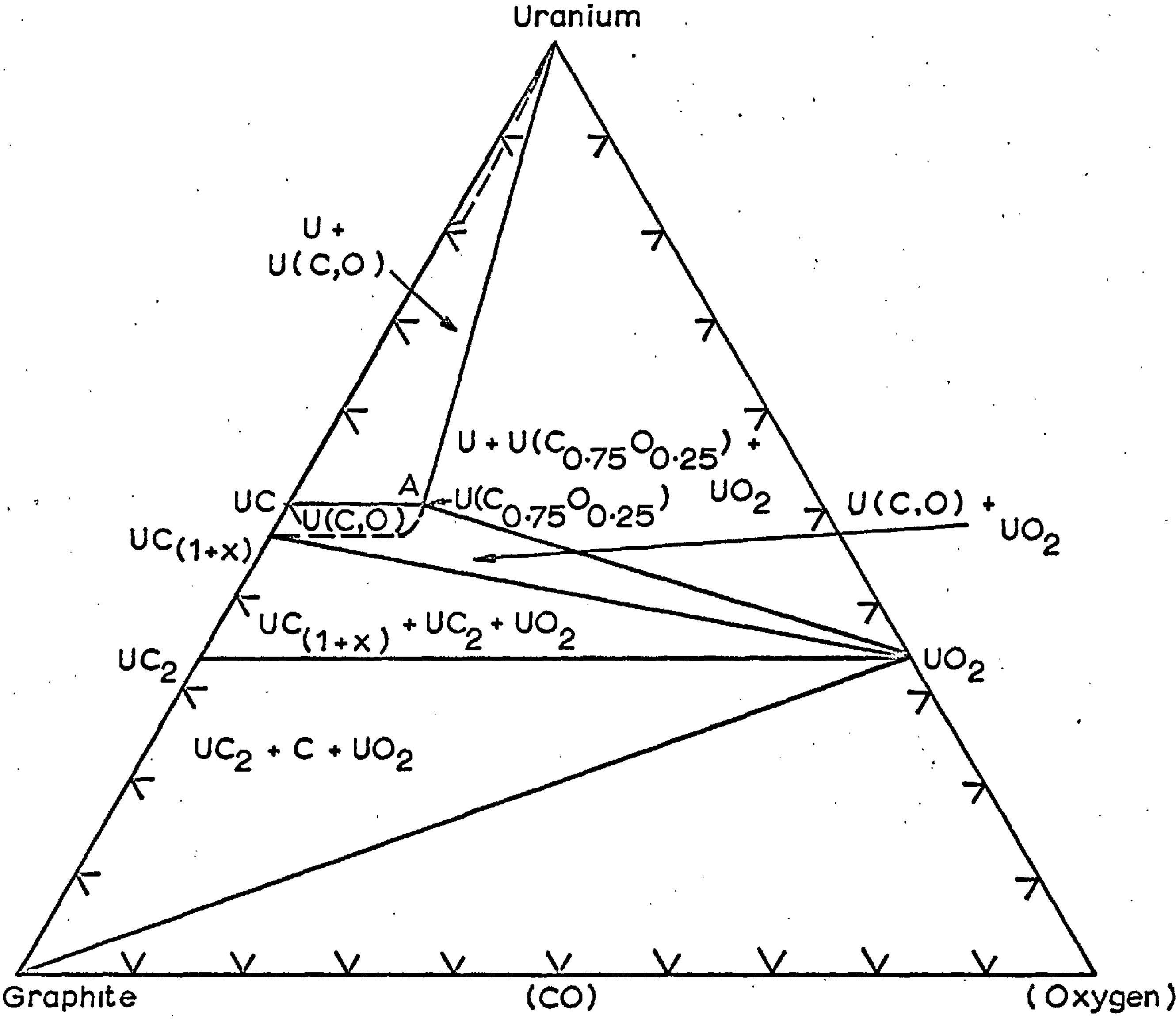


FIG.13 PHASE RELATIONS IN U-C-O MATERIALS FIRED AT 1800°C AND FURNACE COOLED AFTER STOOPS & HAMME[6]

under equilibrium conditions, because according to the phase rule,* a three component system will only be invariant at a particular temperature, if the two other thermodynamic variables are fixed. The only situation so far reported when this condition was fulfilled was when the three solid phases, e.g. UCO, U, UO_2, coexisted in equilibrium (investigated by Stoops and Hamme[6], point A of figure 13). It was impossible therefore, from the work of previous investigators, to obtain any relevant thermodynamic information relating to compositions of the U (CO) phase other than in equilibrium with uranium and uranium dioxide. In general, investigations reported earlier usually refer to non-equilibrium conditions.

These general observations determined the programme of work to be described in this thesis. Thermodynamic data which has been available since this work was commenced will be analysed in subsequent chapters.

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*Will be discussed in the subsequent chapter.

CHAPTER 3

Selection of the Experimental Techniques

3.A General Techniques

As a guide for the treatment of the problem of the uranium oxycarbide system, the phase rule, $F = C - P + 2$, can be used. As the system under study is made up from the three components, i.e. U,C and O; so if the solid solution (UCO) is the only solid phase present ($C=3, P=2, F=3$), then according to the phase rule, the composition of the uranium oxycarbide phase at a particular temperature is only invariant, when two other independent variables (e.g. p_{CO}, a_C) are fixed. The system is also invariant at a particular temperature, when the oxycarbide phase is in equilibrium with two other phases (e.g. U, UO_2).

In order to study the thermodynamics of the uranium oxycarbide phase in the absence of other solid phases, at a certain fixed temperature, it was therefore, necessary to measure the carbon monoxide pressure while the activity of one of the components was fixed, or alternatively the activities of two other components needed to be fixed (e.g. uranium and oxygen). The activity of the third component (e.g. carbon) was thus established and could be calculated by using the Gibbs-Duhem equation.

By knowing the composition of the solid solution phase, i.e. U (CO), the partial molar and integral free energy values can thus be calculated. As $\bar{G}_i - G_i^o = RT \ln a_i$, the quantities $(\bar{S}_i - S_i^o)$ and $(\bar{H}_i - H_i^o)$ may also be determined from the temperature coefficients of the activities.

In order to avoid the formation of UO_2 as a separate phase while preparing the U(CO) phase, the oxygen partial pressure in the system should be lower than needed for the formation of UO_2. The oxygen partial pressures and chemical potentials in equilibrium with liquid uranium and uranium dioxide (stoichiometric) at unit activity of U and UO_2 were calculated at various temperatures of interest and are shown below in table 6.

Table 6

Temperature °C	Oxygen partial pressure (atmosphere)	Oxygen chemical potential (Kcal/mole)
1200	3.388×10^{-30}	-198.59826
1300	9.226×10^{-28}	-194.5567
1400	1.31×10^{-25}	-190.45156
1500	1.1×10^{-23}	-186.228109
1600	5.25×10^{-22}	-182.34607
1700	1.71×10^{-20}	-178.427977

The general techniques and problems encountered in the measurement of chemical potentials in heterogeneous equilibria associated with the various systems are discussed in the reviews of Kubaschewski, Evans[79] and Alcock, Richardson and Alcock[80], Chipman, Elliot, and Averbach[81], and Steele and Alcock[82].

The solid state electromotive force technique exploited by Kiukkola and Wagner[87], and by Steele and Alcock[82], can be used to measure very low oxygen chemical potentials. The ranges over which oxygen-chemical-potentials have been determined by using solid oxide electrolyte are conveniently summarized in figure 14; which is similar to that compiled by Richardson and Jeffes[88].

It is immediately apparent that the oxygen chemical-potentials involved in the present work (table 6) are so low that this technique cannot be employed without an electronic contribution, decreasing the cell e.m.f. by an unknown amount. It should be noted, however, that the thermodynamic properties of uranium and thorium carbides have been successfully determined by using a cell of the type $M, MF_4 / CaF_2(s) / MF_4, MC_x$; by Behl and Egan[26], and Aronson and Sadofsky[89], respectively.

Vapour pressure methods such as the transportation technique are not suitable, as it is difficult to conceive an experimental arrangement which would allow the activities of the various components to be fixed and also measure the relevant weight losses. Knudsen cell, would generally involve the measurements of the partial pressures of a variety of gaseous species, (e.g. U, CO, Au, etc.). These vapour pressure measurements could only be resolved by using a mass-spectrometer. A possible way of studying

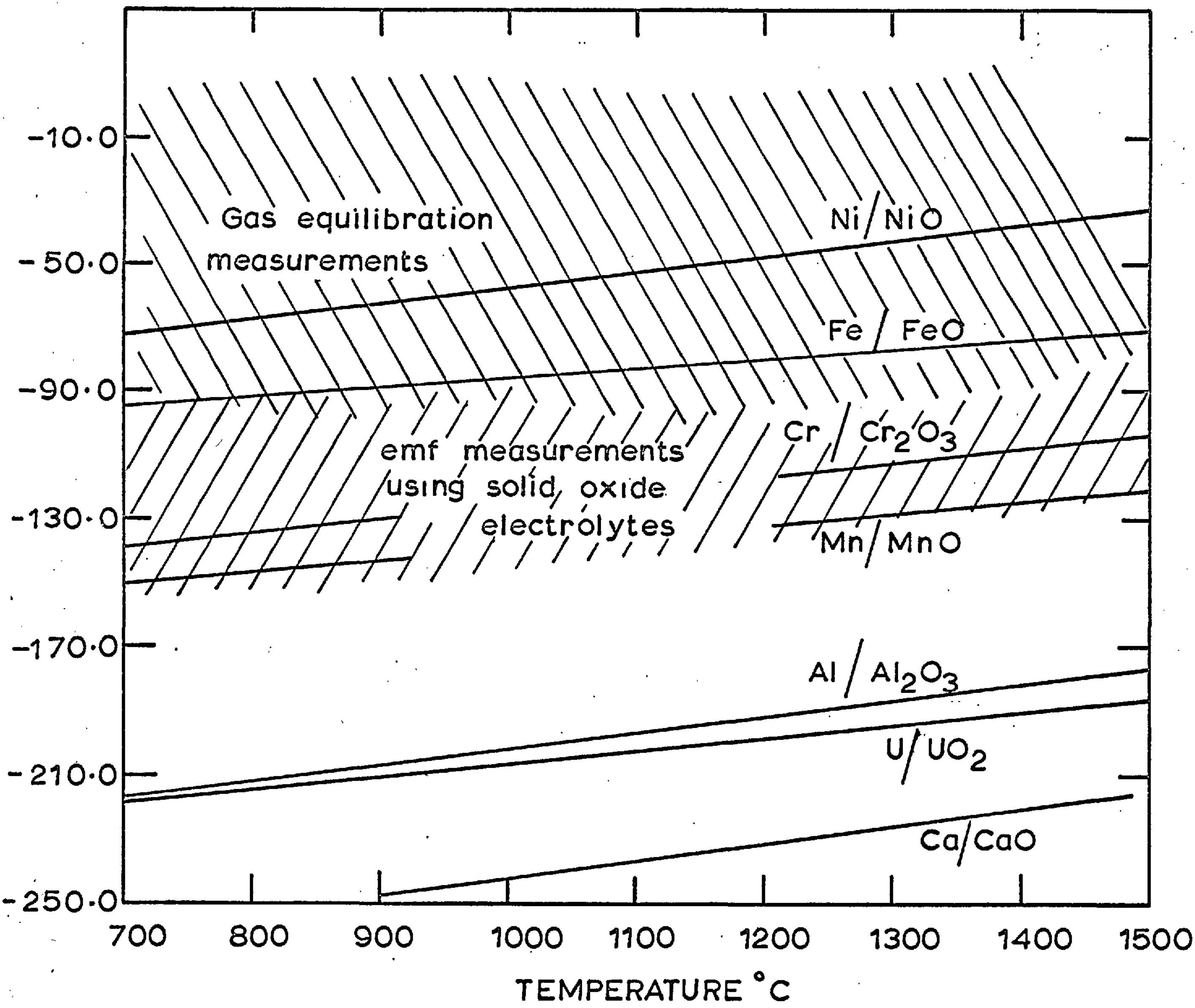


FIG.14 OXYGEN CHEMICAL POTENTIALS IN SELECTED OXIDE SYSTEMS

the activities of uranium and oxygen at the U(CO)-UO_2 phase boundary (see figure 13), is provided by the following experimental arrangement.

Uranium activity	fixed by uranium - gold alloy[*]
Oxygen activity	fixed by the appropriate activities of uranium and activity of $UO_{2.0}$ $(^{a}UO_{2} = 1)$
Crucible for UC and uranium-gold alloy	Uranium-dioxide

Such an arrangement, however, necessitates the presence of solid uranium dioxide phase, along with the U(CO) phase, which is a disadvantage in the subsequent analysis and also would not provide data for a single phase U(CO) and for other phase boundaries.

3.B. Solid-Gas Equilibria

If the uranium activity is fixed by means of U-Au alloy then the activities of carbon and oxygen could be controlled by CO/CO_2[**] ratios for various total gas pressures. Oxygen partial

[*] Activity data about the uranium-gold system are available (reference 17).

pressures were calculated for various CO/CO_2 ratios, for various temperatures of interest which are evident from figure 15, which shows a relationship between $\log_{10}p_{O_2}$ and $\log_{10}CO/CO_2$. The dotted line drawn in figure 15, indicates the stability range of uranium dioxide at various temperatures and CO/CO_2 ratios. The precise values are tabulated in appendix A.

Similarly, the activities of carbon were determined at various temperatures for different total pressures (microns mercury) and CO/CO_2 ratios. These calculated values for the carbon activities are tabulated in appendix B.

The oxygen partial pressure in equilibrium with uranium, uranium dioxide and U(CO) (at unit activities) is 5.25×10^{-22} atm. at a temperature of 1600°C (see page 52). If this oxygen partial pressure was combined with the partial pressure of carbon monoxide (p_{CO}=0.8356 micron Hg or 1.09947×10^{-6} atm.) reported by Hamme and Stoops[6], then the partial pressure of CO_2 (5.315×10^{-14} atm.) could be calculated from the equilibria,

$$2\ CO + O_2 = 2\ CO_2$$

It follows that the experimental ratio CO/CO_2 equals 2.07×10^7, which is in close agreement with the theoretical value of 1.27×10^7. The partial pressures of carbon monoxide reported by Stoops and Hamme[6], were therefore accepted as being accurate and were used to

** It provides the lowest oxygen partial pressure than all other gas mixtures used for fixing the oxygen partial pressure (e.g. H /CO , H /H O etc.)

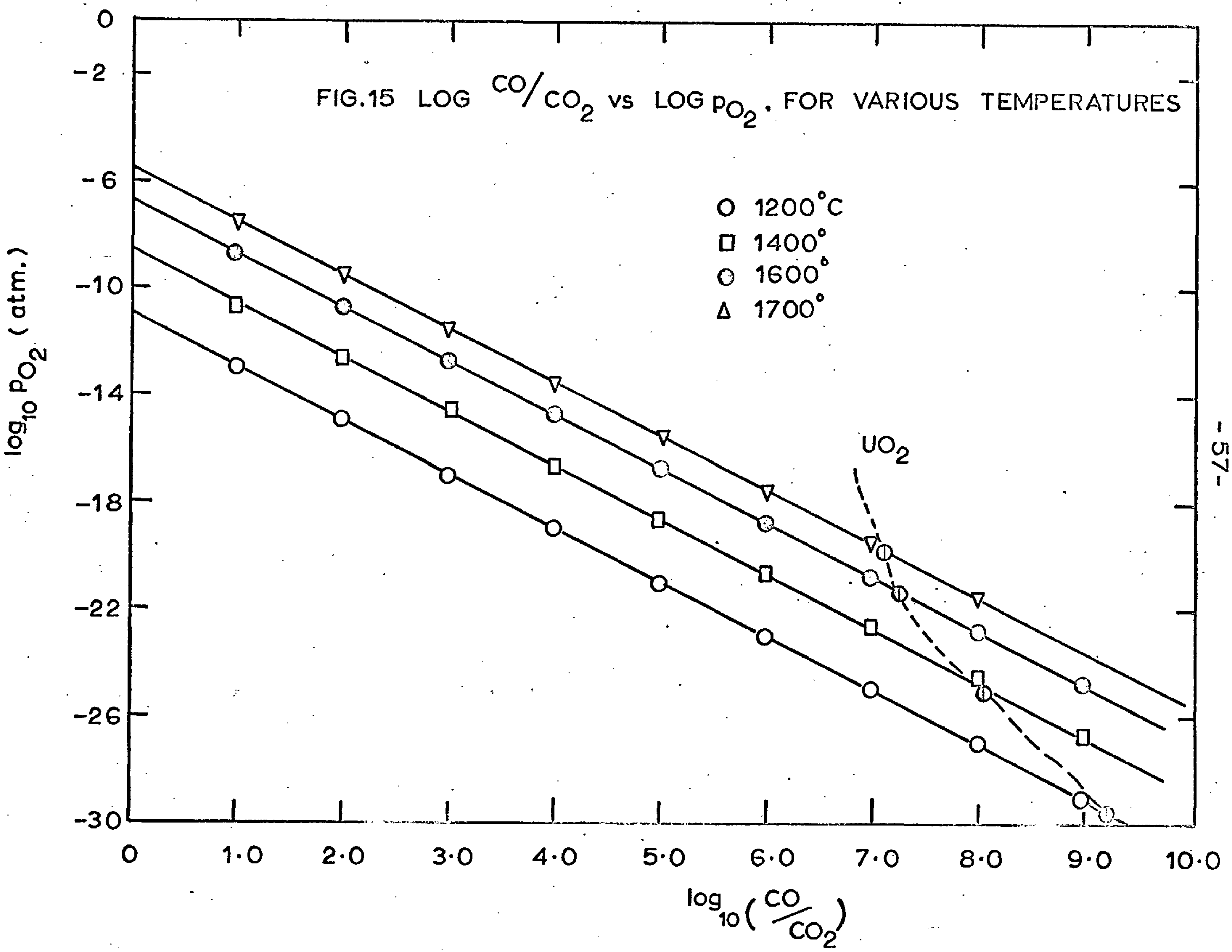


FIG.15 LOG CO/CO_2 vs LOG p_{O_2}. FOR VARIOUS TEMPERATURES

determine the carbon activities ($\simeq 10^{-3}$ at 1600°C) in equilibrium with the three phases, U, UO_2 and $U(C_{1-x}O_x)$. These carbon activities represent the lowest activities of carbon which need be considered in the present investigation. The highest carbon activities will probably be governed by UC-UC_2 equilibria for which the relevant carbon activity approaches unity according to the assessment published by I.A.E.A. panel meeting[18] (reproduced in figure 6). The uranium activities will vary between unity and 3.0×10^{-3} (i.e. uranium activities in the UC-UC_2 system: figure 6, and appendix C). The shaded area in figure 16, therefore, depicts the carbon activities and CO/CO_2 ratios of immediate interest in the present investigation.

It is obvious that the very large CO/CO_2 ratios and low total pressure ($CO+CO_2$), required to establish the necessary carbon and oxygen activities within the uranium oxycarbide phase preclude the use of conventional solid-gas equilibria techniques. Therefore, alternative methods had to be considered.

3.C Solid-Solid Reaction System

3.C.1 General

A useful method for determining extremely low oxygen chemical potentials was first demonstrated by Kubaschewski, et al.,[83-85] in their work on the thermodynamics of oxygen dissolved in vanadium, titanium, and zirconium. The metal understudy, for example, titanium was heat treated with mixtures of molten calcium

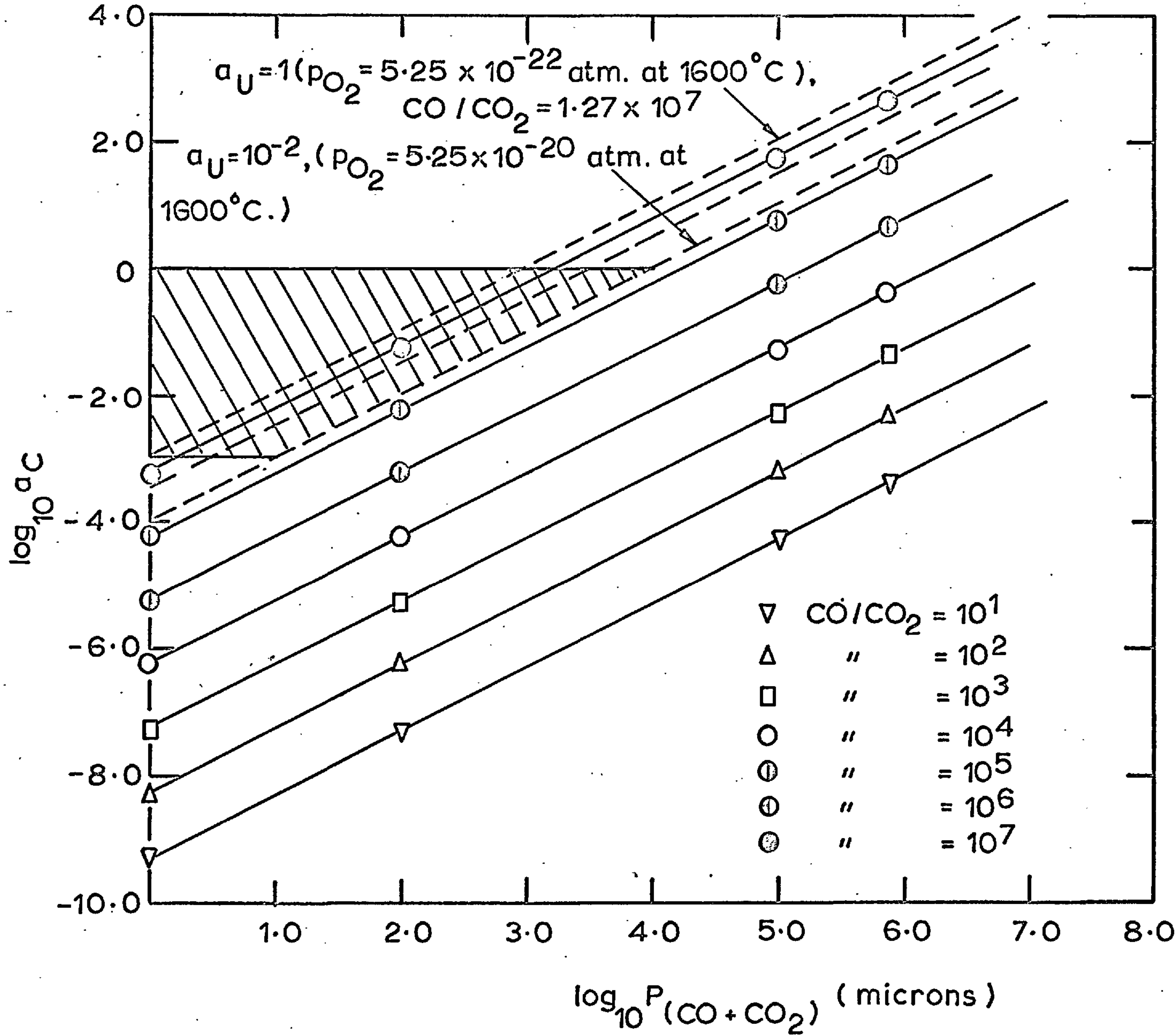


FIG.16 RELATIONSHIP BETWEEN LOG_{10} (CARBON ACTIVITIES) AND $LOG_{10}P_{(CO+CO_2)}$ AT 1600°C, FOR VARIOUS CO/CO_2 VALUES.

magnesium or barium with their respective solid oxides. After equilibration, the surplus reducing metal and oxide were removed and the oxygen content of the refractory metal was determined by vacuum fusion. Obviously, this technique was limited at any one temperature to the three oxygen chemical potentials associated with the Ca/CaO, Mg/MgO and Ba/BaO equilibria.

However, Komarek and co-workers[86], extended the application of this method by combining with an isopiestic technique. The metal specimens in close physical contact with, e.g. CaO, were equilibrated with calcium vapour in an evacuated and sealed titanium tube which was heated vertically in a temperature gradient. The oxygen chemical potential could thus be varied along the temperature gradient by imposing an appropriate calcium vapour pressure, which was kept constant during an experiment by placing the source of calcium at the lowest temperature in the system. These investigators studied the partial molar free energies of oxygen in the metal alloys, Ti-O, Zr-O, and Hf-O, by using this technique.

3.C.2 Experimental Arrangements

3.C.2 (i) Isothermal Method

A: The method devised by Kubaschewski, et al.,[83-85] was considered and the following arrangement proposed:

Temperature	1200 - 1400°C
Closed container	Pure iron *

Crucible for UC and for uranium metal or uranium-gold alloy	Calcium-oxide
Oxygen activity	Fixed by calcium oxide(above), + calcium or calcium-aluminium alloy

When the activity of uranium was unity, this arrangement would provide the oxygen activity data at the U, UCO, phase boundary (see figure 13). Information within the U(CO) phase would be obtained by using uranium at a reduced activity, in the form of U-Au alloy.

Data were available for the Ca-Al[91], and U-Au[17], binary alloy systems, but the extent of the solubility of calcium ($p_{Ca} = 0.57$ atm. at 1400°C) and Al ($p_{Al} = 1.3 \times 10^{-2}$ atm. at 1400°C) in the uranium-gold alloy, was an unknown factor. Although calcium and aluminium form intermetallic compounds with gold ($CaAu_4$, $CaAu_3$, $CaAu_2$, Ca_4Au_3, Ca_2Au, Al_2Au, $AlAu_2$, Al_3Au_5, etc.,) there is a repulsive interaction with uranium, which would tend to reduce the solubility of calcium and aluminium in the alloy.

B: In order to get information about the oxygen chemical potentials, uranium and carbon, activities at the U(CO)-UO_2 phase boundary (see figure 13), the following arrangement proposed:

---

* There is no interaction between pure iron and calcium even at high temperatures [90].

Temperature	1300°C
Closed container	pure iron
Activity of uranium	fixed by uranium-gold alloy
Container for UC and uranium-gold alloy	Stoichiometric uranium-dioxide crucible
Activity of oxygen	fixed by the appropriate activity of uranium, while $a_{UO_2} = 1$

This system had the disadvantage already mentioned, in section 3.A.

3.C.2 Isopiestic Method

(ii) If the previous method (isothermal method A) was combined with an isopiestic technique, as applied by Komarek et al.,[86] then the available range of oxygen partial pressures could be extended without the necessity of alloying the calcium. Accordingly, samples of UC with uranium metal or U-Au alloy are held in close physical contact with the calcium oxide and are equilibrated in an evacuated and sealed pure iron tube, which is held vertically in a temperature gradient. The vapour pressure of calcium during an experiment is kept constant by placing the source of calcium at the lowest temperature in the system and holding this temperature constant.

At equilibrium, the partial molar free energy of oxygen of a sample, i.e. U(CO) can be calculated by using the following equations:

$$Ca_{(1,s)} + \tfrac{1}{2} O_2 = CaO_{(s)} \qquad (3 - a)$$

$$- (Ca)_{(1,s)} = - Ca_{(g)} \qquad (3 - b)$$

$$\overline{\phantom{Ca_{(g)} + \tfrac{1}{2} O_{2\,(g)} = CaO_{(s)}}}$$

$$Ca_{(g)} + \tfrac{1}{2} O_{2\,(g)} = CaO_{(s)} \qquad (3 - (i))$$

The standard free energy for the above reaction is :

$$\Delta G^o_T = - RT \ln K = RT \ln p^{1/2}_{O_2} + RT \ln p_{Ca} \qquad (3 - (ii))$$

and the relative partial molar free energy of oxygen in the U(CO) sample is :

$$\bar{G}_O - G^o_O = \Delta \bar{G}_O = RT \ln a_O = RT \ln p^{1/2}_{O_2} \qquad (3 - (iii))$$

By combining equation (3-(ii)) with equation (3-(iii))

$$\Delta \bar{G}_O = \Delta G^o_T - RT \ln p_{Ca} \qquad (3 - iv)$$

where ΔG^o_T is the standard free energy change of the equation (3-a). The vapour pressure of calcium is constant for each sample of U(CO) and equal to that of the reservoir, but is multiplied by the temperature of the given sample, i.e. U(CO). ΔG^o_T refers, also to the temperature of the specimen..

By varying the calcium vapour pressure from one experiment to another, the chemical potential of oxygen in the Ca-CaO system and in turn the chemical potential of oxygen in the U(CO) sample can be effectively changed.

The isopiestic method (section 3.C.2 (ii)) seemed to be the most attractive and simplest technique, even though the interaction of calcium with uranium-gold alloy was an unknown factor. Thus by applying this technique, information could be obtained about the activities of oxygen and carbon at the U-U(CO) phase boundary (see figure 13), without alloying uranium with gold, and keeping the activity of uranium unity.

However, in order to obtain information about the chemical potentials of oxygen, carbon and uranium, inside the U(CO) single phase area (see figure 13), it would be essential to obtain the relevant data about the uranium-gold-calcium, ternary alloy system.

The activities of uranium in the ternary uranium-gold-calcium alloy system could be calculated by using the ternary Gibbs-Duhem equation[92-95], (appendix D), provided the data about the activities of calcium were available for the whole range of compositions of uranium-gold binary alloys. Thus to study the ternary U-Au-Ca alloy system, the following arrangement was proposed.

Temperature	1300°C
Crucible for uranium-gold alloy	CaO
Closed container	pure iron
Activity of calcium	fixed by Ca vapour pressure by using the isopiestic method

Alternative alloying elements were also considered for fixing the activity of uranium. As elements which form stable carbides. cannot be used,only. Sn, Pb, Ge, Ga, and Cu appeared suitable. Unfortunately, all these elements also interact with calcium to form intermetallic compounds and offer no obvious advantage over gold.

3.C.3. Limitations of the Isopiestic Method, For Studying the Thermodynamics of the U(CO) System.

(i) This method cannot be extended to higher temperatures without using an alternative container material such as molybdenum, which would cause fabrication problems. The vapour pressure of calcium tends to be limiting as well, (boiling point of calcium = 1482°C).

(ii) When the activity of carbon is increased, while the activity of uranium is very low, there is the possibility of the formation of calcium dicarbide (CaC_2). The activities of carbon needed to form UC and CaC_2, at temperatures of interest, i.e. 1200 - 1375°C, taking into account various values of the activities of uranium and calcium, are shown in appendix E; and from there it can be concluded that the uranium activities in the U(CO) phase, may be reduced to a value of $\simeq 0.1$, when $a_{Ca} = 1$, and lower, at the corresponding lower values of the activity of calcium, without any danger of CaC_2 being formed. Though magnesium and lithium, do not form stable carbides at high temperatures, but have high vapour pressures and are not as convenient as the Ca/CaO system, for establishing the oxygen chemical potentials.

(iii) As calcia and urania form solid solutions at high temperatures, so there is the possibility that UO_2 might be present in the solid solution form at an oxygen partial pressure which is low enough to form pure UO_2, when the activity of urania is unity. This would affect the activity of calcia and hence the composition of the U(CO) phase. The oxygen partial pressure was to be kept low enough, at least a factor of 10, than needed, to form UO_2 at the corresponding temperature, to avoid the possible formation of CaO-UO_2 solid solution.

In spite of these disadvantages it was decided to use the isopiestic method 3.C.2 (ii), combined with the isothermal method 3.C.2 (i) B, as being the only methods likely to produce reliable data for the thermodynamics of the uranium oxycarbide system in the temperature range of 1200 - 1375°C.

CHAPTER 4

Experimental Techniques

4.A Equipment

In this section, the equilibration apparatus and the equipment required, for the handling of materials, i.e. the dry box, for the preparation of some of the starting materials and for the chemical analysis, are described. No description is given for other equipment, (e.g. the X-ray diffraction equipment, hydraulic press, argon arc welding apparatus, metallographic equipment, and the vacuum sintering furnace, etc.) which were frequently used during this investigation, as they formed, a part of general equipment facilities, available in the laboratory.

Throughout this section, when a piece of apparatus is standard or in common use, a detailed description is not given.

4.A.1. Apparatus for the Isopiestic Measurements

4.A.1. Temperature Gradient Furnace and Reaction Tube Arrangements

(i) One of the major difficulties in applying the isopiestic technique is the design and construction of a furnace capable of maintaining two regions of constant temperature. These regions must be separated by a reasonable distance and between them there must exist a temperature gradient. Moreover, the absolute temperature of each region must be independently variable.

A vertical platinum - 20% rhodium (20 S.W.G.) wound resistance furnace was considered suitable. The furnace had three separate windings and a tapping in the centre of the middle winding, to facilitate additional temperature control, if required. Each winding had a separate temperature controller and power supply system. Further, each winding had an extra resistor in the circuit, which could be varied to control the temperature in any part of the furnace.

The furnace had a 'Purox' recrystallized alumina winding tube* (75mm. x 65mm. x 680mm.), surrounded by another alumina tube (130mm. x 110mm. x 680mm.). After positioning and tightly securing the terminal leads of the furnace winding tube, the gap between the two tubes was filled with pure alumina powder. The whole unit was then encased in a sindanyo case filled with refractory bricks. The top, middle and bottom windings of the furnace, had resistances 2.4 ohms, 3.5 ohms and 2.0 ohms respectively.

The reaction tube consisted of a 'Purox' recrystallized alumina tube (54mm. x 45mm. x 900mm.). The gap between the winding tube and the reaction tube was sufficient to have three thermocouples with alumina sheaths, connected to three different temperature controllers. The reaction tube had water cooled brass

* Supplied by Morgan Refractories Ltd., Cheshire.

heads containing silicone 'O' ring seals. In addition, both water cooled brass heads had Wilson-seals and gas inlet and gas outlet attachments. The iron rod, half inch in diameter, passed through the bottom Wilson-seal and carried the crucible assembly, which could thus be pushed up **into** the hot zone of the furnace. The bottom water cooled brass head was about twelve inches in length and acted as a quenching chamber for many of the isopiestic runs. It was also possible to evacuate the reaction tube.

As pure iron crucibles were to be used for various equilibration experiments, a purified argon atmosphere ($p_{O_2} < 10^{-12}$ atm.) was essential to avoid oxidation of the iron crucibles at high temperatures.

4.A.1 The Gas Purification Train

(ii) The argon gas was purified by passing it through columns of silica gel, carbest (a special absorbent for CO_2) and magnesium perchlorate, and finally deoxidised with titanium granules at 900°C. The other end of the furnace tube having titanium granules was connected to the reaction tube by means of rubber 'O' ring joints and copper tubing. All rubber tubing connections were avoided by using either glass or copper tubing. In certain cases when titanium granules of sufficient purity were not available, calcium metal granules, heated between 600-650°C were quite good for the removal of oxygen; but the calcium metal became exhausted relatively quickly.

In order to reduce the oxygen partial pressure still further inside the reaction tube while doing an equilibration run, a titanium-zirconium alloy getter was used in the top zone of the reaction tube. The Ti-Zr alloy was placed inside the alumina crucible, which in turn was placed in a pure iron container having holes drilled all around it. The iron container was welded to an iron rod, half inch in diameter, and was suspended in the top zone of the reaction tube by means of a Wilson-seal.

4.A.1. Temperature Control and Temperature Survey of the Temperature Gradient Furnace

(iii) The supply of current to the three separate windings of the furnace was made by means of three separate variable transformers. The furnace temperature was controlled by three separate Smith's temperature controllers (Mark 4), each connected with a Pt - (Pt-13% Rh) thermocouple, placed in the centre of each winding. Each temperature controller was connected with a mercury switch in the circuit, having a rheostat across it. Each mercury switch varied the current through the appropriate winding of the furnace, depending upon the amount of additional resistance in the circuit.The amount of this additional resistance was adjusted by varying the rheostat. In this way, temperatures of three zones of the furnace were controlled within $\pm$ 1°C. The relevant temperature was obtained, both by controlling the current input in any winding, and by varying the amount of extra resistance in the appropriate circuit. The whole furnace assembly is shown in figure 17.

A typical temperature survey of temperature gradient furnace is shown in figure 18, which shows a temperature gradient of about 200°C over a length of five inches.

4.A.2 Apparatus for the Isothermal Measurements

(i) For carrying out some of the equilibration experiments isothermally, a furnace having constant zone of at least one inch in length, over a temperature range of 1200 - 1375°C was required. A vertical, platinum- 10% rhodium (20 S.W.G.), wound resistance furnace was designed and built. The furnace had one winding and was wound in such a way that the turns were closer together towards the ends of the winding tube than in the middle, i.e. about six turns per inch towards the ends and four turns per inch in the central part. This had the object of constant temperature than would be produced with a uniform winding.

The winding tube was of 'Purox' recrystallized alumina, 54mm. outside diameter, 45mm. inside diameter and 310mm. in length. The winding tube was surrounded by another alumina tube. The space between the winding tube and the outer alumina tube was filled with alumina powder. The whole unit was encased in a sindanyo case and filled with the asbestos wool.

The reaction tube consisted of 'Purox' recrystallized alumina, 39mm. outside diameter, 31mm. inside diameter and 650mm.

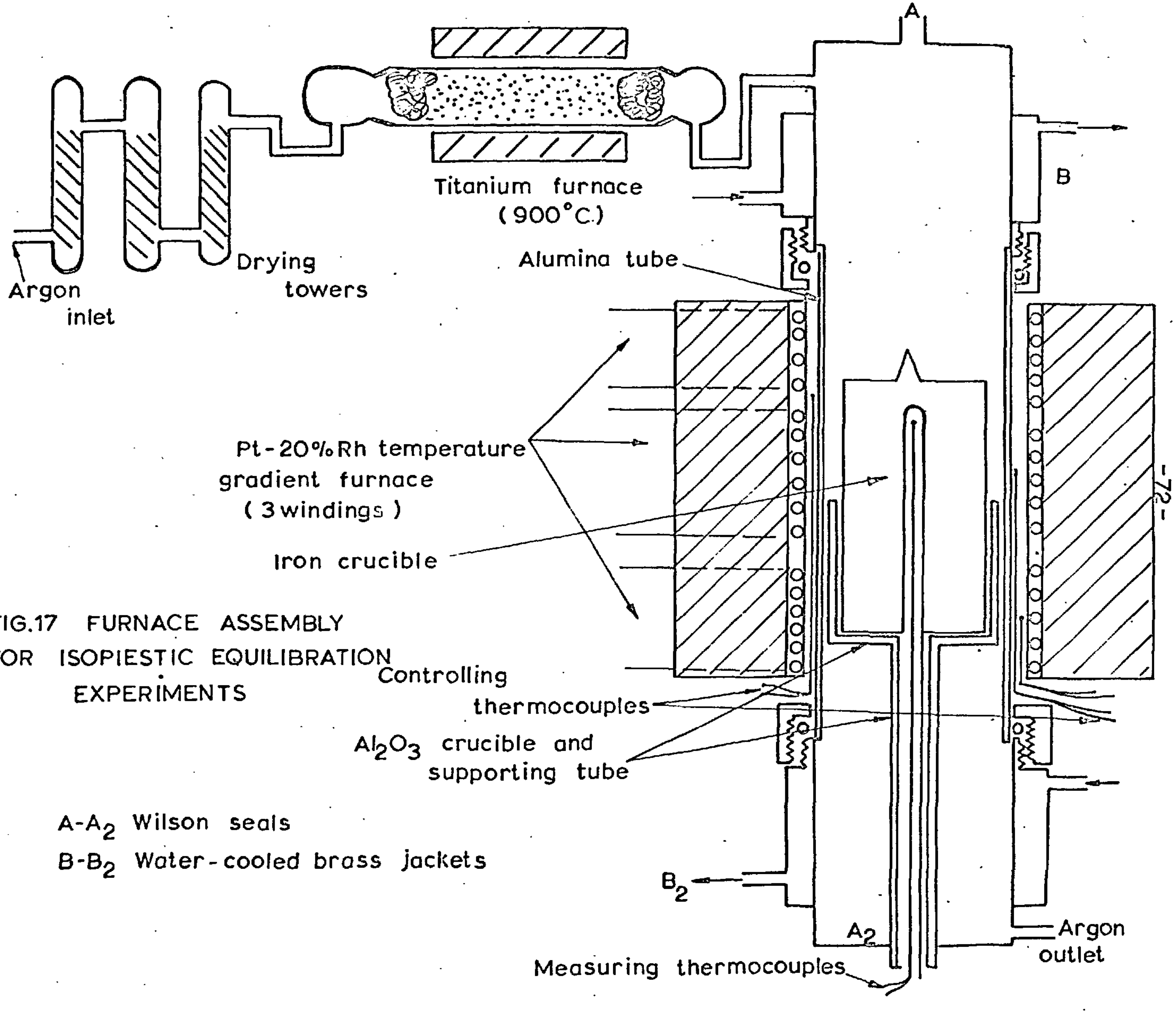


FIG.17 FURNACE ASSEMBLY FOR ISOPIESTIC EQUILIBRATION EXPERIMENTS

A-A_2 Wilson seals

B-B_2 Water-cooled brass jackets

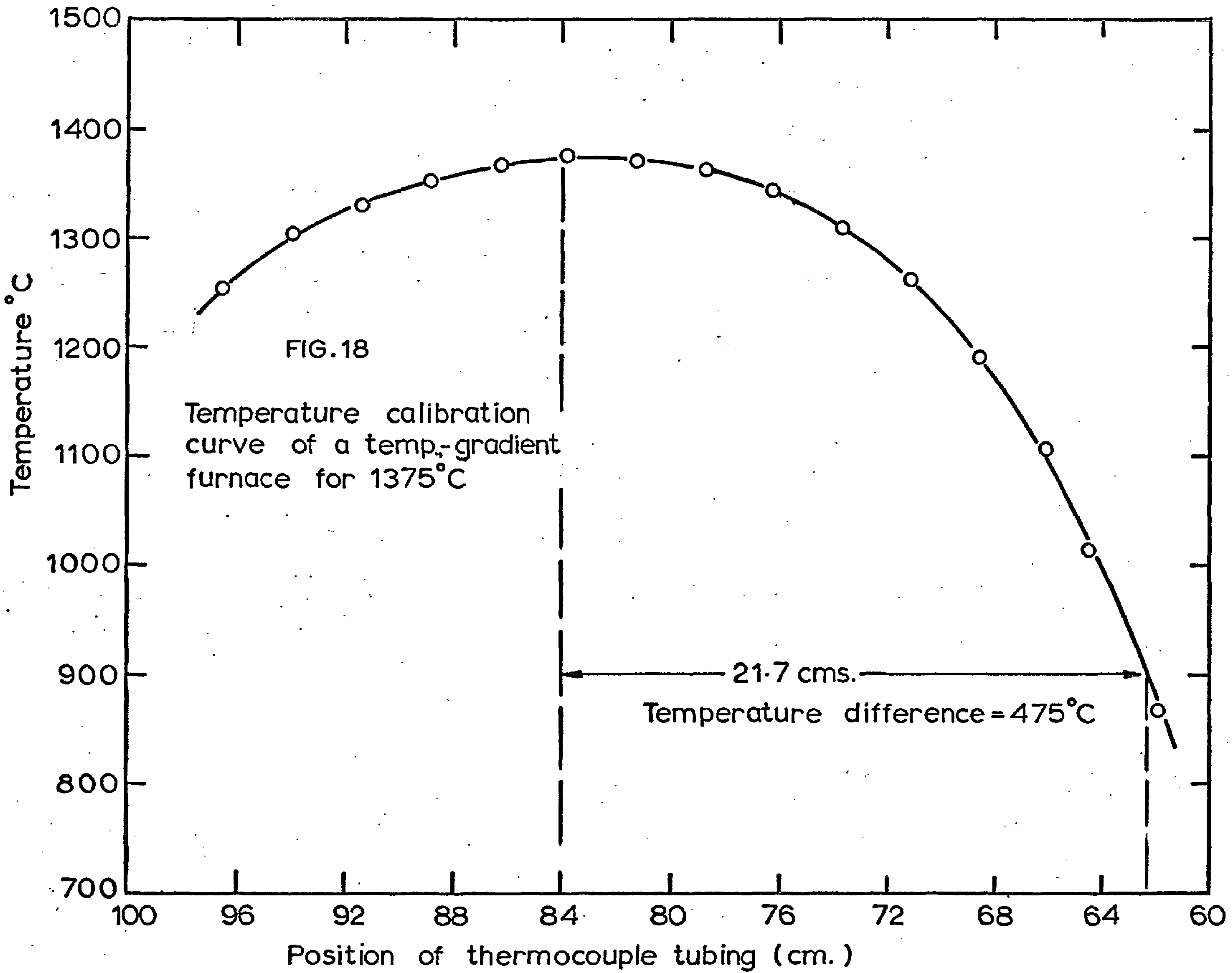


FIG.18

Temperature calibration curve of a temp.-gradient furnace for 1375°C in length. The ends of the reaction tube were ground to the size of B - 40 cone, so that the corresponding size of glass sockets, could be fitted. Both ends of the reaction tube were water cooled. The space between the winding tube and the reaction tube contained a Pt - (Pt - 13% Rh.) thermocouple with alumina sheathing to control the temperature of the furnace. At the bottom end of the reaction tube , an alumina tube with one end closed, was supported by means of a leaktight 'O' ring arrangement. This carried a Pt, (Pt - 13% Rh) thermocouple to measure the correct temperature during the equilibration. The assembly at the top end of the reaction tube allowed the crucible assembly to be removed from the hot zone and quenched. The top end of the reaction tube was also connected with an argon gas purification train. The whole apparatus is shown as in figure 19.

4.A.2 The Temperature, Control and Measurements

(ii) The temperature was measured by means of a Pt - (Pt-13%Rh.) thermocouple. The current was supplied to the furnace from a variable transformer. The furnace temperature was controlled by a Smith's temperature controller (Mark 5), operating a mercury switch which varied the current through the winding by means of an additional resistance of about one ohm in the circuit. The presence of this additional resistor in the circuit reduced the current by about 20% when incorporated in the circuit. At 1300°C, the temperature did not vary by more than 1°C, over a length of about one inch

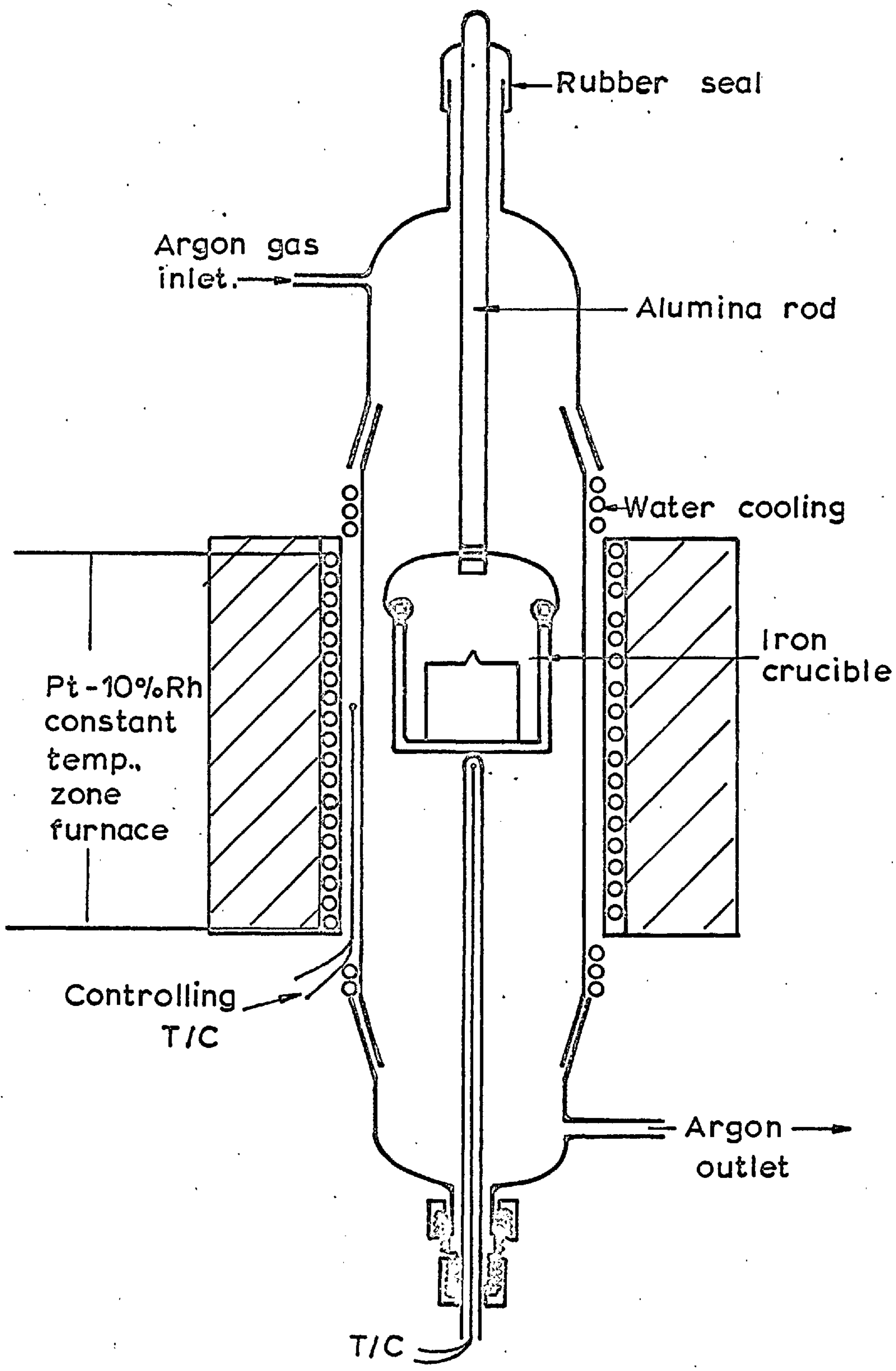


FIG.19 FURNACE ASSEMBLY FOR ISOTHERMAL EQUILIBRATION EXPERIMENTS

inside the reaction tube.

4.A.3. Equipment for the Handling of Materials

4.A.3. The Dry Box

In order to avoid air contamination of the specimens of uranium carbides, it was necessary to handle and store the equilibrated specimens in an inert atmosphere.

A dry box of fibre glass frame with perspex window, was designed and built, having special ports to introduce the iron crucibles. One of the ports was horizontal, about six inches in diameter and fourteen inches in length; while the other port was vertical and about twelve inches long and three inches in diameter. In order to saw open the iron crucible inside the dry box, arrangements were made for securing the crucible in a brass assembly.

A positive pressure of dry argon gas, between 0.25 - 1.1 inch wg. was maintained inside the box, by means of two, three way magnetic valves* in the circuit, operated automatically by means of a pressure switch (type PS/A, Londex Ltd., London). Arrangements were also made for the supply of electric power inside the box by fitting a miniature plug and socket (Ether's BHM 7, plug and socket) with one of the side panels of the box. Neoprene gloves (supplied by Lewis-Gilder and Co. Ltd., London) were used with this box. Initially a Watson-Marlow H.R. flow inducer (type MHRK, supplied by Watson-Marlow Ltd., England) was also introduced

*Supplied by the Magnetic Valve Co. Ltd., 7 Kendall Place, London, W.1.

into the gas supply circuit, but later on it was taken out from the circuit, as it was not very useful.

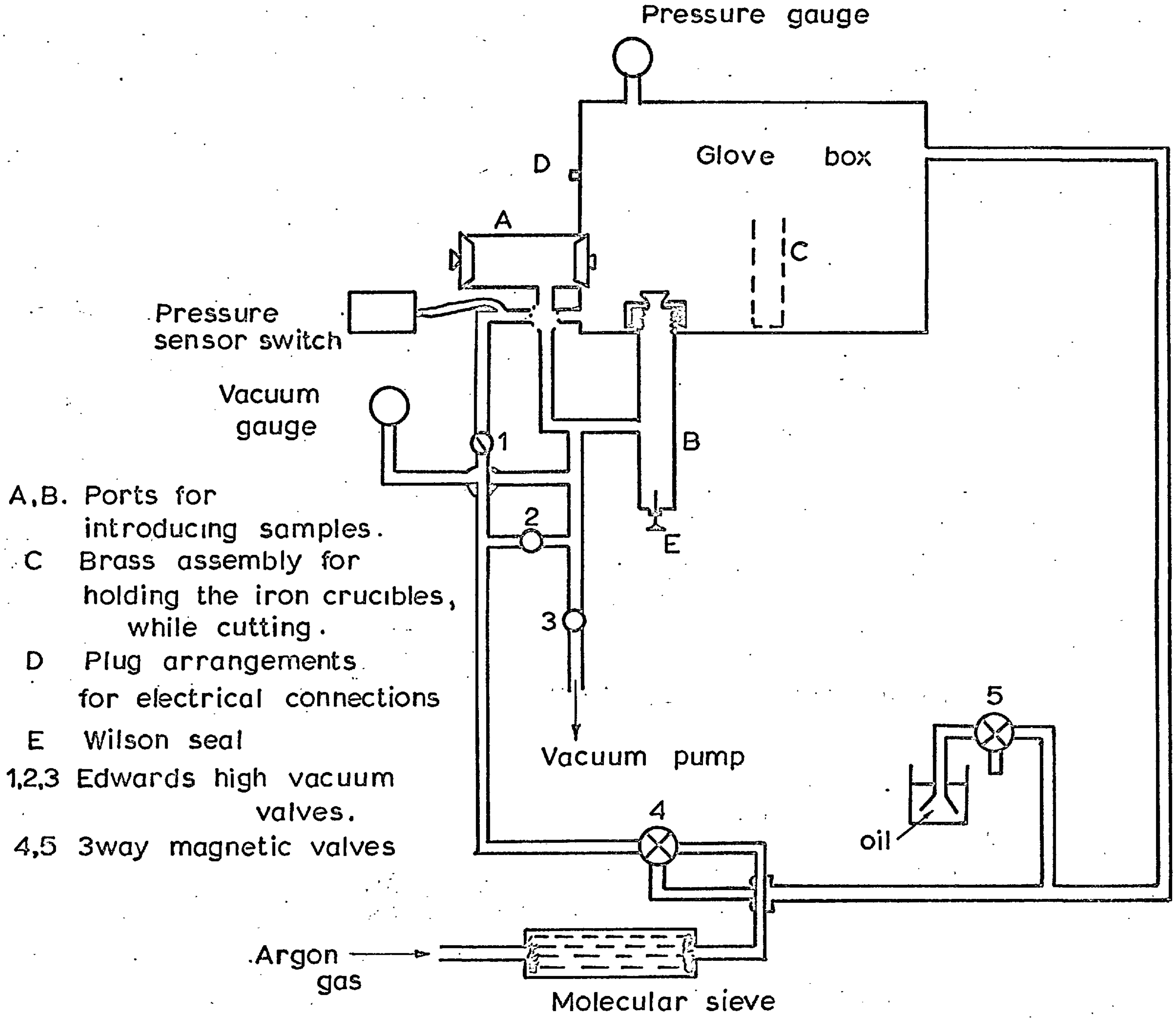
The argon gas was purified by means of a molecular sieve type 4A, before it entered into the box. Some sodium metal and molecular sieve were also placed inside the dry box to further purify the argon atmosphere. Equilibrated samples were stored in desiccators having phosphorus pentoxide and the sodium metal at the base. These desiccators were always kept in the dry box.

A schematic diagram of the dry box is shown in figure 20.

4.A.4. Equipment for the Preparation of Uranium and Gold Alloys

At high temperatures uranium gets oxidised to form its various oxides, even at very low oxygen partial pressures. The uranium-gold alloys were prepared, therefore, by melting the two metals in required proportion under a good vacuum (e.g. 10^{-5} torr.). Induction heating was used to melt these alloys and the apparatus used is shown in figure 21.

The furnace A was heated with a water cooled induction coil consisting of five turns, of one quarter inch copper tubing, energized by 6 KW. Philips H.F. induction heating generator. This gave about half an inch zone with the temperature variation of about 10-15°C. By means of this apparatus temperature of the order of about 1500°C was easily obtained. Temperature was measured by means of an optical pyrometer.



A,B. Ports for introducing samples.
C Brass assembly for holding the iron crucibles, while cutting.
D Plug arrangements for electrical connections
E Wilson seal
1,2,3 Edwards high vacuum valves.
4,5 3way magnetic valves

FIG.20 SCHEMATIC DIAGRAM OF THE DRY-BOX.

A - B 50 silica socket as furnace.

B - Induction coils.

C - Molybdenum susceptor

D - Alumina crucible

G - " disc.

F - " tube having slits to facilitate evacuation.

H - Brass B 50 cone

E - BeO crucible as container for melting Uranium and Gold

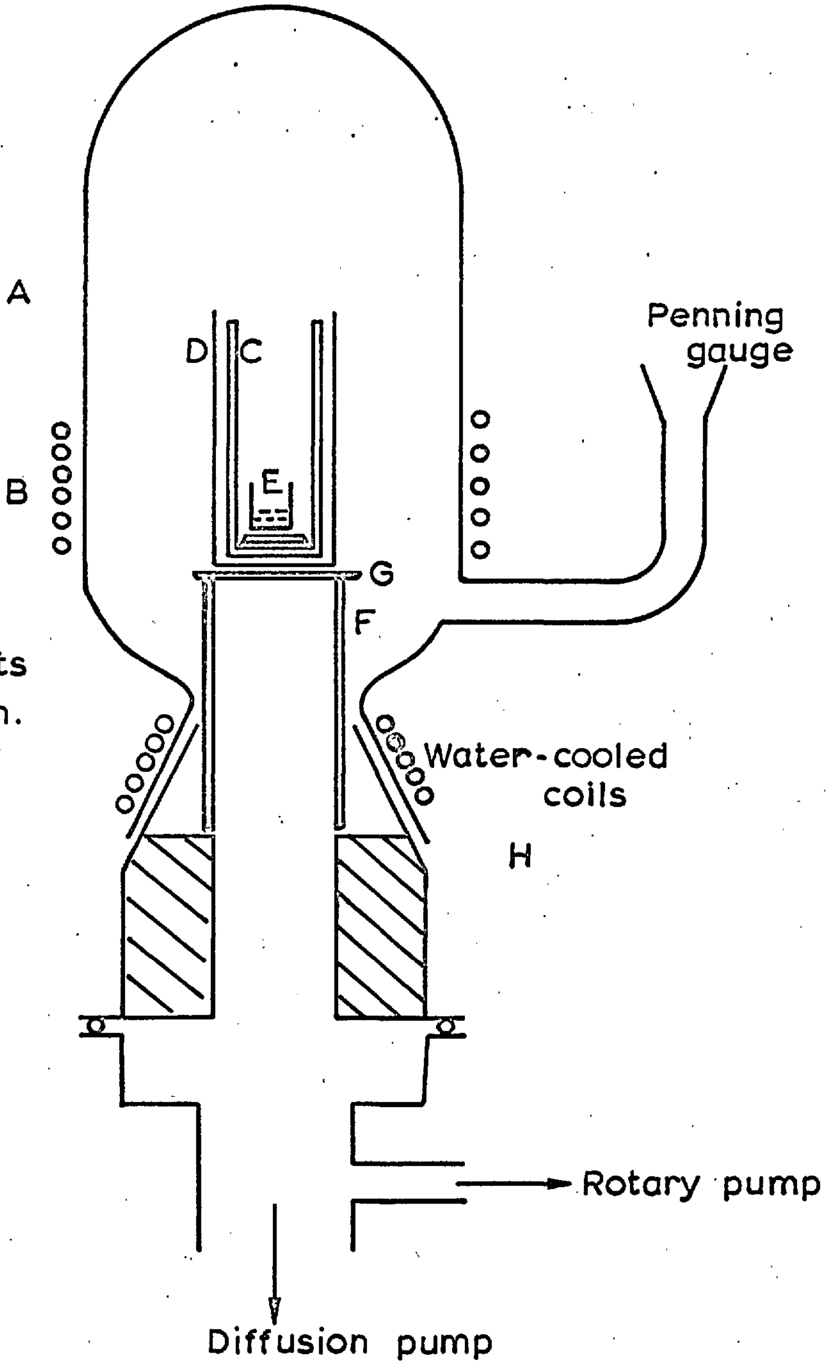


FIG.21 APPARATUS FOR THE PREPARATION OF URANIUM - GOLD ALLOYS UNDER VACUUM.

4.A.5. Apparatus for Chemical Analysis

4.A.5. General

(i) The equilibrated specimens of uranium carbides (e.g. UCO, $UC_{2-x}O_x$, U_2C_3), were to be analysed for uranium, carbon, oxygen and nitrogen. Oxygen was analysed at the A.E.R.E. Harwell and nitrogen as an impurity, was determined from the residual gas after the determination of oxygen. In certain cases to check the exact amount of nitrogen impurity present in the specimens of uranium oxycarbides, Micro-kjeldahl's method (described in appendix F) was used. No special apparatus was required to analyse other elements (e.g. uranium, gold and calcium) which were in the form of binary uranium-gold and ternary, uranium-gold-calcium alloys; except the usual laboratory glass ware and other facilities. For the determination of impurities such as calcium and iron in uranium and in the uranium oxycarbide specimens, introduced after equilibration; an electron microprobe analysis was carried out in the Analytical services Laboratory of Imperial College.

The only apparatus needed was, for the determination of carbon and uranium.

4.A.5 (ii) Apparatus for the Determination of Uranium and Carbon

4.A.5. (ii) a Principle

Samples of uranium carbides were ignited at about 900°C in a stream of oxygen. Any carbon dioxide produced was absorbed in a bulb filled with carbest. The increase in weight of the bulb was a measure of the amount of carbon present in the sample. The residue, i.e. U_3O_8, after the ignition was weighed, from which the weight of uranium was calculated.

4.A.5 (ii) b Apparatus

The apparatus used for the determination of carbon and uranium was built and a schematic diagram is shown in figure 22. The whole apparatus consisted of four parts:

A. Oxygen Gas Purifying Train

Impurities which interfered with the determination of carbon and uranium were removed from the oxygen gas using the purifying train, shown in figure 22.

B. Combustion Furnace and Sample Introducing Arrangement

The combustion furnace was made by winding Kanthal wire, over an alumina tube which was 35.5mm. outside diameter, 28.5mm. inside diameter and about 300mm. in length. The combustion tube was made of alumina with dimensions 28.5mm x 22.5mm x 600mm., and both ends of it, were ground to B-24 cone size. The combustion tube had both ends water cooled. Arrangements were made to introduce the samples in the combustion tube at X, using a silica rod carrying a silica boat at one end and a piece of iron the other end.

C Furnace for the Conversion of CO to CO_2

Any carbon monoxide produced in the combustion furnace had to be converted into carbondioxide. An alumina tube with both ends ground to the size of B-14 cone was wound with Kanthal wire, so that

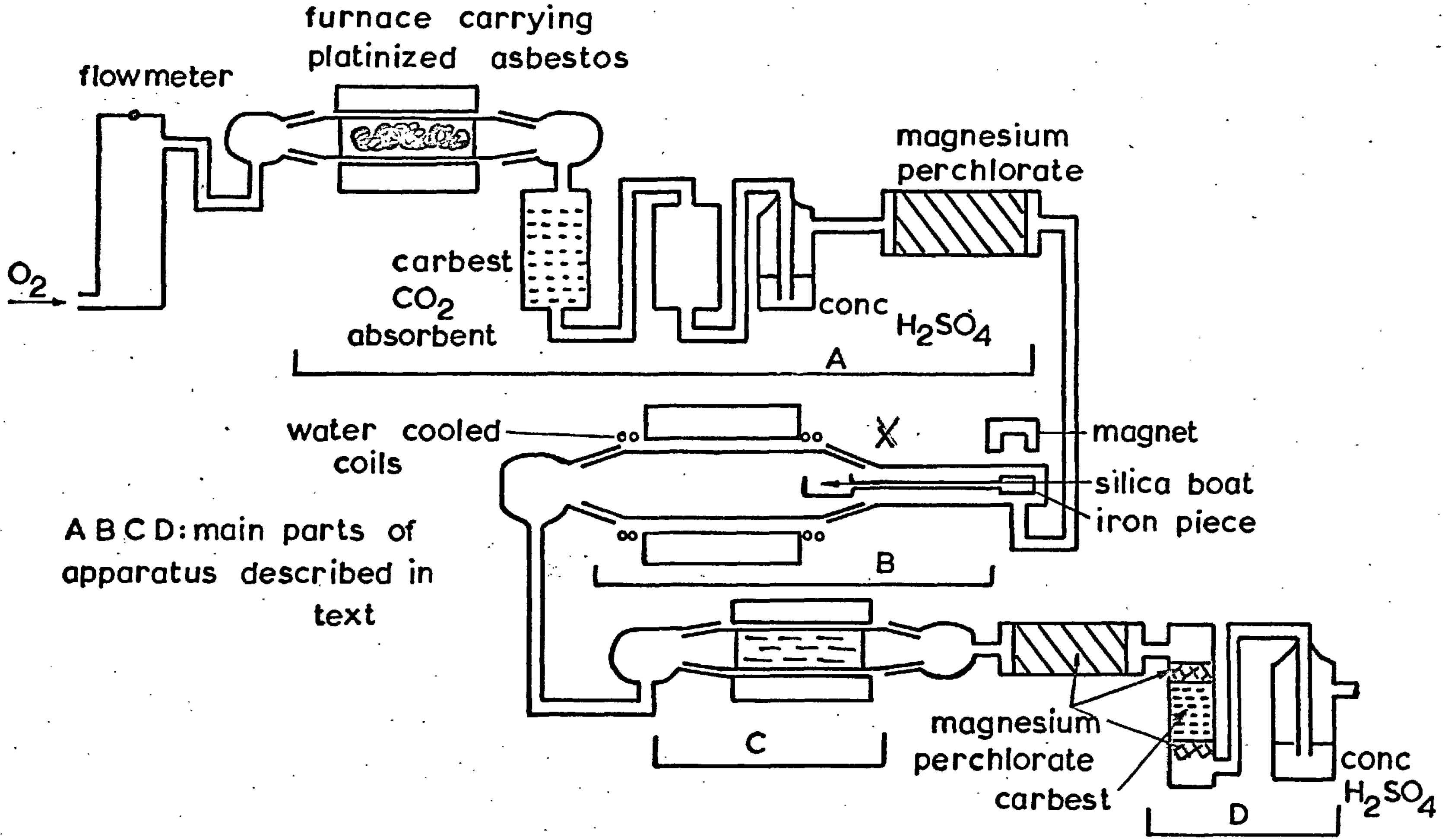


FIG.22 COMBUSTION TRAIN FOR CARBON AND URANIUM ANALYSES

a temperature of 400-500°C could easily be obtained. This furnace tube contained CuO.

Five ampere variable transformers supplied the current to the furnaces used in this apparatus.

D. Absorption Bulbs.

Semi-micro Flaschentrager tubes (A.D. Wood Ltd., England), filled with carbest and small amounts of magnesium perchlorate on both sides of it, were used for absorbing carbon dioxide. The small size of such tubes was useful as they could be weighed on a semi-micro balance. A concentrated H_2SO_4 bubbler was connected at the end of the absorption bulb.

4.B. Materials

Details of the chemical materials used in the present investigation are as follows:

4.B.1. Uranium Carbides

All the uranium-carbides, i.e. UC, UC_2, U_2C_3, needed for the various equilibria were supplied by A.E.R.E. Harwell. Uranium-monocarbide was usually the starting material for the formation of the uranium oxycarbide phase, but a few equilibration experiments required UC_2 and U_2C_3 to be used as well.

Uranium monocarbide was supplied in four different forms:

(i) UC, sintered pellets containing 0.2 wt.% Ni, and the lattice parameter determined in the laboratory was = 4.9606 Å.

(ii) UC, sintered pellets containing no nickel. The lattice parameter determined was 4.9604 Å.

(iii) UC, in the form of small granules prepared by arc-melting. The lattice parameter varied but in most cases it was 4.9524 Å.

(iv) Zone refined UC, this gave the lattice parameter as 4.9612 Å.

In most of the experiments UC, sintered pellets were used and a typical analysis, as supplied by the A.E.R.E. Harwell, was

Carbon = 4.75 - 4.85 wt.%
Oxygen = 0.1 - 0.2 wt.%
Nitrogen = - 0.02 wt.%
Nickel = - 0.2 wt.%

Uranium dicarbide and uranium sesquicarbide were also supplied in the form of sintered pellets. The lattice parameters determined for the UC_2 and U_2C_3 were:

a = 3.5215 Å
c = 5.9955 Å
and a = 8.0889 Å respectively.

4.B.2. Uranium Metal

The uranium metal chips were obtained from Koch-Light Laboratories (England). These uranium chips had the following impurities in ppm.

Al	Ca	Fe	Pb	Th	C	H_2	N_2	O_2
1500	60	400	<1	5	1500	10	100	300

Some uranium in the form of metallic powder, and metal chips was also supplied by A.E.R.E. Harwell.

4.B.2. Cleaning of Uranium Metal

The uranium metal chips were degreased by washing with carbon tetrachloride, followed by an acetone wash. After the degreasing operation the chips were pickled in one part concentrated HNO_3, with about five parts water until bright, indicating that the oxide coating had been removed. After pickling,the chips were washed with five rinses using distilled water, followed by five rinses in ethyl alcohol. After finally rinsing again with acetone, the chips were dried with flowing argon. The dried chips were then ready for use.

4.B.3. Uranium Dioxide

Uranium dioxide was often used in the form of a crucible. The stoichiometric uranium dioxide crucibles were fabricated and sintered from the uranium dioxide powder supplied by A.E.R.E. Harwell. The preparation procedure of the stoichiometric urania crucibles is explained in appendix G.

Some sintered pellets of stoichiometric urania were also obtained frpm the U.K.A.E.A., Dounreay.

4.B.4. Calcium Oxide

Calcium oxide was always used in the form of crucibles. For preliminary experiments, calcium oxide crucibles were fabricated and sintered in the laboratory (appendix H). However, the bulk supply of the calcia crucibles was made by 'Consolidated Beryllium Ltd., (England). Some single crystal calcia cubes (1 cm^3) were obtained from Muscle Shoals Electrochemical Corporation (U.S.A.) and W.and C. Spicer Ltd., (England).

4.B.5. Magnesium Oxide

Magnesium oxide was also used in the form of crucibles. These crucibles were supplied by Thermal Syndicate Ltd., (England).

4.B.6. Beryllia Crucibles

Beryllia crucibles, were obtained from Cambria Chemicals Ltd., England.

4.B.7 Calcium Metal

Calcium metal grains possessing the following impurities in ppm.

Al	B	Cd	Cl	Fe	Li	Mg	Mn	Si	C	N_2
100	0.2	0.2	80	30	<10	<1000	15	<50	40	<50

were supplied by Koch Light Laboratories,(England).

4.B.8 Magnesium Metal

Magnesium metal turnings possessing the following impurities in ppm.

Al	Cu	Fe	Pb	Mn	Ni	Si	Zn	C	N_2	O_2
<10	<5	30	<5	20	<1	<10	<10	<30	15	<30

were supplied by Koch Light Laboratories,(England).

4.B.9 Gold

Pure gold in the form of thin sheets was obtained from Johnson- Matthey Co. Ltd., (England). It was used in the form of binary alloys with uranium in order to fix the activity of uranium for the various equilibrias.

4.B.9 Preparation of Uranium and Gold Alloys

(i) The alloys of various compositions of uranium and gold were prepared by using the apparatus shown in figure 21 . The required amounts of cleaned uranium metal piece and gold were weighed and put in the beryllia crucible. The loaded beryllia crucible was then placed in the molybdenum susceptor, with thoria lid in between the molybdenum susceptor and the beryllia crucible. The system was evacuated for several hours to obtain good vacuum, ($\sim 10^{-5}$ torr.), and the temperature was raised slowly to about 1450°C, making sure that there was always good vacuum in the system. The whole system was maintained at this temperature for some time to ensure that a homogeneous alloy was produced, and then cooled.

4.B.10. Carbest

Carbest is a graded form of soda asbestos used as a special absorbent for carbon dioxide. It was supplied by 'Beecroft and Partners' Retort Works, Suffolk Road, Sheffield, 2. (England).

4.B.11 Pure Iron

All the iron crucibles were made from Remko's pure iron (a Swedish product), supplied by Ernst B. Westman Ltd., (England).

4.C Experimental Procedures

In this section the experimental procedures adopted during this investigation, for the various equilibration experiments, X-ray diffraction, metallographic examinations and chemical analysis of various elements, are described.

4.C.1 Procedures for the Equilibration Experiments

Procedures for the two techniques (i.e. the isothermal method and the isopiestic method) applied for the various equilibrias are described here.

4.C.1 The Isothermal Method

(i) The iron crucible arrangements adopted for this system are shown in figure 23. Cleaned uranium metal piece or uranium-gold alloy, and UC, were weighed and placed in a stoichiometric urania crucible, which was located in a recess in the base of the pure iron crucible, figure 23 , as UO_2 and pure iron are compatible. The lid and the attached spout of the iron crucible were pressed into position, and sealed by argon arc welding. The assembled iron crucible assembly was immediately transferred to the evacuation apparatus, figure 24 .

The iron crucible was evacuated to less than 0.1 micron mercury pressure and then sealed under vacuum by squeezing the spout over a length of 1-2 cms. by means of a specially made vice. The wall thickness (0.5mm.- 1.0mm.) and outer diameter (4mm.) of the spout of the crucible was such that a good seal was made. The top end of the spout was further sealed by argon-arc welding. This procedure of sealing the iron crucible, under vacuum was tested by taking a similarly sealed iron crucible

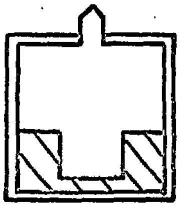


FIG.23

PURE IRON CRUCIBLE USED AS A CONTAINER FOR ISOTHERMAL EQUILIBRATION EXPERIMENTS

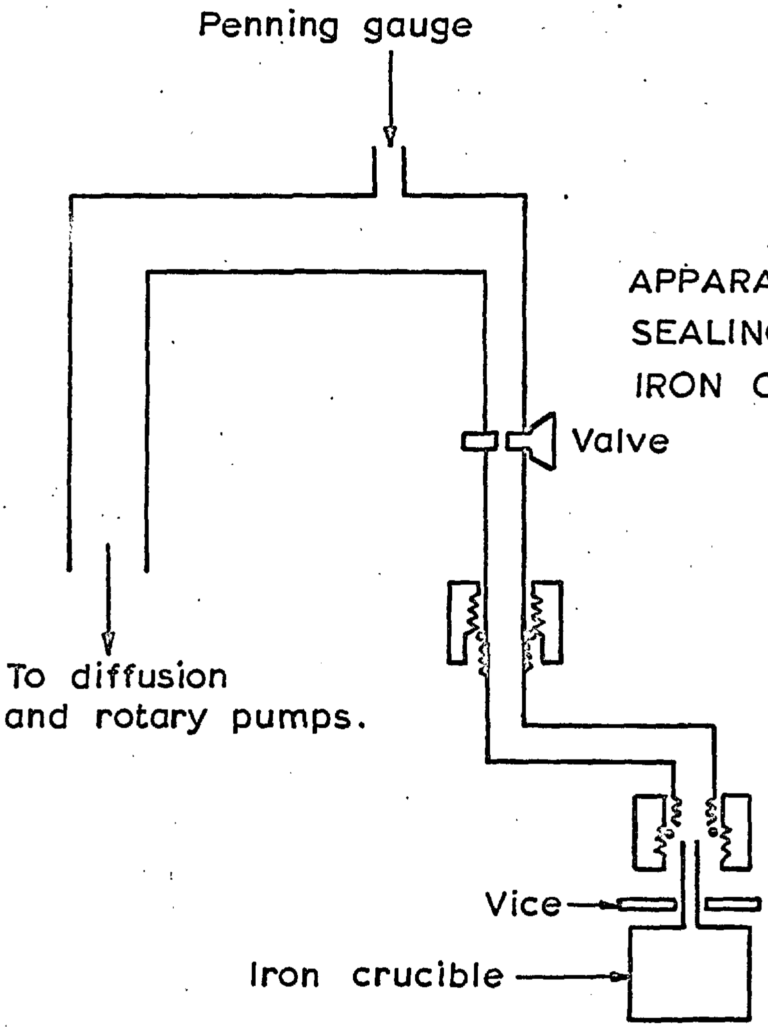


FIG.24

APPARATUS FOR THE SEALING OF PURE IRON CRUCIBLE UNDER VACUUM having calcium metal in it. This iron crucible was heated under vacuum inductively at about 1000°C. As no calcium vapour escaped from the iron crucible, this sealing procedure was therefore, considered to be acceptable.

The sealed iron crucible was placed in an alumina crucible, which was attached to an alumina rod by means of a thick Pt - 5% Rh wire. An inert atmosphere was maintained within the furnace by a continuous stream of purified argon. The whole apparatus is shown in figure 19 .

The iron crucible assembly was introduced into the top zone of the furnace and kept cool, until the argon removed any traces of oxygen inside the reaction tube. This iron crucible assembly was then lowered slowly into the hot zone. The bottom end of the alumina crucible was just touching the thermocouple carrying alumina tube introduced from the bottom end of the reaction tube, so that the temperature of the reaction crucible could be measured. The crucible assembly was kept in the hot zone for an appropriate equilibration time. After equilibration the crucible assembly was quenched, and the temperature drop from the equilibrium temperature to 40 - 50°C, was in three to four minutes. The iron crucible was then sawn open inside the dry box to avoid the possible contamination of U(CO) with moisture, oxygen and nitrogen. As soon as the equilibrated specimens were taken out from the iron crucible, they were immediately transferred to a desiccator and stored in the dry box.

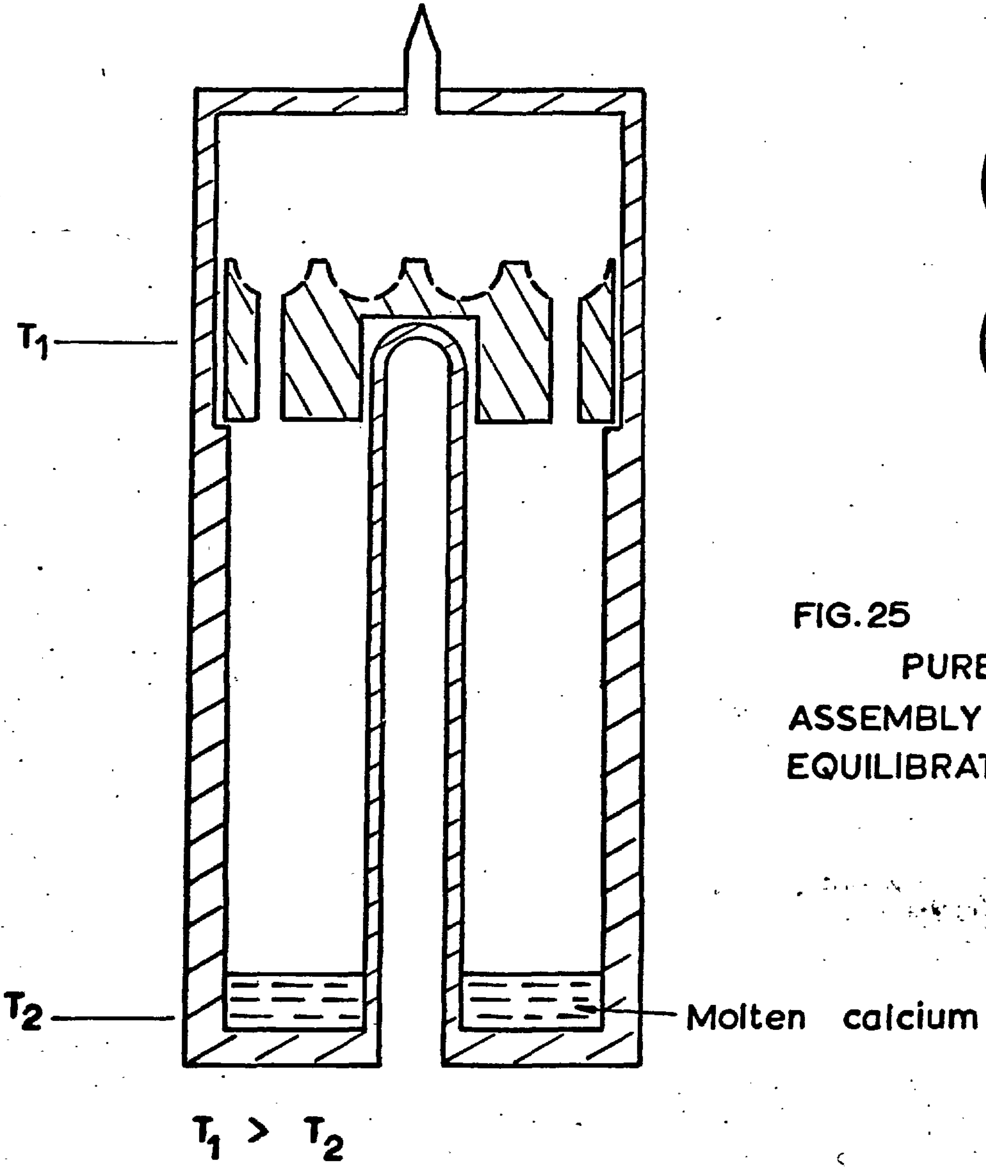
A similar procedure was adopted for the experiments in which Ca/CaO ($a_{Ca}=1$) was used to fix the activity of oxygen; except in this case some calcium metal grains were placed around the calcia crucible at the base of the pure iron crucible.

The same procedure was adopted for other equilibration experiments (e.g. U-Au, UC-UC_2, BeO (crucible); U-Au, UC-UC_2, UO_2 (crucible); UC-UC_2, Ca, CaO (crucible).

However, for the fixed composition equilibria of UC, U_2C_3, UO_2, small platinum crucible was used as a container, which was placed in a small alumina crucible in turn, which was located in a recess at the base of the iron crucible.

4.C.1 The Isopiestic Technique

(ii) The iron crucible arrangement adopted for this method is indicated in figure 25 . The calcium metal grains were placed at the bottom of the iron crucible, while the actual specimens i.e. U, UC or U-Au, UC were contained in four calcia crucibles, which in turn were located in iron cups, placed in such a way, that they were all at the same temperature. The four iron cups were made from a block of pure iron by drilling four grooves, so that calcia crucibles could be easily located in them. The iron block having four cups was supported in the shoulder, made inside the iron crucible at an appropriate depth. The position of the thermocouple wall was arranged in such a way that the top



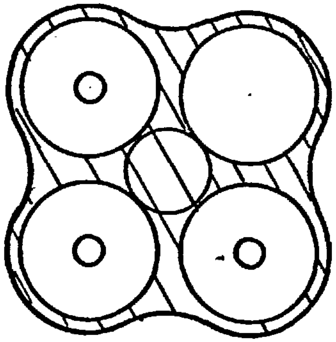


FIG. 25
PURE IRON CRUCIBLE ASSEMBLY FOR ISOPIESTIC EQUILIBRATION EXPERIMENTS

closed end of it was in line with the centres of all the four cups, so that the temperature of the specimen under study could be measured accurately.

Initially, the iron crucible assembly was designed in which pure iron cups could be placed at different heights of the iron crucible along the thermocouple well, in order to equilibrate the specimens at three temperatures of interest, i.e. 1200°C, 1300°C, and 1375°C. The calcium metal grains were to be placed at the bottom of the iron crucible. This design was changed into a simple design as shown in figure 25 , because it was difficult to arrange the required temperatures at the prefixed heights.

After loading the iron crucible with the specimens, the lid and the attached spout were pressed into position and sealed by argon arc welding. The crucible was evacuated and sealed as outlined in the section previous to this, (4.C.1. (i)) of this chapter.

The sealed iron crucible assembly was placed in an alumina crucible (39mm. x 36mm. x 91mm.), having a 7mm. hole in the centre, cemented with an alumina tube about 90 cms. long. The alumina tube was further surrounded by a stainless steel tube , to give it support. The whole assembly was supported by means of a Wilson-seal arrangement at the bottom end of the quenching chamber. Using a multibore thermocouple tube, two thermocouples were used to measure the temperatures of calcium and that of specimens; and the thermocouple wires passed through the rubber seal and then connected with a potentiometer.

The iron crucible assembly was introduced into the bottom end of the water cooled zone of the furnace, and purified argon gas was passed through the reaction tube of the furnace, until argon gas removed all traces of oxygen. The crucible assembly was then introduced slowly into the hot zone of the furnace,by pushing the supporting rod through the Wilson-seal. Temperature measurements were made from time to time during the equilibration period. In case of temperature variations of either end of the iron crucible, adjustments of current supply to the furnace were made by varying the positions of rheostats.

The whole apparatus is shown in figure 17 .

After the appropriate time of equilibration, the iron crucible assembly was quenched into the water cooled part of the furnace reaction tube, by pulling down the supporting rod through the Wilson-seal. The quenched iron crucible assembly was taken to the dry box and sawn open. The samples were taken out from the iron crucible and transferred to the desiccator inside the dry box.

The same procedure was adopted for other isopiestic equilibration experiments, (e.g. U, UC, Mg/MgO; U-Au, Ca/CaO;)

4.C.2 X-Ray Diffraction Analysis

All the samples (e.g. UC, UCO, UC_2, U_2C_3, UO_2) obtained after equilibration for the various equilibria were subjected to the X-ray diffraction analysis, employing the Debye-Scherrer technique, using a Philips camera of 114.83mm. in diameter (type no. PW 1084) and copper $K\alpha_1$, $K\alpha_2$ nickel filtered radiation, generated from a Philips X-ray generator. The specimen under study was ground inside the dry box and introduced into the 0.3mm. diameter Lindemann glass capillary. The top end of the capillary was sealed by means of plasticine inside the dry box and finally the capillary was sealed using a bunsen burner as soon as it was brought outside the dry box. After alignment of the capillary the camera was loaded with Kodirex X-ray film in the dark room and exposed. The exposure time varied from 4-5 hours. The phases present in the samples were identified and the lattice parameters of the phases of interest for this investigation, i.e. UCO. UC_2, U_2C_3 and UO_2 were determined. The lattice parameter of the U(CO) phase was calculated from the 620, 600, 531, 440 and 511 reflections. The lines obtained from the 440 plane, often were not as sharp as the ones above, however, when they were sharp they too were used to calculate the lattice parameter. Systematic errors were corrected by using the Nelson-Riley method. Corrections were made for changes in the film while processing, and films with length changes greater than $\pm$ 0.07% were discarded.

The estimated precision of the calculated lattice parameter was from ± 0.0005 Å to ± 0.0007 Å.

4.C.3 Metallographic and Electron Probe Examinations

A few samples obtained after equilibration were subjected to metallographic and electron probe examinations. The sample under study was mounted vertically in cold setting resin, inside the dry box. Attempts were made to grind and polish the specimen inside the dry box using cyclohexane as lubricant (the solubility of water in cyclohexane is virtually zero). However, on examination under microscope it was found that fine polish was not obtained. It was then decided to grind and polish the specimens outside the dry box, but in cyclohexane media to avoid the contamination of samples with oxygen, nitrogen and moisture. Coarse grinding was accomplished by using silicon carbide papers and fine grinding was carried out with fine silicon paper and 14 micron diamond paste. The final polishing was done on Selvyt cloth using diamond grits of 8 micron size, 3 micron size and ¼ micron size with cyclohexane as lubricant.

The specimen under study was transferred to a desiccator, after it was finally polished. Metallographic examination was done by using a Reichert projection microscope, whereas the microprobe examination was performed in the analytical service laboratory of Imperial College, with the help of Mr. N.G. Ware.

4.C.4. Chemical Analysis Procedures.

4.C.4. Determination of Total Carbon and Uranium in Uranium Carbides

(i) Details of the analytical procedure used for the dtermination of total carbon and uranium in the specimens of $U C_{1-x} O_x$, UC_2 and U_2C_3 are given in appendix I. The techniques developed for carbon and uranium analysis produced good reproducible data, as shown in the following table 7.

Table 7

Sample NUMBER	Weight of UC, taken (mgm.)	Percentage of carbon determined (wt.%)	Percentage of uranium determined (wt.%)
1	201.76	4.589	95.145
2	95.955	4.590	95.371
3	121.48	4.578	95.150
4	110.99	4.586	95.196
5	105.595	4.598	95.208
6	94.87	4.586	95.310
7	91.91	4.587	95.123

TYPICAL RESULTS OF THE DETERMINATION OF URANIUM AND CARBON IN UC*.

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*Uranium monocarbide granules prepared by arc melting and supplied by A.E.R.E. Harwell were used.

A further check was made of the errors involved in the determination of uranium, by igniting a weighed amount of cleaned uranium-metal and determining the weight of the resulting U_3O_8. The results are shown in table 8.

Table 8

Sample NUMBER	Weight of uranium metal taken (mgm.)	Weight of uranium determined (mgm.)	Percentage of uranium (wt.%)
1	262.24	262.114	99.952
2	370.485	370.2961	99.949
3	216.555	216.462	99.957

It can be seen from table 8, that determining uranium metal by ignition to U_3O_8, produced results close to 100%. The small error (approximately 0.05%) could possibly be attributed to small deviations from stoichiometry exhibited by U_3O_8.

However, the average uranium and carbon contents of the UC were shown to be 4.588 wt.% and 95.214 wt.% respectively (table 7); whereas the theoretical uranium and carbon contents of the stoichiometric UC should be 95.197 wt.% and 4.8028 wt.% respectively. The discrepancy can probably be accounted for, either by the presence of oxygen or the hypostoichiometric nature, of the UC material as supplied.

4.C.4 Oxygen Analysis

(ii) The oxygen content in the equilibrated specimens of uranium oxycarbide, uranium dicarbide and uranium sesquicarbide was determined at A.E.R.E. Harwell (analytical chemistry division), using a semi micro vacuum fusion technique[96].

4.C.4 Nitrogen Analysis

(iii) In most cases the residual gas after the determination of oxygen was considered to be nitrogen. However, when the nitrogen content determined by this procedure was higher than expected as an impurity, then a micro Kjeldahl's method was used to check the actual nitrogen content in the particular specimen. The procedure adopted for the determination of nitrogen is mentioned in appendix F.

4.C.4 Analysis of Uranium-Gold and Uranium-Gold-Calcium, Alloys

(iv) The analytical procedure adopted for the binary uranium-gold alloys was the same as applied by Grieveson[97]. However, a new procedure for the analysis of ternary alloys of uranium-gold-calcium was developed, which is described in appendix J. This procedure was laborious and the error involved was rather high (2-3 wt.%), so it was decided to have most of these alloys analysed by the analytical service laboratory of Imperial College.

CHAPTER FIVE

Results and Discussion

5.A. General

The experimental results are reported and discussed in three separate sections according to the region of the phase diagram under examination:

a = U, U (C,O), boundary

b = UO_2, U (C,O), boundary

c = inside the single phase U (C,O) region.

Equilibration experiments using either uranium dicarbide or uranium sesquicarbide, with uranium monocarbide at various oxygen partial pressures are also reported in the section of UO_2 - U(C,O) boundary.

An indirect method of calculating the activity coefficients of UC in the U(C,O) solid solutions of various compositions is also described.

A tentative phase diagram of the U - C - O, system has been constructed, based on the experimental results obtained during the present investigation and relevant data available in the literature.

5.B. Attainment of Equilibrium

Before oxygen analyses of the equilibrated specimens of U(C,O) were available, decrease in the lattice parameter was taken as the criterion for the oxygen solubility in the uranium monocarbide lattice. According to most investigators[5-8], uranium oxycarbide exhibits the maximum oxygen content when in equilibrium with both uranium metal and uranium dioxide. Experiments were accordingly carried out at 1573°K and 1648°K, in which uranium, uranium monocarbide and uranium dioxide were equilibrated for different times and the lattice parameters of the quenched samples measured.

The initial experiments were done at 1648°K using UC granules (prepared by arc melting method). However, the chemical analyses of these granules was not reliable as their small size made it impossible to obtain a central homogeneous piece of the equilibrated specimen, free from interfering phases, such as UO_2 and uranium. Later, it was decided to use uranium monocarbide pellets, having a density, 13.2 g/c.c.* and containing about 0.2 wt.% nickel, as the starting material, to form the uranium oxycarbide phase. The size of the pellets, i.e. 3mm. x 5mm., and high density made it possible to analyse chemically the central part of the equilibrated pellet.

Figure 26, indicates that equilibration was achieved much more quickly for the UC granules, compared to the sintered pellets. In the case of sintered UC pellets, the equilibration time

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* determined by the A.E.R.E. Harwell staff.

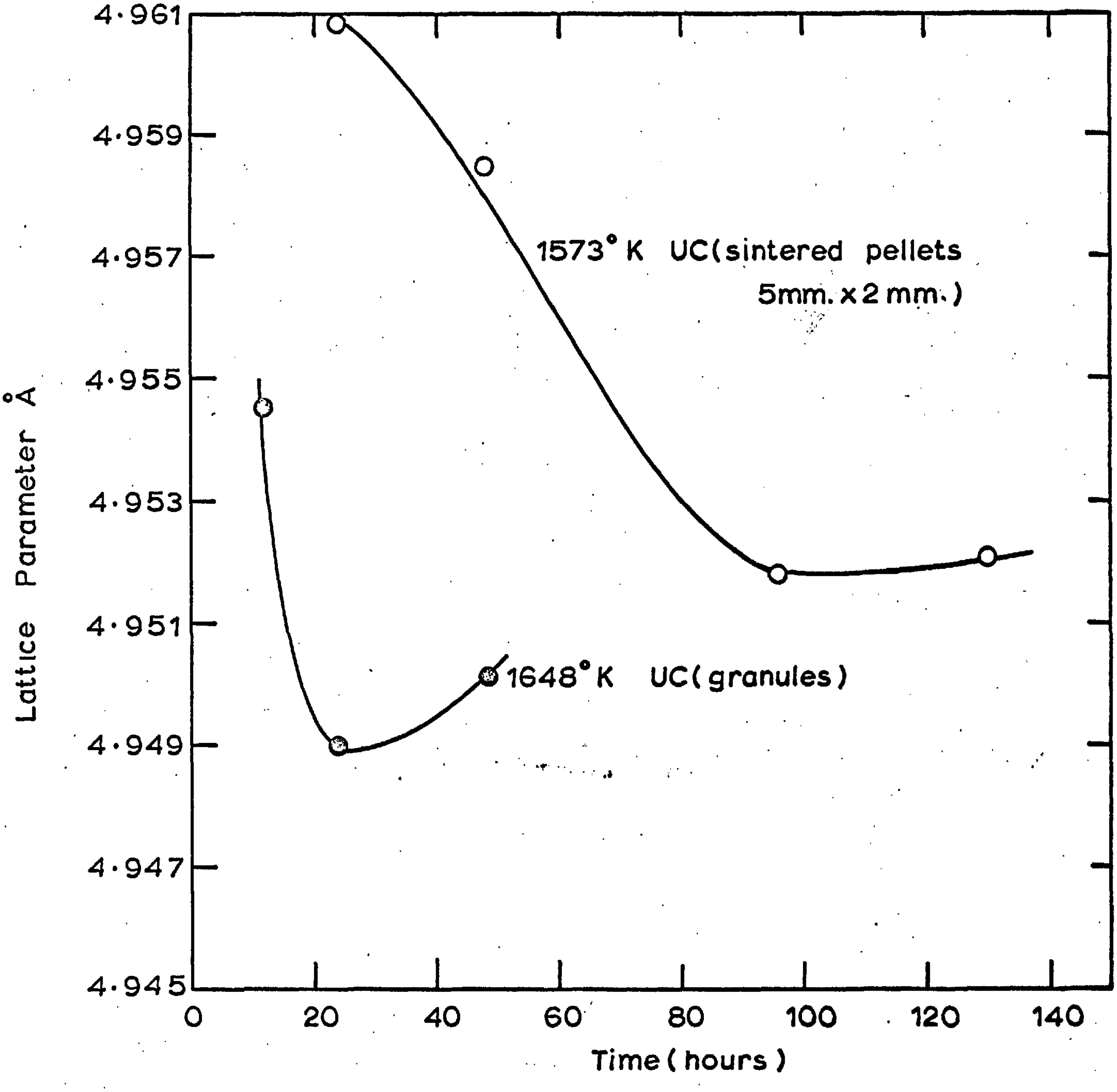

FIG.26 LATTICE PARAMETER OF U(C,O) PHASE vs. TIME FOR EQUILIBRATION

was about 100 hours. The results of chemical analysis of these experiments are reported in section 5.C.1.

5.C. Experimental Results

5.C.1. U - U(C,O), Phase Boundary

In order to get thermodynamic information for the U(C,O) phase in equilibrium with uranium, experiments were conducted at the three temperatures, 1473°K, 1573°K and 1648°K. In all these experiments the activity of uranium was maintained as unity, by having excess uranium metal in contact with the UC, whilst equilibrating at a fixed oxygen partial pressure.

The results of these equilibration experiments at 1473°K, 1573°K and 1648°K are reported in tables 9, 10; 11, 12; and 13, 14; respectively. The results of preliminary experiments in which arc melted granules were the starting materials, are also included in the relevant tables; and only the calculated lattice parameters are reported as the chemical analysis results were not reliable, due to the reasons mentioned earlier, in section 5.B. The accuracy of these preliminary experimental results is further doubtful, as adequate facilities were not available to handle the equilibrated samples.

The results reported in tables 9, 10; 11, 12; and 13, 14; are based primarily upon the chemical analyses of oxygen, carbon and uranium, in conjunction with X-ray analysis. To provide Additional information, certain samples were also subjected to either metallographic or electron microprobe examination, whichever was considered most appropriate.

In order to calculate the relevant oxygen partial pressures at which the various samples were equilibrated, the following thermodynamic data were taken from the literature:

(i) standard free energy of formation of UO_2, for the reaction, $U_{(l)} + O_{2(g)} = UO_{2(s)}$.

$$\Delta G^{o}_{T} = -269,700 + 97.0T - 15.4T \log T \text{ (cals.)}$$

from Rand and Kubaschewski[50].

(ii) standard free energy of formation of CaO, for the reaction, $2\,CaO_{(s)} = 2\,Ca_{(l)} + O_{2(g)}$

$$\Delta G^{o}_{T} = 307,100 - 51.28T \text{ cals } (\pm 3 \text{ Kcals})$$

from Kubaschewski, Evans and Alcock[79].

(iii) standard free energy of formation of MgO, for the reaction, $MgO_{(s)} = Mg_{(l)} + 1/_2\, O_{2(g)}$

$$\Delta G^{o}_{T} = 181,600 + 7.37\, T \log T - 75.7\, T \text{ (cals.)} \quad (\pm 3 \text{ Kcals.})$$

from reference 79.

(iv) vapour pressures for liquid calcium and magnesium were calculated from the equations,

$$\log p_{Ca} = -8,920\, T^{-1} - 1.39 \log T + 12.45 \text{ (mm.Hg)},$$

and

$$\log p_{Mg} = -7550\, T^{-1} - 1.41 \log T + 12.79 \text{ (mm.Hg)}$$

TABLE 9

Equilibration Conditions For Experiments At 1473°K

Experiment Number	Starting materials for equilibration	Equilibration time (hours)	Activity of the metal used to fix the oxygen chemical potential	Oxygen partial pressure during the equilibration (atm.)
1C	U, UC, UO_2	170	$a_U = 1$	3.3×10^{-30}
2C	U, UC, UO_2	142	"	"
3C	U, UC, Mg/MgO	191	$a_{Mg} = 0.53$	3.5×10^{-31}
4C	U, UC, Ca/CaO	170	$a_{Ca} = 0.15$	1.9×10^{-33}
5C	U, UC, Ca/CaO	150	$a_{Ca} = 0.45$	2.2×10^{-34}
6C	U, UC, Ca/CaO	160	$a_{Ca} = 1$	4.3×10^{-35}
7C	U, UC, Ca/CaO	144	$a_{Ca} = 1$	4.3×10^{-35}

TABLE 10

X-Ray And Chemical Analysis Data, Of The Reaction Products At 1473°K

Experimental	Chemical Analyses (wt.%)				Phase	Lattice	Lattice
Number	Uranium	Carbon	Oxygen	Nitrogen	identification by X-ray*	parameter of the U(C,O) phase (Å)	parameter of the UO_2 phase (Å)
1C	95.19	3.31	2.2	0.04**	$U(C,O)UO_2$	4.95220	5.4694
2C	95.19	3.40	1.83	0.1	U(C,O)	4.95115	5.4704
3C	95.20	3.91	1.1	0.05	U(C,O)	4.95374	-
4C	95.19	4.22	0.77	0.1	U(C,O)	4.95815	-
5C	95.19	4.42	0.48	0.05	U(C,O)	4.9604	-
6C	95.21	4.55	0.22	0.09	U(C,O)	4.95975	-
7C	95.20	4.57	0.21	0.002	U(C,O)	4.95935	-

* The central core of the U(C,O) sample was examined by X-ray.

** Nitrogen determined by Microkjeldahl's method.

TABLE 11

Equilibration Conditions For Experiments At 1573°K

Experiment Number	Starting materials for equilibration	Equilibration time (hours)	Activity of the metal used, to fix the oxygen chemical potential	Oxygen partial pressure during the equlibration (atm.)
1A	U, UC*, UO_2	24	$a_U = 1$	$9.2x10^{-28}$
2A	U, UC*, UO_2	48	"	"
3A	U, UC, UO_2	24	"	"
4A	U, UC, UO_2	48	"	"
5A	U, UC, UO_2	96	"	"
6A	U, UC, UO_2	130	"	"
7A	U, UC, Mg/MgO	165	$a_{Mg} = 0.5$	$8.4x10^{-28}$
8A	U, UC, Ca/CaO	48	$a_{Ca} = 0.01$	$2.0x10^{-28}$
9A	U, UC*, Ca/CaO	"	"	"
10A	U, UC, Ca/CaO	96	$a_{Ca} = 0.04$	$2.3x10^{-39}$
11A	U, UC, Ca/CaO	100	$a_{Ca} = 0.1$	$3.5x10^{-30}$
12A	U, UC**, Ca/CaO	"	"	"
13A	U, UC, Ca/CaO	48	$a_{Ca} = 0.15$	$1.4x10^{-30}$
14A	U, UC, Ca/CaO	120	$a_{Ca} = 0.27$	$4.7x10^{-31}$
15A	U, UC, Ca/CaO	98	$a_{Ca} = 0.28$	$4.3x10^{-31}$
16A	U, UC, Ca/CaO	51	$a_{Ca} = 1$	$3.4x10^{-32}$
17A	U, UC, Ca/CaO	96	"	"
18A	U, UC, Ca/CaO	120	"	"
19A	U, UC**, UO_2	104	$a_U = 1$	$9.2x10^{-28}$
20A	U, UC***, UO_2	105	"	"
21A	U, UC*, Ca/CaO	24	$a_{Ca} = 1$	$3.4x10^{-32}$

* Uc was in the form of small granules prepared by arc melting method. ** Zone refined UC. *** UC sintered pellet without any nickel in it, density=12.68g/cc

TABLE 12

X-Ray And Chemical Analysis Data Of The Reaction Products At 1573°K

Experiment	Chemical Analyses (wt.%)				Oxygen obtained by difference for $U(C_{1-x}O_x)$ (wt.%)	Phase identification by X-ray **	Lattice parameter of U(C,O) phase (Å)	Lattice parameter of UO_2 phase (Å)
Number	Uranium	Carbon	Oxygen	Nitrogen				
1A	-	-	-	-	-	U(C,O),UO_2	4.9492	5.4695
2A	-	-	-	-	-	"	4.9495	5.4690
3A	95.19	4.72	0.12	.03	0.1	U(C,O)	4.9609	-
4A	95.24	4.59	0.27	0.01	0.29	"	4.9585	-
5A	95.2	3.23	3.1	0.05*	2.08	U(C,O),UO_2	4.9518	5.4695
6A	95.18	3.24	4.0	0.2	2.07	"	4.9521	5.4704
7A	95.2	3.39	1.93	0.1*	-	U(C,O)	4.9525	-
8A	95.49	3.65	-	-	1.51	U(C,O)	4.9591	-
9A	-	-	-	-	-	U(C,O)	4.9453	-
10A	95.19	3.70	1.48	0.04*	1.46	U(C,O)	4.95505	-
11A	95.20	3.96	1.1	-	1.12	U(C,O)	4.95515	-
12A	-	-	-	-	-	U(C,O)	4.95665	-
13A	-	-	-	-	-	U(C,O)	4.9613	-
14A	95.19	4.05	0.58	0.05	0.64	U(C,O)	4.9586	-
15A	95.21	4.17	0.45	0.05	0.54	U(C,O)	4.95935	-
16A	95.19	4.76	0.23	0.11	0.32	U(C,O)	4.9681	-
17A	95.19	4.49	0.43	0.01	0.43	U(C,O)	4.9612	-
18A	95.19	4.49	0.41	0.03	0.42	"	4.96135	-
19A	95.20	3.23	2.8	0.04*	2.08	U(C,O)	4.9513	-
20A	95.19	3.24	-	-	2.07	U(C,O),UO_2	4.9515	5.4695

* Nitrogen determined by micro Kjeldahl's method. ** Central piece of U(C,O) was taken for X-ray analysis.

TABLE 13

Equilibration Conditions For Experiments At 1648°K

Experiment Number	Starting materials for equilibration	Equilibration time (hours)	Activity of the metal used to fix the oxygen chemical potential	Oxygen partial pressure during equilibration (atm.)
1B	U,UC*,UO_2	12	$a_U = 1$	4.0×10^{-26}
2B	U, UC*,UO_2	24	"	"
3B	U, UC*, UO_2	48	"	"
4B	U, UC*, UO_2	12	"	under high vacuum
5B	U, UC, UO_2	100	"	4.0×10^{-26}
6B	U, UC, UO_2	75	"	"
7B	U. UC, UO_2	120	"	"
8B	U, UC, Ca/CaO	110	$a_{Ca} = 0.11$	2.3×10^{-28}
9B	U, UC, Ca/CaO	105	$a_{Ca} = 0.16$	1.1×10^{-28}
10B	U, UC, Ca/CaO	106	$a_{Ca} = 0.38$	2.1×10^{-29}
11B	U, UC, Ca/CaO	110	$a_{Ca} = 0.42$	1.7×10^{-29}
12B	U, UC*, Ca/CaO	24	$a_{Ca} = 1$	3.0×10^{-30}
13B	U, UC, Ca/CaO	107	"	"
14B	U, UC, Ca/CaO	96	"	"
15B	U, UC**, Ca/CaO	101	$a_U = 1$	4.0×10^{-26}

* UC in the form of granules, prepared by arc melting method. ** Uc Sintered pellet, having no nickel.

TABLE 14

X-Ray And Chemical Analysis Data Of The Reaction Products At 1648°K

Experiment Number	Chemical Analyses (wt.%) Uranium	Carbon	Oxygen	Nitrogen	Phase identification by X-ray **	Lattice parameter of the U(C,O) phase (Å)	Lattice parameter of the UO_2 phase (Å)
1B	-	-	-	-	$U(C,O),UO_2$	4.9545	5.4705
2B	-	-	-	-	"	4.9495	5.4710
3B	-	-	-	-	"	4.95015	5.4704
4B	-	-	-	-	"	4.94795	5.4701
5B	95.19	3.28	2.0	0.05*	$U(C,O),UO_2$	4.9517	5.4690
6B	95.19	-	-	-	U(C,O)	4.9535	-
7B	95.19	3.28	2.3	0.04*	$U(C,O),UO_2$	4.9514	5.4695
8B	95.19	3.75	1.45	0.01	U(C,O)	4.9545	-
9B	95.20	3.95	1.1	0.1	U(C,O)	4.9555	-
10B	95.20	4.15	0.8	0.1	U(C,O)	4.9569	-
11B	95.19	4.41	0.53	0.05	U(C,O)	4.9573	-
12B	-	-	-	-	U(C,O)	4.95775	-
13B	95.20	4.46	0.43	0.02	U(C,O)	4.9605	-
14B	95.19	4.49	0.41	0.1	U(C,O)	4.95905	-
15B	95.18	3.31	-	-	U(C,O)	4.9511	-

* Nitrogen obtained by micro Kjeldahl's method.

** Central piece of U(C,O) pellet was used for X-ray analysis.

respectively and were taken from reference 79.

In figure 27, $\log_{10} p_{O_2}$ (the oxygen partial pressure in atm.) versus lattice parameter values are plotted for various equilibration experiments, for each temperature, i.e. 1473°K, 1573°K and 1648°K. Nitrogen contamination occured in varying amounts in all of the reaction products, but the amount was in the range of 0.05-0.1 wt.%. Assuming, the ideal **UC-UN solid solution behaviour, the associated** [illegible] -compositions, i.e. $U(C_{0.99},N_{0.01})$ and $U(C_{0.98},N_{0.02})$ respectively, decrease the lattice parameter by about 0.0006 Å, which is almost within the precision of lattice parameter measurements; the effect of nitrogen on the lattice parameter of U(C,O) phase was therefore, neglected. It can be seen from figure 27, that at the U-U(C,O) phase boundary, there is a decrease of lattice parameter with the increase of oxygen partial pressure, at all the temperatures of interest involved for this investigation. It has been reported by many investigators[5-8], that the decrease in lattice parameter is due to the replacement of carbon by oxygen in the UC lattice, and the results shown in tables 10, 12, and 14, support this conclusion. The results plotted in figure 27, suggest that the presence of nickel in UC used as a starting material for U(C,O), did not affect the oxygen solubility; as the experiments carried with UC pellets containing no nickel and with the zone refined UC, as the starting materials, under the same experimental conditions gave similar lattice parameter values.

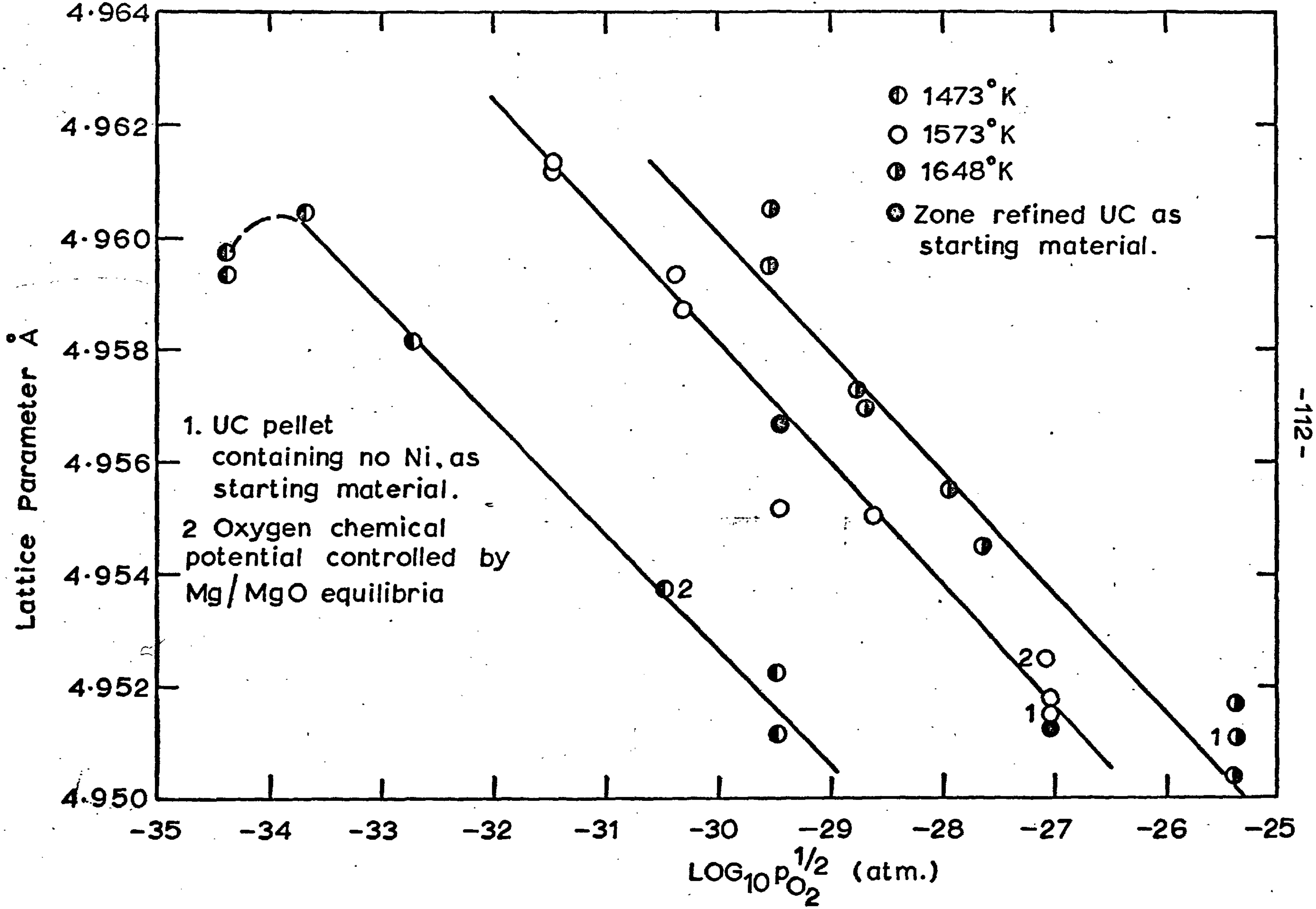

FIG.27 LATTICE PARAMETER OF THE U(C,O) PHASE, AS A FUNCTION OF $LOG_{10}p_{O_2}$ AT 1473°, 1573° & 1648°K

The lower lattice parameter observed in the case of preliminary experiments, in which granular UC was used might be due to nitrogen contamination. Further, the lowest lattice parameter observed at all the temperatures was in the same range, i.e. 4.951-4.952 Å, which suggests that the maximum solubility of oxygen in UC lattice is almost independent of temperature, which is contrary to the findings of Sano, et al.,[9] but is in agreement with the work of Russell[8], and Brett, et al.,[7]. Magnier and Accary[5], Anselin, et al.,[68] and Brett, et al.,[7] observed a maximum in their curves of lattice parameter versus oxygen content, at the lower oxygen contents, i.e. $U(C_{0.973},O_{0.027})$, but this observation could not be confirmed in the present work at 1573°K and 1648°K, as the minimum oxygen content was higher, i.e. $UC_{0.94}\,O_{0.06}$. At 1473°K, however there was some indication of a maximum at the relevant oxygen content.

In order to demonstrate the effect of oxygen solubility upon the lattice parameter of U(C,O), a typical plot is shown in figure 28, for the experimental results at 1573°K. Comparison has been made in this figure, with the oxygen contents determined for various lattice parameter values, from the curve of lattice parameter versus oxygen present in U(C,O), reported by Magnier and Accary[5], and the oxygen contents determined by difference, i.e. O = 1-C, during the present investigation. Oxygen contents determined by the vacuum fusion method are also included in

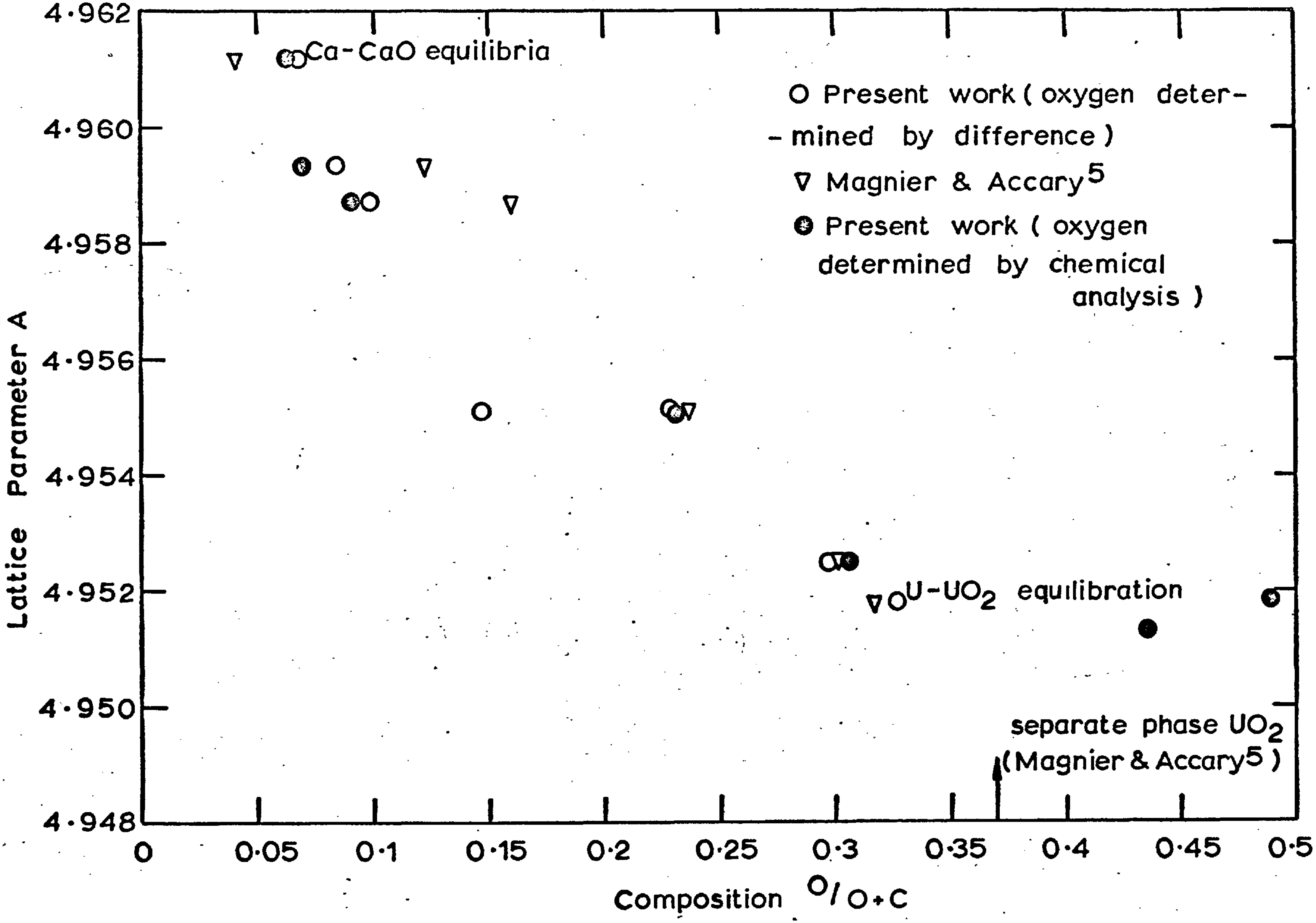

FIG.28 LATTICE PARAMETER AS A FUNCTION OF U(C,O) COMPOSITION, FROM EQUILIBRATION EXPERIMENTS AT 1573°K.

figure 28. It is clear from figure 28, that the oxygen contents determined by difference and by the vacuum fusion method are in good agreement when the U(C,O) is in equilibrium with uranium only. The disagreement at the higher oxygen contents might be attributed to the presence of traces of UO_2, in the samples analysed for oxygen.

5.C.1.(i) Thermodynamic Calculations

If U (C,O) is assumed to be a pseudobinary solid solution of UC and UO, then the results presented in tables 10, 12 and 14, can be written in terms of UC and UO mole fractions. The results presented in tables 15, 16 and 17, are those obtained for samples equilibrated at the longer times, i.e. in excess of 100 hours. Moreover, the chemical analyses of these experiments were relatively more reliable. Oxygen analysis by vacuum fusion technique was accepted as being most reliable when it agreed with the value calculated by difference for the carbon analysis. If the discrepancy was large, it was assumed that either there was a large nitrogen contamination or an error in either the carbon analysis or in the oxygen determination and the results were discarded. For experiments in which UO_2 was present with uranium and the U(C,O), the oxygen content determined by difference was considered to be more reliable, as already deduced in connection with figure 28.

While calculating the formula of U(C,O), from the chemical analysis results, the atom fraction of uranium was taken as unity,

TABLE 15

Compositions of U (C,O) Phase at 1473°K

Experiment Number	U(C,O) formula calculated from chemical analyses	N_{UC} (mole fraction)	N_{UO} (mole fraction)	p_{O_2} (atm.)	$\frac{p_{O_2}^{1/2}}{N_{UO}}$	$\log_{10} \frac{p_{O_2}^{1/2}}{N_{UO}}$	$\frac{N_{UC}}{N_{UC}}$
1C	$UC_{0.69}O_{0.31}$*	0.69	0.31	3.3×10^{-30}	5.81×10^{-15}	-14.24	0.453
2C	$UC_{0.71}\ O_{0.29}$	0.71	0.29	3.3×10^{-30}	6.33×10^{-15}	-14.2	0.404
3C	$UC_{0.82}\ O_{0.17}$	0.82	0.17	3.45×10^{-31}	3.42×10^{-15}	-14.47	0.211
4C	$UC_{0.87}\ O_{0.12}$	0.87	0.12	1.92×10^{-33}	3.66×10^{-16}	-15.4	0.137
5C	$UC_{0.92}\ O_{0.08}$	0.92	0.08	2.2×10^{-34}	1.96×10^{-16}	-15.7	0.082
6C	$UC_{0.95}\ O_{0.04}$	0.95	0.04	4.35×10^{-35}	1.94×10^{-16}	-15.7	0.036

* Oxygen substituted in the formula of U(C,O), was obtained by difference.

TABLE 16

Compositions Of U(C,O) Phase At 1573°K

Experiment Number	U(C,O) furmula calculated from chemical analyses	N_{UC} (mole fraction)	N_{UO} (mole fraction)	p_{O_2} (atm.)	$\frac{p^{1/2}_{O_2}}{N_{UO}}$	$\frac{\log p^{1/2}_{O_2}}{N_{UO}}$	$\frac{N_{UO}}{N_{UC}}$
5A	$UC_{0.67},O^{*}_{0.33}$	0.67	0.33	9.2×10^{-28}	9.29×10^{-14}	-13.03	0.486
6A	$UC_{0.68},O^{*}_{0.32}$	0.68	0.32	"	9.32×10^{-14}	-13.03	0.484
7A	$UC_{0.71},O_{0.3}$	0.71	0.30	8.43×10^{-28}	9.46×10^{-14}	-13.02	0.435
10A	$UC_{0.77},O_{0.23}$	0.77	0.23	2.35×10^{-29}	2.09×10^{-14}	-13.68	0.3
14A	$UC_{0.9},O_{0.091}$	0.9	0.091	4.67×10^{-31}	7.53×10^{-15}	-14.12	0.1
15A	$UC_{0.92},O_{0.07}$	0.92	0.07	4.35×10^{-31}	9.42×10^{-15}	-14.03	0.076
18A	$UC_{0.93},O_{0.065}$	0.93	0.065	3.43×10^{-32}	2.89×10^{-15}	-14.54	0.068

* Oxygen employed in the formula was obtained by difference.

TABLE 17

Compositions Of U(C,O) Phase At 1648°K

Experiment Number	U(C,O) formula calculated from the chemical analyses	N_{UC} (mole fraction)	N_{UO} (mole fraction)	p_{O_2} (atm.)	$\frac{p_{O_2}^{1/2}}{N_{UO}}$	$\log \frac{p_{O_2}^{1/2}}{N_{UO}}$	$\frac{N_{UO}}{N_{UC}}$
7B	$UC_{0.68},O_{0.32}$*	0.68	0.32	4.0×10^{-26}	6.29×10^{-13}	-12.20	0.466
5B	$UC_{0.68},O_{0.32}$	0.68	0.32	"	6.29×10^{-13}	-12.20	0.466
8B	$UC_{0.78},O_{0.22}$	0.78	0.22	2.32×10^{-28}	6.73×10^{-14}	-13.17	0.289
9B	$UC_{0.82},O_{0.17}$	0.82	0.17	1.12×10^{-28}	6.15×10^{-14}	-13.21	0.209
10B	$UC_{0.86},O_{0.13}$	0.86	0.13	2.1×10^{-29}	3.65×10^{-14}	-13.44	0.145
11B	$UC_{0.92},O_{0.08}$	0.92	0.08	1.72×10^{-29}	5.06×10^{-14}	-13.3	0.089
13B	$UC_{0.93},O_{0.07}$	0.93	0.07	3.6×10^{-30}	2.59×10^{-14}	-13.59	0.072

* Oxygen associated with the U(C,O) formula, was obtained by difference.

as the uranium content obtained by chemical analysis did not deviate (tables 10, 12 and 14), much from the stoichiometric value, i.e. 95.19 wt.%.

In the results presented in tables 15, 16 and 17, no corrections are made in the formula for U(C,O), due to the nitrogen content which was invariably present. If it is assumed that nitrogen is present in the form of UN as solid solution in U(C,O), then the mole fraction of UN is between 0.009-0.018, which is neglected in the subsequent calculations.

5.C.1.(i).a. Method of Calculating the Activity Coefficient of UC in the U(C,O), Solid Solution

Generally for a three component system if the activity coefficients for the two components are known over a range of composition, the activity coefficient for the third component may be calculated by using the Gibbs-Duhem equation:

$$N_1 \, d \ln \gamma_1 + N_2 \, d \ln \gamma_2 + N_3 \, d \ln \gamma_3 = 0$$

$$\text{i.e.} \quad \ln \gamma_1 = - \int_{N_1=1}^{N_1=N_1} \frac{N_2}{N_1} \, d \ln \gamma_2 - \int_{N_1=1}^{N_1=N_1} \frac{N_3}{N_1} \, d \ln \gamma_3$$

In order to calculate the activity coefficient data for carbon in U(C,O), from the known activity coefficients of uranium and oxygen, the above equation can be written as:

$$\int_{N_C=1}^{N_C=N_C} d \ln \gamma_C = - \int_{N_C=1}^{N_C=N_C} \frac{N_U}{N_C} \, d \ln \gamma_U - \int_{N_C=1}^{N_C=N_C} \frac{N_U}{N_C} \, d \ln \gamma_O$$

which means the activity coefficient data for uranium and oxygen should be available in the range of pure carbon to any carbon content in the U(C,O) solid solution. These data are not possible to obtain for the U(C,O) system.

Further, no thermodynamic data are available about the controversial compound UO. Thus, in view of these problems, the following, an indirect method, for calculating the activity coefficients of UC in the U(C,O) solid solution was eventually used.

$$U + {}^{1}/_{2}\, O_2 \; = \; UO$$

$$K \; = \; \frac{a_{UO}}{a_U \cdot p_{O_2}^{1/2}}$$

and $$a_{UO} \; = \; K \cdot a_U \cdot p_{O_2}^{1/2}$$

$$\gamma_{UO} \; = \; K \cdot \frac{a_U}{N_{UO}} \cdot p_{O_2}^{1/2}$$

or

$$\ln \gamma_{UO} \; = \; \ln K + \ln \left(\frac{a_U}{N_{UO}} \cdot p_{O_2}^{1/2} \right)$$

differentiating

$$d \ln \gamma_{UO} \; = \; d \ln \left(\frac{a_U}{N_{UO}} \cdot p_{O_2}^{1/2} \right) \quad \ldots. \quad (5\text{-a})$$

If it is assumed that U(C,O) is a pseudobinary solid solution of UC and UO, then the Gibbs-Duhem equation in the form of a binary system can be written for this solid solution:

$$N_{UC} \; d \ln \gamma_{UC} + N_{UO} \; d \ln \gamma_{UO} = 0$$

i.e.

$$\ln \gamma_{UC} = - \int_{N_{UC=1}}^{N_{UC} = N_{UC}} \frac{N_{UO}}{N_{UC}} \cdot d \ln \gamma_{UO} \qquad \ldots\ldots (5\text{-}b)$$

If the value of d ln γ_{UO} derived in equation (5-a) is substituted in equation (5-b), then:

$$\ln \gamma_{UC} = - \int_{N_{UC=1}}^{N_{UC}=N_{UC}} \frac{N_{UO}}{N_{UC}} \cdot \; d \ln \left(\frac{a_U \cdot p_{O_2}^{1/2}}{N_{UO}} \right) \qquad \ldots\ldots (5\text{-}c)$$

Equation (5-c), makes it possible to calculate the activity coefficient of UC as a function of composition, even though the thermodynamic data for the solid uranium monoxide are not known. Moreover, once the activity of UC is known then the activity of carbon can be calculated from the available standard free energy data for the reaction:

$$U + C = UC \qquad \ldots\ldots(5\text{-}d)$$

The relevant CO and CO_2 partial pressures can also be calculated for any particular equilibrium, using the relevant carbon activity and equilibrium oxygen partial pressure, and applying the thermodynamic data for the reactions:

$$C + {}^1/_2 \, O_2 = CO$$

and $$C + O_2 = CO_2$$

Values of $\dfrac{p_{O_2}^{1/2}}{N_{UO}}$ $(a_U = 1)$

and N_{UO}/N_{UC} were taken from tables 15,16 and 17, and the values of γ_{UC} were evaluated graphically at three temperatures, i.e. 1473°K, 1573°K and 1648°K. One of the modified Gibbs-Duhem plot is shown in figure 29.

The UC activity values for various compositions of U(C,O) are shown in table 18, for the relevant temperatures. Results from table 18 indicate that there is a negative deviation from Raoult's law for the UC and UO solid solution at all the temperatures of this investigation.

Accepting the values for the standard free energy of formation of UC recommended by the I.A.E.A. panel 1962[18], i.e. - 22.8 Kcals./mole at 1473°K and 1573°K, and - 22.6 Kcals./mole at 1648°K, then the corresponding values for the activities of carbon in the U(C,O) solid solution, could also be calculated using equation (5-d), and are included in table 18.

5.C.1.(ii).b. Evaluation of Thermodynamic Data

Values of the relative partial molar enthalpies and entropies of oxygen in the U(C,O) solid solution are derived by using the following equations:

$$\left[\frac{\partial\left(\frac{\Delta\bar{G}_{\frac{1}{2}O_2}}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right]_{x_O} = \Delta\bar{H}_{\frac{1}{2}O_2} \qquad (5\text{-}e)$$

and

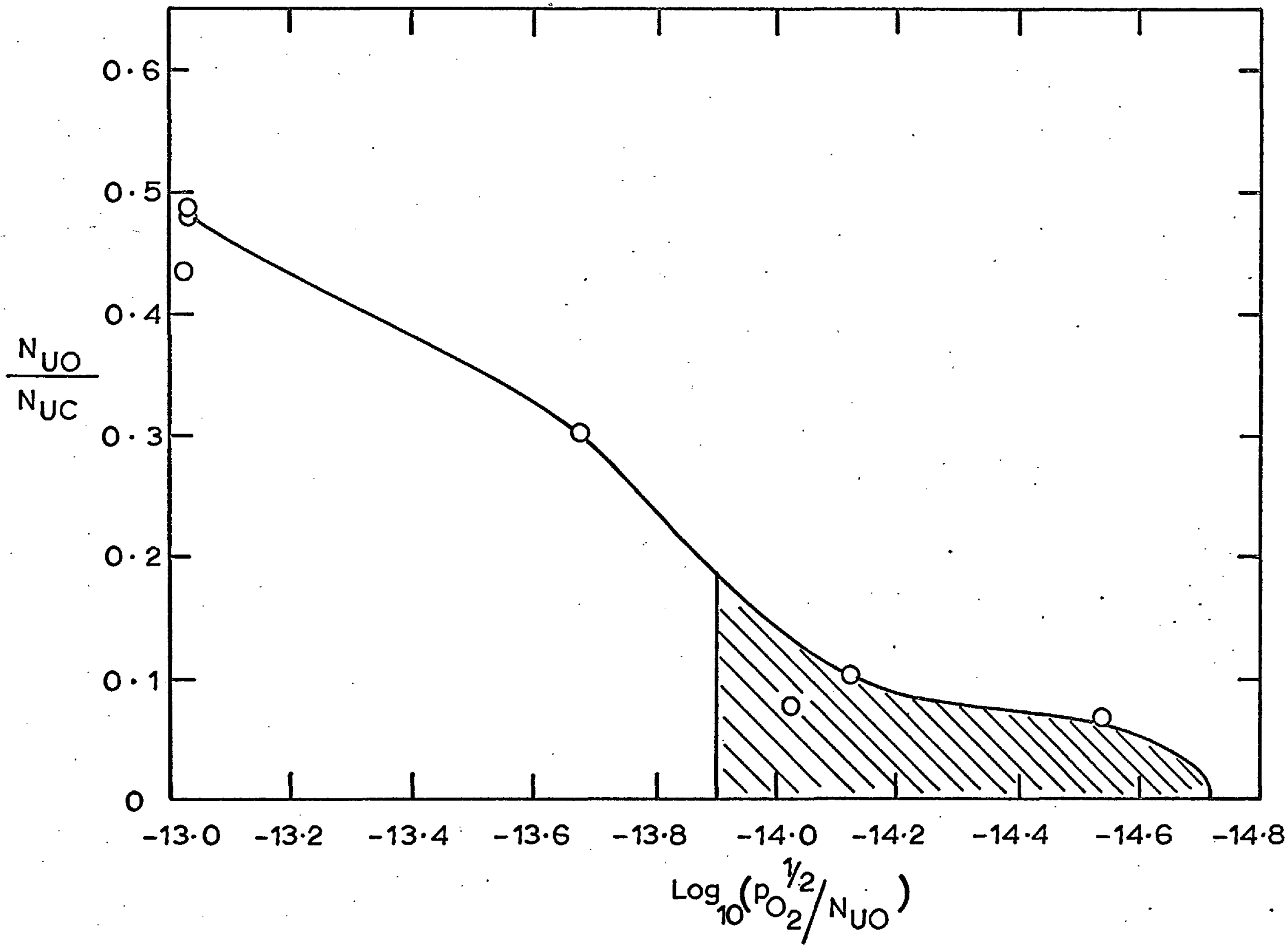

FIG.29 DETERMINATION OF γ_{UC} IN U(C,O) IN EQUILIBRIUM WITH U, AT 1573°K, USING THE MODIFIED GIBBS-DUHEM RELATIONSHIP (see p.121)

TABLE 18

Calculated Activities of UC, And Carbon, In U(C,O) Phase, As A Function Of Composition, At 1473°K, 1573°K And 1648°K.

N_{UC}	1473°K		1573°K		1648°K	
mole fraction of UC in U(C,O)	Activity of UC (a_{UC})	Activity of carbon (a_C)	Activity of UC (a_{UC})	Activity of carbon (a_C)	Activity of UC (a_{UC})	Activity of carbon (a_C)
0.909	0.895	3.7×10^{-4}	0.83	5.64×10^{-4}	0.864	8.69×10^{-4}
0.9	0.879	3.64×10^{-4}	0.81	5.5×10^{-4}	0.845	8.5×10^{-4}
0.869	0.776	3.21×10^{-4}	0.763	5.17×10^{-4}	0.774	7.79×10^{-4}
0.8	0.517	2.14×10^{-4}	0.648	4.4×10^{-4}	0.657	6.61×10^{-4}
0.769	0.472	1.95×10^{-4}	0.571	3.88×10^{-4}	0.615	6.19×10^{-4}
0.74	0.417	1.73×10^{-4}	0.492	3.33×10^{-4}	0.512	5.65×10^{-4}
0.714	0.386	1.547×10^{-4}	0.396	2.69×10^{-4}	0.462	4.64×10^{-4}
0.7	0.372	1.54×10^{-4}	0.383	2.6×10^{-4}	0.42	4.2×10^{-4}
0.68	0.365	1.51×10^{-4}	0.28	1.94×10^{-4}	0.22	2.25×10^{-4}

$$\left[\frac{\partial(\Delta\bar{G}_{\frac{1}{2}O_2})}{\partial T}\right]_{x_O} = -\Delta\bar{S}_{\frac{1}{2}O_2} \quad \ldots\ldots \quad (5\text{-}f)$$

The suffix x_O, indicates constant composition of oxygen in the U(C,O) solid solution. The plots of $\log_{10} p_{O_2}^{1/2}$ versus 1/T, and $\Delta\bar{G}_{\frac{1}{2}O_2}$ versus T °K, are shown in figures 30 and 31, respectively.

The values of $\Delta\bar{H}_{\frac{1}{2}O_2}$ and $\Delta\bar{S}_{\frac{1}{2}O_2}$, thus derived are shown in the following table 19.

TABLE 19

N_{UO} (Mole fraction)	$-\Delta\bar{H}_{\frac{1}{2}O_2}$ (Kcals./mole)	$-\Delta\bar{S}_{\frac{1}{2}O_2}$ (e.u.)
0.1	130.7	6.15
0.2	131.5	15.38
0.25	137.2	16.38
0.32	139.2	17.06

The values thus obtained are valid between 1473°K to 1648°K. The oxygen partial pressures for various mole fractions of UO were taken from plots of oxygen content versus log p_{O_2}, for three different temperatures.

From the calculated carbon activity data, shown in table 18 and the known oxygen partial pressures, at a fixed activity of uranium ($a_U = 1$), it is possible to derive the standard free energy of formation value of U(C,O) phase, for selected compositions at various temperatures, using the equation:

$$U_{(l)} + C_{(s)} + \tfrac{1}{2}\ O_{2(g)} \rightleftharpoons U(C,O)_{(s)}$$

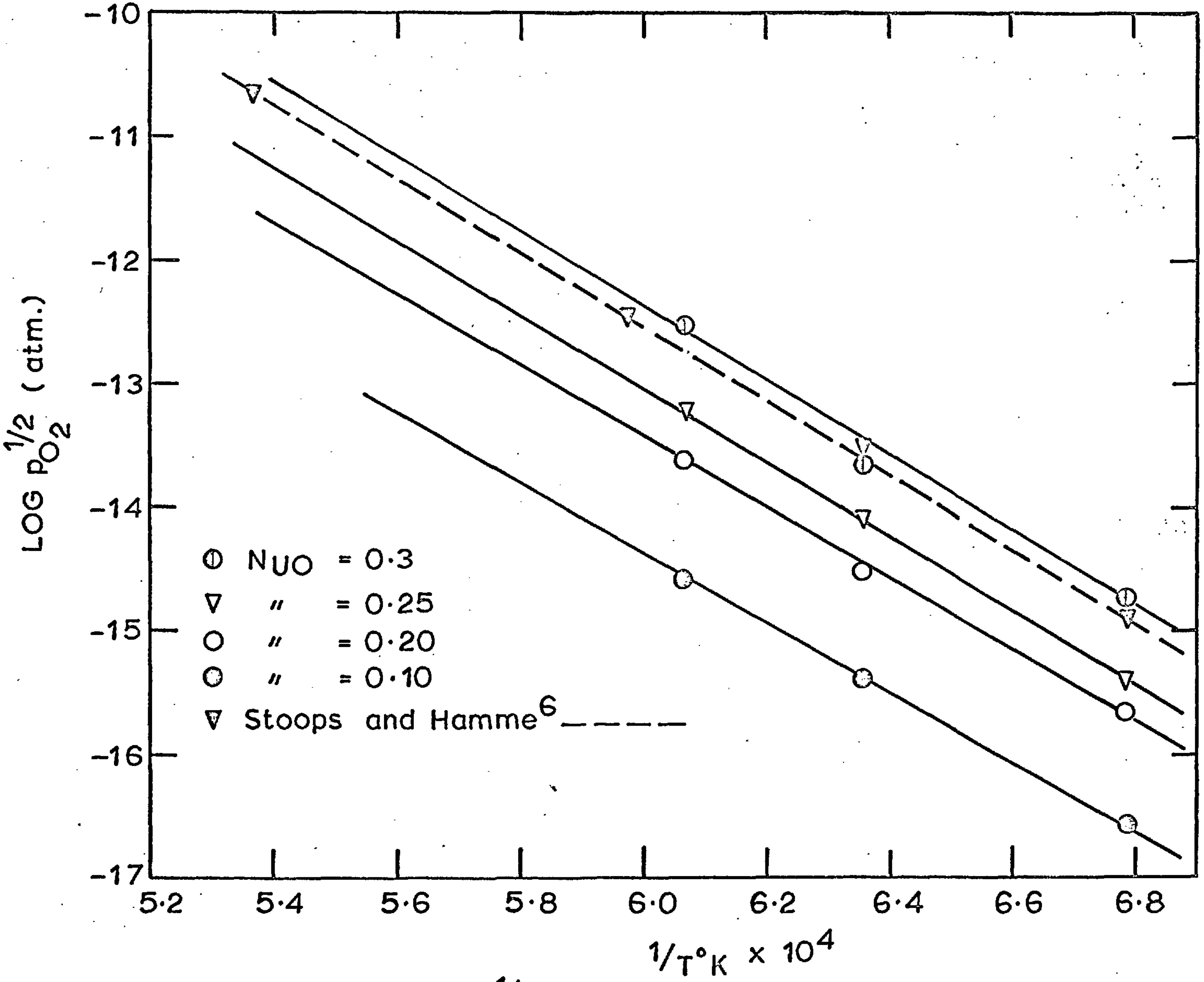

FIG.30 PLOT OF $LOG_{10} P_{O_2}^{1/2}$ vs. 1/T°K FOR VARIOUS UO MOLE FRACTIONS IN U(C,O) SOLID SOLUTION.

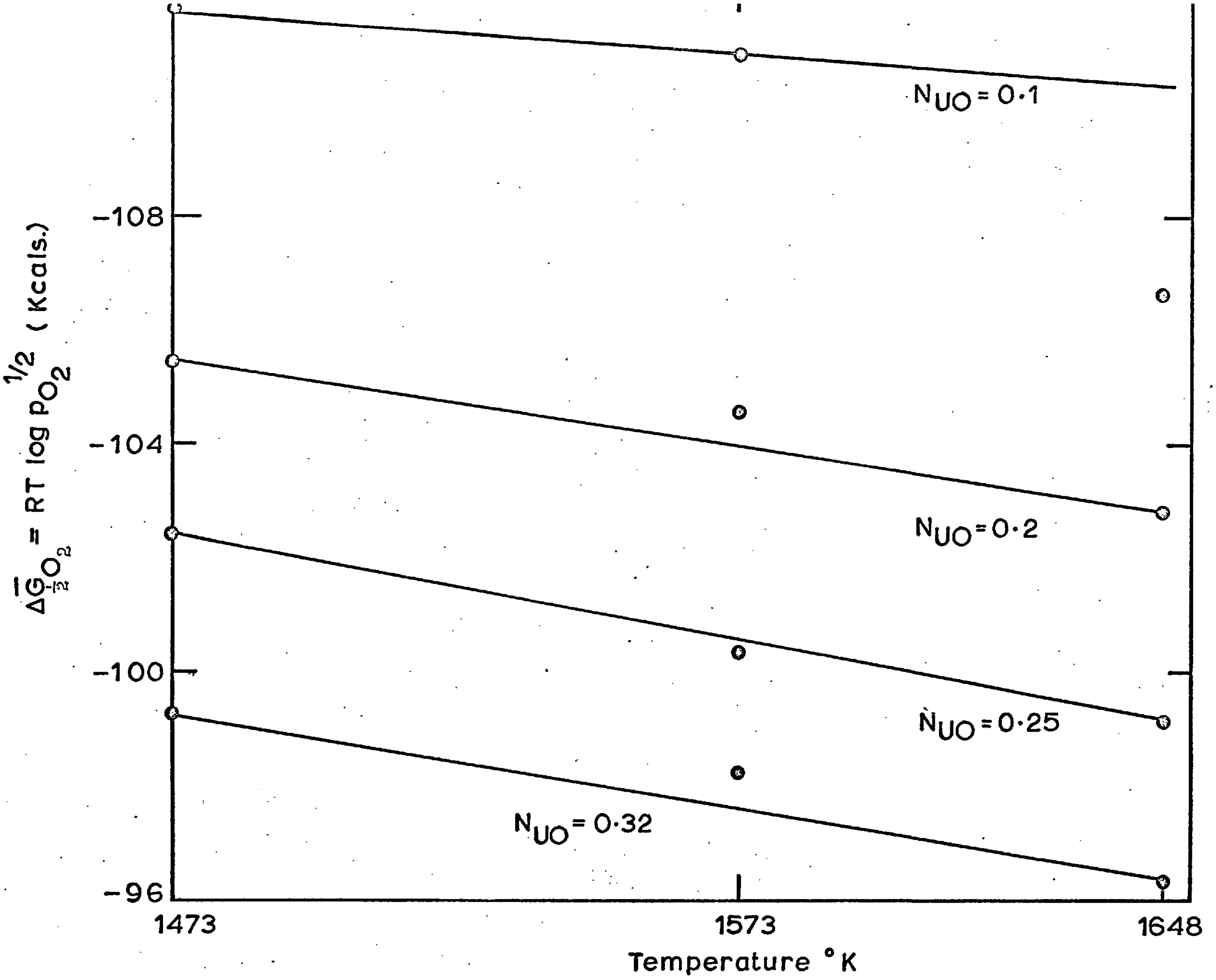

FIG.31. RELATIVE PARTIAL MOLAR FREE ENERGY OF OXYGEN IN U(C,O), AS A FUNCTION OF TEMPERATURE, FOR VARIOUS COMPOSITIONS.

The calculated values are shown in table 20.

TABLE 20

Standard Free Energy Of Formation Of U(C,O) Phase, For Various Compositions At Different Temperatures.

Formula for U(C,O)	$\Delta G^{o}_{U(C,O)}$, (Kcals./mole) 1473°K	1573°K	1648°K
$U(C_{0.9},O_{0.1})$	-32.0	-32.20	-31.77
$U(C_{0.8},O_{0.2})$	-40.88	-40.23	-39.76
$U(C_{0.75},O_{0.25})$	-44.54	-44.0	-43.24
$U(C_{0.68},O_{0.32})$	-49.30	-49.30	-49.20

From the data of Stoops and Hamme[6], it is also possible to calculate the standard free energy of formation, for the saturated uranium oxycarbide ($U(C_{0.75},O_{0.25})$). The calculated value of $\Delta G^{o}_{U(C_{0.75},O_{0.25})}$, from the data of these investigators is -42.2 Kcals/mole, at 1873°K.

By applying the relation:

$$\frac{\partial(\Delta G^{o}/_{T})}{\partial(\frac{1}{T})} = \Delta H^{o}$$

the value of ΔH^{o}, i.e. the standard heat of formation for $U(C_{0.68},O_{0.32})$ is also derived, by plotting $\Delta G^{o}/_{T}$ versus $\frac{1}{T}$, as shown in figure 32.

From the slope of figure 32, the value of ΔH^{o} is -47.6 Kcals./mole, and is valid in the temperature range of 1473°K to 1648°K.

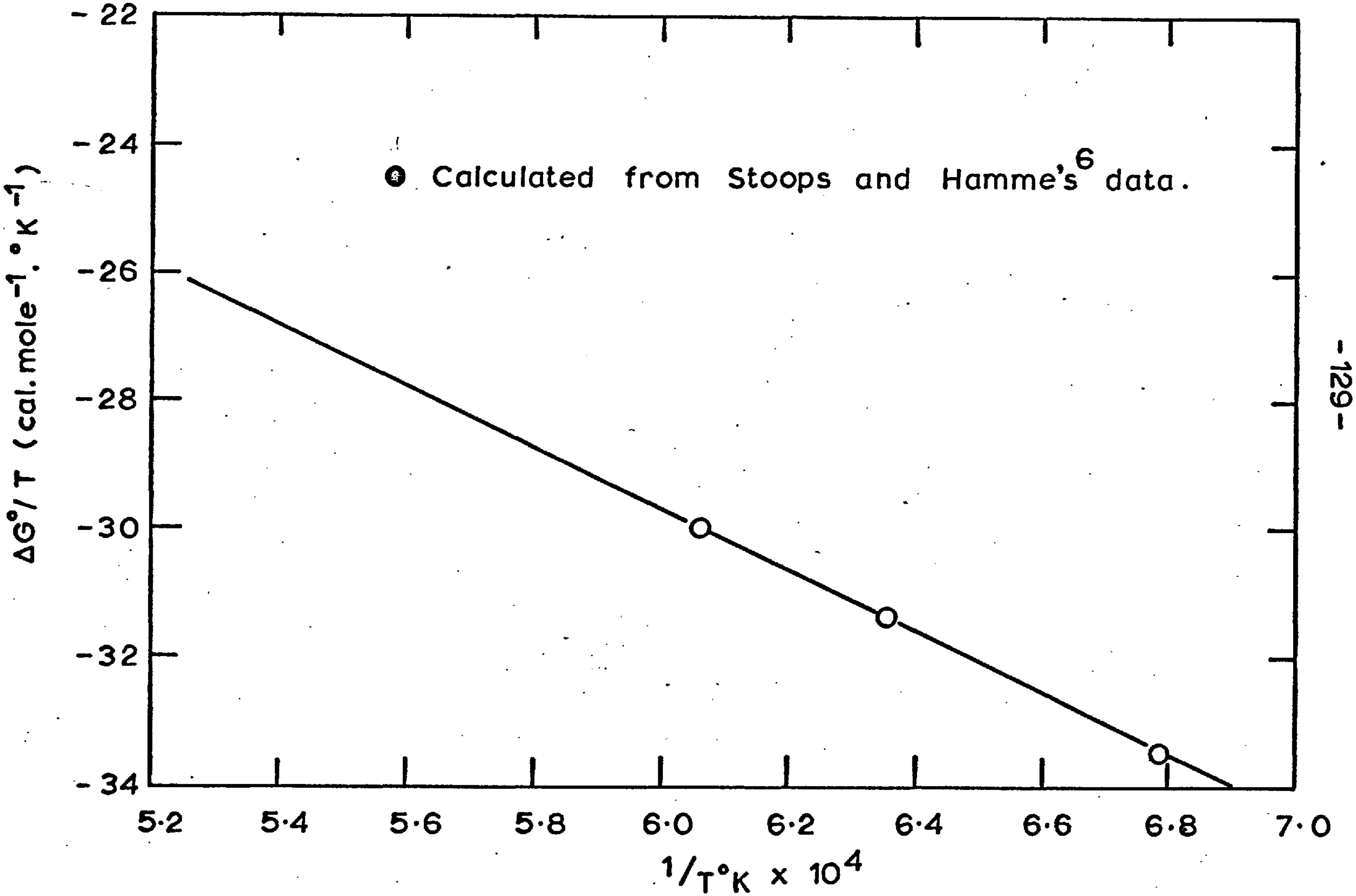

FIG.32 PLOT OF $\Delta G^\circ/T$ vs. $1/T^\circ K$ IN ORDER TO CALCULATE ΔH° FOR $UC_{0.68}O_{0.32}$.

Recently, Chiotti, et al.,[51], studied the thermodynamics of uranium oxycarbide system, by measuring the emf of fused galvanic cells of the type:

$$U/KCl/LiCl \ - \ UCl_3/U(C_{1-x},O_x),C,$$

over a temperature range of 723°K to 1023°K, and for oxycarbide compositions of 0.11 - 0.82 mole fraction of UO. These investigators derived the following relations from their data, assuming that the U(C,O) is a pseudobinary solid solution of UC and UO:

$$\Delta \bar{G}^{xs}\ UC/(1-x_{UC})^2 = -24{,}000 + X_{UC}\ (24230 - 44.7\ T)$$

and

$$\Delta \bar{G}^{xs}\ UO/(1-x_{UO})^2 = -24{,}000 + (X_{UC}-0.5)(24230 - 44.7\ T)$$

The $\Delta \bar{G}^{xs}_{(UC)}$, i.e. $R\ T \ln \gamma_{UC}$, data reported by Chiotti, et al.,[51], and values derived in the present investigation are shown in table 21.

TABLE 21

Effect Of Temperature And Composition, Upon $\Delta \bar{G}^{xs}_{(UC)}$ Values.

N_{UC}	Present Work			Chiotti, et al.,[51]
mole fraction of UC in U(C,O)	$-\Delta \bar{G}^{xs}_{UC}$ at 1473°K (cals.)	$-\Delta \bar{G}^{xs}_{UC}$ at 1573°K (cals.)	$-\Delta \bar{G}^{xs}_{UC}$ at 1648°K (cals.)	$-\Delta \bar{G}^{xs}_{UC}$ at 1023°K (cals.)
0.9	66.7	328.8	206.6	430
0.8	1277.0	658.5	644.6	1650
0.7	1848.5	1884.8	1691.9	3510

From the data reported by Stoops and Hamme[6], it is possible to calculate the value of the activity coefficient of UC, for $N_{UC} = 0.75$ (mole fraction), at 1873°K. This value of the activity coefficient of UC is, i.e. $\gamma_{UC} = 0.505$, and corresponds to a $\Delta\bar{G}^{xs}_{UC}$ of -2554 (cals.).

It is difficult to compare Chiotti, et al[51]., results, with those obtained in the present investigation, as in view of the lower temperature involved, i.e. 450 - 750°C; and the fact that the U(C,O) phase was always in contact with pure graphite. It is to be recalled that the results of the present work refer to the U - U(C,O) phase boundary. Additional uncertainties associated with the preparation of U(C,O) of known compositions, used by Chiotti, et al.,[51] and the degree of equilibrium referred to 'later' do not make it worthwhile to evaluate the thermodynamic data.

However, the data reported by Stoops and Hamme[6], were manipulated to provide a comparison with the present work, whenever possible and in general the agreement is fair. Mainly, the chemical analysis of oxygen could be a source of discrepancy. Most of the experiments carried out by Stoops and Hamme[6], were such that UO_2 was present as a separate phase along with U(C,O) phase, and it was therefore, difficult to assign an accurate value for the oxygen content of their U(C,O) phase.

The accuracy of the results of present investigation, is affected by a variety of errors, which are discussed in details in appendix K. Reference to appendix K, indicates that the experimental errors involved in the present work are relatively small, compared with other errors associated with the literature values for the various equilibrias.

5.C.2. $U(C,O) - UO_2$ Phase Boundary

Preliminary experiments were carried out at 1648°K, in which uranium-gold alloys were equilibrated with UC granules in stoichiometric urania crucibles. The equilibrated reaction product U(C,O) gave lattice parameters as low as 4.946 Å. These low lattice parameters suggested that the U(C,O) single phase could accomodate more oxygen than the composition $U(C_{0.68},O_{0.32})$, in equilibrium with both uranium and UO_2. Accurate chemical analysis was difficult due to the reasons mentioned in the earlier section of this chapter. An alternative explanation might include reaction between the UC and uranium-gold alloy. Therefore, Electron micro probe analysis was made of a polished specimen containing uranium-gold alloy and U(C,O). It was found that uranium-gold remained as a separate phase in contact with the U(C,O) phase and contained no carbon, within the detection limits of the Electron micro probe. In addition, analyses of the U(C,O) phase never revealed the presence of significant (less than 0.1%) quantities of gold.

The micro probe analysis however, did reveal the presence of nitrogen, as well as the expected oxygen and carbon. The presence of nitrogen might account for the anonomously low lattice parameters of U(C,O).

Subsequent equilibration experiments incorporated the sintered uranium monocarbide pellets which enabled the equilibrated samples to be analysed, both chemically and by using X-ray and metallographic techniques. Experiments were performed at the temperature, i.e. 1573°K, for which the most data were available, for other phase boundary of U(C,O) phase, i.e. U - U(C,O).

It was observed that when the activity of uranium was reduced to a value as low as $\lesssim 3.5 \times 10^{-3}$, very weak line of an unidentified phase were present on the X-ray photograph of the U(C,O) phase. As these lines might have been due to the presence of a second carbide phase, resulting from the high carbon activity associated with the low uranium activity. Therefore, some additional experiments were carried out in which both UC and UC_2 were equilibrated at various activities of uranium, and oxygen chemical potentials. Moreover, it was thought that such experiments might also help to resolve the difference in the observations of various investigators (19, 20, 26, 100) regarding the relative stability of the UC_2 phase in the presence of oxygen at 1573°K, rather than the U_2C_3 phase. Many workers including Alcock and Grieveson[17], had not observed U_2C_3 phase, during their equilibration experiments at 1773°K, which is certainly below the generally accepted temperature for which UC_2 is stable, i.e. above 1973°K.

The reaction products of the various equilibration experiments were separated mechanically and identified by means of X-ray analyses. Metallographic examinations were carried out for all those equilibrated samples which included UC_2 along with UC as the starting materials, in order to provide information about the amount and distribution of the resulting phases. The identified carbide phases were individually separated, and chemically analysed for uranium, carbon and oxygen. No analyses were carried out for nitrogen contamination, as the experimental results for the U-U(C,O) phase boundary, had indicated that there was little contamination for this element. Therefore, the effect of little nitrogen contamination upon the lattice parameter and composition of the U(C,O) phase was negligible.

The uranium-gold alloy bead for each experiment was mechanically separated and cleaned for any carbide contamination, using hydrochloric acid and then analysed. The activity data about the uranium-gold solutions, obtained by Grieveson[97], at 1723°K, were used to calculate the activities of uranium at 1573°K (appendix L). Phase diagram of the uranium-gold binary system presented by Smithells[101], was used to construct the activity composition plot (see appendix L) for uranium at 1573°K.

The results of the various equilibration experiments are shown in tables 22 and 23.

TABLE 22

Experimental Conditions For Experiments At 1573°K

Experiment Number	Starting materials for equilibration	Equilibration time (hours)	Composition of uranium-gold alloys after equilibration (mole fraction)		Activity of uranium (a_U)	Oxygen partial pressure during the equilibration (atm.)
			N_{AU}	N_U		
101 A	10 mole % gold + 90 mole % uranium, UC, UO_2	124	0.09	0.091	0.88	8.1×10^{-28}
102 A	10 mole % gold + 90 mole % uranium, UC, UO_2	109	0.11	0.89	0.84	7.75×10^{-28}
103 A	20 mole % gold + 80 mole % uranium, UC, UO_2	128	0.16	0.84	0.75	6.9×10^{-28}
104 A	30 mole % gold + 70 mole % uranium, UC, UO_2	120	0.22	0.78	0.64	5.9×10^{-28}
105 A	40 mole % gold + 60 mole % uranium, UC, UO_2	124	0.46	0.54	0.44	4.0×10^{-28}
106 A	50 mole % gold + 50 mole % uranium, UC, UO_2	121	0.5	0.5	0.44	4.0×10^{-28}
107 A	60 mole % gold + 40 mole % uranium, UC, UO_2	115	0.67	0.33	0.44	4.0×10^{-28}
108 A	70 mole % gold + 30 mole % uranium, UC, UO_2	120	0.73	0.27	3.5×10^{-3}	2.6×10^{-25}
109 A	80 mole % gold + 10 mole % uranium, UC, UO_2	116	0.73	0.27	3.5×10^{-3}	2.6×10^{-25}

TABLE 22 continued

Experiment Number	Starting materials for equilibration	Equilibration time (hours)	Composition of uranium-gold alloys after equilibration (mole fraction)		Activity of uranium (a_U)	Oxygen partial pressure during the equilibration (atm.)
110 A	90 mole % gold + 10 mole % uranium, UC, UO_2	145	0.79	0.21	3.5×10^{-3}	2.6×10^{-25}
111 A	85 mole % gold + 15 mole % uranium, UC, UC_2, BeO*	130	0.81	0.19	3.5×10^{-3}	-
112 A	60 mole % gold + 40 mole % uranium, UC, UC_2, BeO*	135	0.79	0.21	3.5×10^{-5}	-
113 A	70 mole % gold + 30 mole % uranium, + UC, UC_2, BeO*	96	0.74	0.26	3.5×10^{-3}	-
114 A	85 mole % gold + 15 mole % uranium, UC, UC_2, UO_2	101	0.82	0.18	3.5×10^{-3}	2.6×10^{-25}
115 A	60 mole % gold + 40 mole % uranium, UC, UC_2, UO_2	100	0.72	0.28	3.5×10^{-3}	2.6×10^{-25}
116 A	UC, UC_2 Ca/CaO	96	-	-	$a_{Ca} = 1$	3.43×10^{-32}
117 A	UC, U_2C_3 UO_2	119	-	-	-	-

* Experiments similar to Alcock and Grieveson[17], performed at 1573°K.

TABLE 23

X-Ray and Chemical Analyses Of The Reaction Products At 1573°K

Experiment Number	Phase identification	Chemical Analyses of U(C,O) (wt.%) Uranium	Carbon	Oxygen	Chemical Analyses of $UC_{2-x}O_x$ or U_2C_3 (wt.%) Uranium	Carbon	Oxygen	Lattice parameter of U(C,O) phase (Å)	Lattice parameter of the $UC_{2-x}O$ or U_2C_3 phase (Å)
101 A	U(C,O)	95.19	3.48	1.8	-	-	-	4.9523	-
102 A	U(C,O), UO_2	95.20	3.51	1.8	-	-	-	4.9525	-
103 A	U(C,O)	95.19	3.92	1.3	-	-	-	4.9535	-
104 A	U(C,O)	95.18	3.86	1.2	-	-	-	4.9556	-
105 A	U(C,O)	95.18	4.15	0.9	-	-	-	4.9574	-
106 A	U(C,O)	-	4.16	1.0	-	-	-	4.9583	-
107 A	U(C,O), UO_2	-	4.15	0.5	-	-	-	4.9575	-
108 A	U(C,O)*, UO_2	95.18	4.28	0.75	-	-	-	4.9615	-
109 A	U(C,O)*, UO_2	-	4.27	1.0	-	-	-	4.95730	-
110 A	U(C,O)*, UO_2	95.18	4.28	0.7	-	-	-	4.95825	-
111 A	U(C,O), U_2C_3	-	4.47	0.5	-	7.0	0.12	4.96450	8.08890
112 A	U(C,O), U_2C_3	95.18	4.452	0.4	92.97	6.9	0.2	4.96155	8.08850
113 A	U(C,O), UO_2, UC_2**	-	4.29	0.7	-	8.5	2.2	4.95870	a = 3.5210 c = 5.9910
114 A	U(C,O), UC_2**	95.18	4.37	0.7	90.80	8.45	0.5	4.96690	a = 3.5240 c = 5.9960
115 A	U(C,O), UC_2**	95.19	4.31	0.7	91.15	8.65	0.4	4.9601	a = 3.5185 c = 5.9950
116 A	C, U_2C_3	-	-	-	92.81	7.1	0.1	-	8.0889
117 A	U(C,O), U_2C_3, UO_2	-	4.51	0.5	-	7.3	0.2	4.96120	8.0885

* Very very weak lines of an unidentified phase. ** For UC_2 phase containing oxygen in it.

5.C.2.(i) Lattice Parameters Of U(C,O), UC_2^*, U_2C_3 and UO_{2+x} Phases, As A Function Of Oxygen Partial Pressure At 1573°K

a Uranium Oxycarbide Phase

From the results shown in table 23, there appears to be no simple relationship between the lattice parameters of the U(C,O) phase and the relevant oxygen partial pressures at 1573°K. Lattice parameters as low as 4.9523 Å and as high as 4.9669 Å are observed for the U(C,O) phases prepared at high and low uranium activities respectively. This trend probably reflects the fact, that as uranium activity decreases, the activity of carbon is increased and consequently the solubility of oxygen in UC lattice might be expected to be reduced. However, the decrease in the activity of uranium, increases the corresponding oxygen partial pressure, so ultimately it is the resulting carbon monoxide partial pressure which becomes the controlling factor.

From the results of the chemical analyses of U(C,O) samples from the various equilibria, it is apparent that the oxygen content of the U(C,O) specimens decreases with the decrease of the activity of uranium and this results in the increase of the lattice parameter of the corresponding U(C,O) phase.

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* for UC_2 containing oxygen in its lattice.

The lattice parameters of the U(C,O) phase resulting from experiments 111A, and 114A, are higher than expected, i.e. 4.9645Å and 4.9669Å respectively. High lattice parameters, i.e. 4.970Å, 4.968Å, 4.966Å and 4.964-4.966Å, have already been reported for UC, by Kehl and Mendel[23], Burdick, et al.,[22], Henney[20], and Stoops and Hamme[6], respectively. Various explanations have been given by these investigators, for their high lattice parameter values. Kehl and Mendel[23], attribute the high lattice parameter, i.e. 4.970Å to some unknown impurities in UC. Stoops and Hamme[6], think that the accepted value of the lattice parameter of stoichiometric UC, i.e. 4.961Å, might be too low. Burdick, et al.,[22] suggest that the high lattice parameter, i.e. 4.968Å is due to the solid solution of UC_2 in UC. An alternative explanation by Shenan and Nicholls[102], is that these phases are hyperstoichiometric ($\frac{U}{C+O} < 1$), with respect to carbon and oxygen, and that the resulting compound has uranium vacancies. The latter statement is probably more accurate and is not in disagreement with the present results. It is apparent, that accurate analyses of the U(C,O) phase is essential, before an exact formula is assigned to such U(C,O) phases.

However, an explanation of results in table 23 clearly indicates that a lattice parameter in the region of 4.960-4.961Å, which is a characteristic of the stoichiometric UC, free from oxygen (section 5.C.1.), can also be possessed by various uranium oxycarbide compositions in equilibrium with UC_2-UO_2 and U_2C_3-UO_2.

A lattice parameter of 4.960Å is therefore, not necessarily the criterion for the presence of oxygen in UC, often assumed by other investigators[100,103]. The fact that the uranium oxycarbide phase containing finite quantities of oxygen can have lattice parameters equal to or greater than exhibited by pure UC (experiments,112A, 114A, 115A and 117A), might be due to hyperstoichiometry of the U(C,O) phase, as mentioned earlier.

b Uranium Dicarbide

The results of experiments 113A-115A suggest that uranium dicarbide*, is the stable phase under the relevant experimental conditions even at temperatures as low as 1573°K, which is in disagreement with the proposed phase diagrams for the UC system shown in figures 1 and 2. Chemical analysis results of the relevant experiments indicate that some oxygen goes into the UC_2 lattice and causes a slight decrease in the lattice parameter of the 'C' axis, but has little effect upon the lattice parameter of the 'a' axis. An oxygen content of 0.4-0.5 wt.% was determined for two equilibrations (114A, 115A) and 2.2 wt.% in another experiment (113A). However, the carbon content varied from 8.45 - 8.65 wt.%. These consistently high carbon contents suggest that the solubility of oxygen in the UC_2 lattice cannot be as high as 2.2 wt.% and this high oxygen content of 2.2 wt.% might have been due to the presence

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* Oxygen stabilized UC_2.

of UO_2 as an impurity. However, an oxygen solubility of 0.5 wt.% appears to be possible and could produce a phase having the composition $UC_{1.92}O_{0.08}$, instead of the stoichiometric formula, UC_2. It is suggested therefore, that the solution of 0.5 wt.% oxygen in UC_2, stabilizes this phase in preference to the U_2C_3 phase. However, in the presence of a strong reducing agent (e.g. calcium), insufficient oxygen dissolves in the UC_2 phase and the UC_2 phase should transform to the U_2C_3 phase. Evidence for this suggestion is available from the results of experiment 116A. The same arguement could be applied to the exepriments 111A and 112A, in which a beryllia crucible was used instead of the urania crucible and the equilibrated samples contained U_2C_3 instead of UC_2*.

However, in experiment 113A, which was carried out at a temperature 100°C higher (i.e. 1673°K), UC_2 containing oxygen was observed instead of U_2C_3; a state of affair which might be explained by the high temperature involved or the use of less pure UC_2 as the starting material. The absence of U_2C_3 in the experiments of Alcock and Grieveson[17], may be attributed to the stabilization of the UC_2 phase by oxygen at the high temperature used or the relatively short time, allowed for equilibration.

Results of experiments 113A-115A, indicate that at an activity of uranium $\simeq 3.5 \times 10^{-3}$, the oxygen content in the U(C,O) is 0.7 wt.%, and remains constant. Henney, et al.,[19], and Henney[20] also observed that oxygen dissolved in UC_2, but the concentration of oxygen in their samples prepared at 1773°K differed from the value obtained in the present investigation, at 1573°K.

Several investigators[109,110] have found that it is not possible to prepare stoichiometric UC_2, and a composition in the range of $UC_{1.8}$ to $UC_{1.9}$, is often proposed. If it is assumed that oxygen occupies the vacant carbon sites then the lattice parameter could increase first until all sites are occupied and decrease only after further replacement of oxygen for carbon. Only a relatively small decrease in the lattice parameter was observed in these experiments, this suggests that oxygen only occupies the vacant carbon sites and does not replace the carbon atoms.

c Uranium Sesquicarbide

Uranium sesquicarbide had always the same lattice parameter i.e. $a = 8.0889 \pm 0.0005$ Å, even in equilibrium with different phases, which suggests that it exhibits a negligible solubility of oxygen. The oxygen found by chemical analyses, varied between 0.1 - 0.2 wt.%, which is within the experimental error (± 0.2 wt.%) of oxygen analyses. Results from experiment 117A, indicate that U_2C_3 may exist in equilibrium with UO_2 and the U(C,O) phase, having an oxygen content of about 0.5 wt.%. This is in agreement with the work of Anselin, et al.,[68], who reported that uranium oxycarbide in equilibrium with U_2C_3 and UO_2 had the composition, $U(C_{0.95},O_{0.05})$. These results appear to contradict the earlier comments about the enhanced stability of the UC_2 phase containing oxygen and in equilibrium with the U(C,O) and UO_2 phases. It should be remembered however, that in experiment 117A, U_2C_3 was the actual starting material, and a possible explanation of these conflicting observations may be due to the fact, that U_2C_3 does not dissolve any oxygen, so transformation from oxygen free U_2C_3 to oxygen stabilized UC_2 phase may not take place easily at these temperatures (1573°K), and therefore, U_2C_3 could exist as a metastable phase in equilibrium UO_2.

Results of experiment 116A are important, in that they indicate that in the absence of any UO_2 or in the presence of an extremely reducing metal (e.g. calcium), U_2C_3 is then the stable phase in equilibrium with free carbon at 1573°K.

d Uranium Dioxide

Utilizing, the change in the lattice parameter of the UO_{2+x} phase, after equilibration at various activities of uranium, assessment in the change of the activity of uranium dioxide can be made. The values of the lattice parameters of uranium dioxide reported by various investigators are reported in table 24, and comparison is made with the lattice parameter values of the UO_{2+x} phase formed during the equilibration experiments of this investigation, particularly when the activity of uranium was lowest, i.e. 3.5×10^{-3} (table 25).

TABLE 24

Reference	Compound	Lattice Parameter (Å)
Rundle, et al; (33)	$UO_{2.0}$	5.4691 ± 0.0005
Swanson and Fuyat (104)	$UO_{2.0}$	5.46820
Hering and Perio (30)	$UO_{2.0}$	5.468 ± 0.001
do	$UO_{2.35}$	5.427 ± 0.001
Piazza (100)	UO_2	5.4707 ± 0.0005
Bazin and Accary (103)	UO_2	5.4707 ± 0.0009

TABLE 25

Experiment Number	Lattice Parameter of the UO_{2+x} Phase (Å)
101 A	5.4685 ± 0.0005
103 A	5.4705 ± 0.0005
110 A	5.4695 ± 0.0005
114 A	5.4704 ± 0.0005

Comparison of the lattice parameter values of the UO_{2+x} phase formed during the present investigation and those calculated by other workers, indicates that the deviation from stoichiometry was negligible and the corresponding activity of the uranium dioxide is therefore essentially unity.

5.C.2. (ii) Evaluation of Thermodynamic Data

The data shown in table 26 were used to calculate the activity

TABLE 26

Compositions Of The U(C,O) Phase At 1573°K, At Various Oxygen Partial Pressures.

Experiment Number	U(C,O) formula calculated from the chemical analyses	N_{UC} (mole fraction)	N_{UO} (mole fraction)	$p_{O_2}^{1/2}$ (atm.)	$\frac{N_{UO}}{N_{UC}}$
5 A	$UC_{0.67}O_{0.33}$	0.67	0.33	3.04×10^{-14}	0.49
101 A	$UC_{0.72}O_{0.28}$	0.72	0.28	2.85×10^{-14}	0.39
103 A	$UC_{0.8}O_{0.2}$	0.8	0.2	2.64×10^{-14}	0.25
104 A	$UC_{0.8}O_{0.19}$	0.8	0.19	2.44×10^{-14}	0.23
105 A	$UC_{0.86}O_{0.14}$	0.86	0.14	2.05×10^{-14}	0.16
106 A	$UC_{0.86}O_{0.15}$	0.86	0.15	2.08×10^{-14}	0.18
115 A	$UC_{0.89}O_{0.11}$	0.89	0.11	5.13×10^{-13}	0.12

coefficient of uranium monocarbide in the U(C,O) solid solution. The calculation method for the activity coefficient of UC in the U(C,O) solid solution, was the same as that described in section 5.C.1.(i).a, of this chapter. The activities of UC and carbon thus calculated for various compositions of UC in U(C,O) are reported in table 27, which indicates a negative deviation from Raoult's law.

TABLE 27

Calculated Activities of UC in U(C,O), As a Function of Composition at 1573°K

N_{UC} (mole fraction)	Activity of UC (a_{UC})	Activity of Carbon (a_C)
0.72	0.47	3.62×10^{-4}
0.82	0.54	4.92×10^{-4}
0.89	0.88	0.17

It can be seen that the activity of carbon is about 0.17, when $U(C_{0.89}, O_{0.11})$ is in equilibrium with uranium dioxide and the oxygen stabilized uranium dicarbide phase, at an activity of uranium $\simeq 3.5 \times 10^{-3}$.

Using the values of the activities of the various components, the standard free energy of formation values for $U(C_{0.89}, O_{0.11})$ and $U(C_{1.92}, O_{0.08})$, are calculated at 1573°K by using the following reactions respectively.

$$U_{(l)} + 0.89\ C_{(s)} + 0.11\ (\tfrac{1}{2}\ O_2)_g = \underset{(s)}{U(C_{0.89}, O_{0.11})}$$

and

$$U_{(l)} + 1.92\ C_{(s)} + 0.08\ (\tfrac{1}{2}\ O_2)_{(g)} = \underset{(s)}{U(C_{1.92}, O_{0.08})}$$

The values of the standard free energy of formation are thus -32.33 Kcals./mole and -35.38 Kcals./mole, respectively. The standard free energy of formation of UC_2, reported by Piazza[100], from the data obtained for the reaction:

$$UO_2 + 3\ UC_2 = 4\ UC + 2\ CO$$

for 1573°K is -27.2 Kcals./mole.

The difference between the values could be partly due to the activity of UC (= 0.95) assumed by Piazza[100], and calculated (0.88) during this investigation, and partly the errors involved in the measurements of exact equilibrium partial pressures of CO, under the conditions stated by Piazza[100].

The integral free energies of formation per gram atom, of the relevant phases investigated in the present studies are all combined as shown in figure 33.

5.C.3. Equilibrium Carbon-Monoxide Partial Pressures, At The U-U(C,O) And UO_2-U(C,O) Phase Boundaries, As A Function Of Temperature, And Composition Of The U(C,O) Phase.

Using the carbon activity data, reported in tables 18 and 27, the corresponding equilibrium oxygen partial pressures, and the recommended thermodynamic data for the equilibria:

$$C + \tfrac{1}{2}\ O_2 = CO$$

$$\text{i.e. } \Delta G^o_T = -26{,}700 - 20.95\ T \text{ (cals.)}$$

taken from Kubaschewski, et al.,[79], the partial pressures of CO have been calculated for the U-U(C,O) and UO_2-U(C,O), phase boundaries

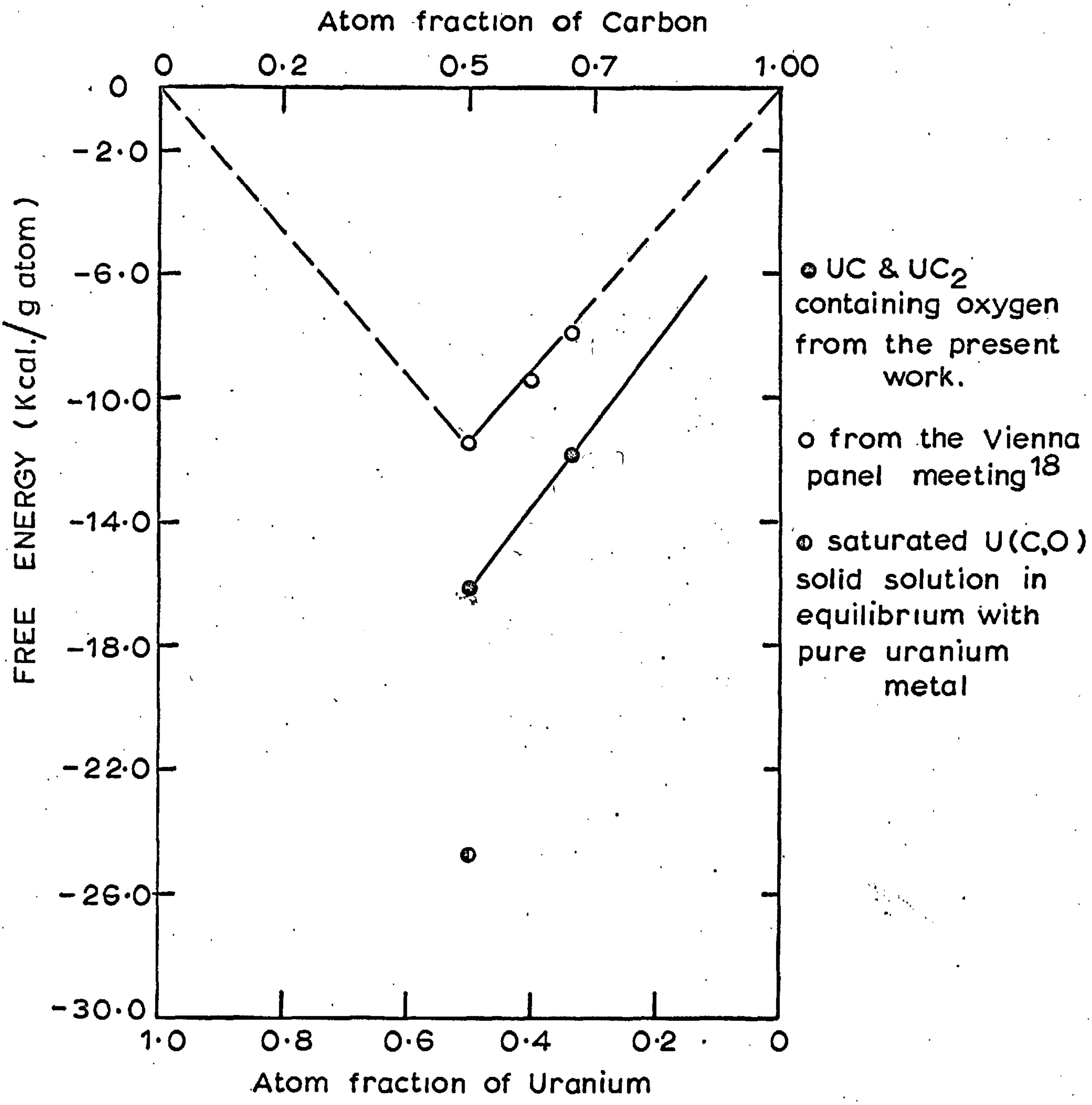

FIG.33 PARTIAL AND INTEGRAL FREE ENERGIES OF PURE URANIUM CARBIDES & OXYGEN SATURATED URANIUM CARBIDES AT 1573°K

respectively. These carbon monoxide (CO) partial pressures are shown in tables 28 and 29.

TABLE 28

Partial Pressures Of CO, At The U-U(C,O) Phase Boundary As A Function Of Temperature And Composition Of U(C,O).

Mole fraction of UC in U(C,O) (N_{UC})	Partial Pressures Of CO (mm.Hg)		
	1473°K	1573°K	1648°K
0.9	2.56×10^{-9}	3.24×10^{-8}	2.70×10^{-7}
0.8	1.26×10^{-8}	1.94×10^{-7}	1.48×10^{-6}
0.75	3.0×10^{-8}	4.22×10^{-7}	3.50×10^{-6}
0.68	7.24×10^{-8}	8.73×10^{-7}	4.54×10^{-6}

TABLE 29

Equilibrium Partial Pressures Of CO At The UO_2-U(C,O) Phase Boundary As A Function Of U(C,O) Composition, At 1573°K.

Number	Mole fraction of UC in U(C,O)	Partial pressure of CO (mm.Hg)
1	0.72	1.52×10^{-6}
2	0.82	1.92×10^{-6}
3	0.89	1.29×10^{-2}

From the CO partial pressures (P_{CO}) values reported in tables 28 and 29, it appears that for a certain fixed equilibrium temperature (e.g. 1573°K), P_{CO} increases with the decrease of UC mole-fraction in U(C,O), at the U-U(C,O) phase boundary, but decreases at the UO_2-U(C,O) phase boundary. This is in agreement with the conclusion drawn by Dutta and White[105], from their study of the stability relationships of uranium carbides in the U-C-O system.

Figure 34, shows the relationship between log p_{CO}(mm.Hg) and molefraction of UC in U(C,O) phase at 1573°K, for the U-U(C,O) phase boundary. It indicates a linear relationship, and log p_{CO} (mm.Hg) increases as the UC molefraction (N_{UC}) decreases.

In figure 35, which shows a relationship between log p_{CO} (mm.Hg), as a function of temperature, for various compositions of the U(C,O) phase for the U-U(C,O) phase boundary, also contains data calculated from the results reported by Stoops and Hamme[6], and Henry, et al.,[73], at 1873°K and 1923°K respectively. These data are for the three phase equilibria, i.e. U, $U(C_{1-x},O_x)$ and UO_2, and are to be compared with the values obtained in the present investigation, for the composition $U(C_{0.68},O_{0.32})$. It can be seen that the CO partial pressures reported by Stoops and Hamme[6] and Henry, et al.[73], are higher than the value calculated from the results of this investigation by factors of $\simeq 4$ and about 10, respectively. The discrepancy in these values could be attributed to the fact, that Stoops and Hamme[6], and Henry, et al.,[73], were measuring the total pressure in a vacuum system, and assuming that the observed value corresponded to the CO pressure. Apart from the difficulty of correlating a pressure recorded by a Penning gauge with the pressure exhibited by a system some distance away; other objections to this simple assumption include the possibility that leaks would contribute to

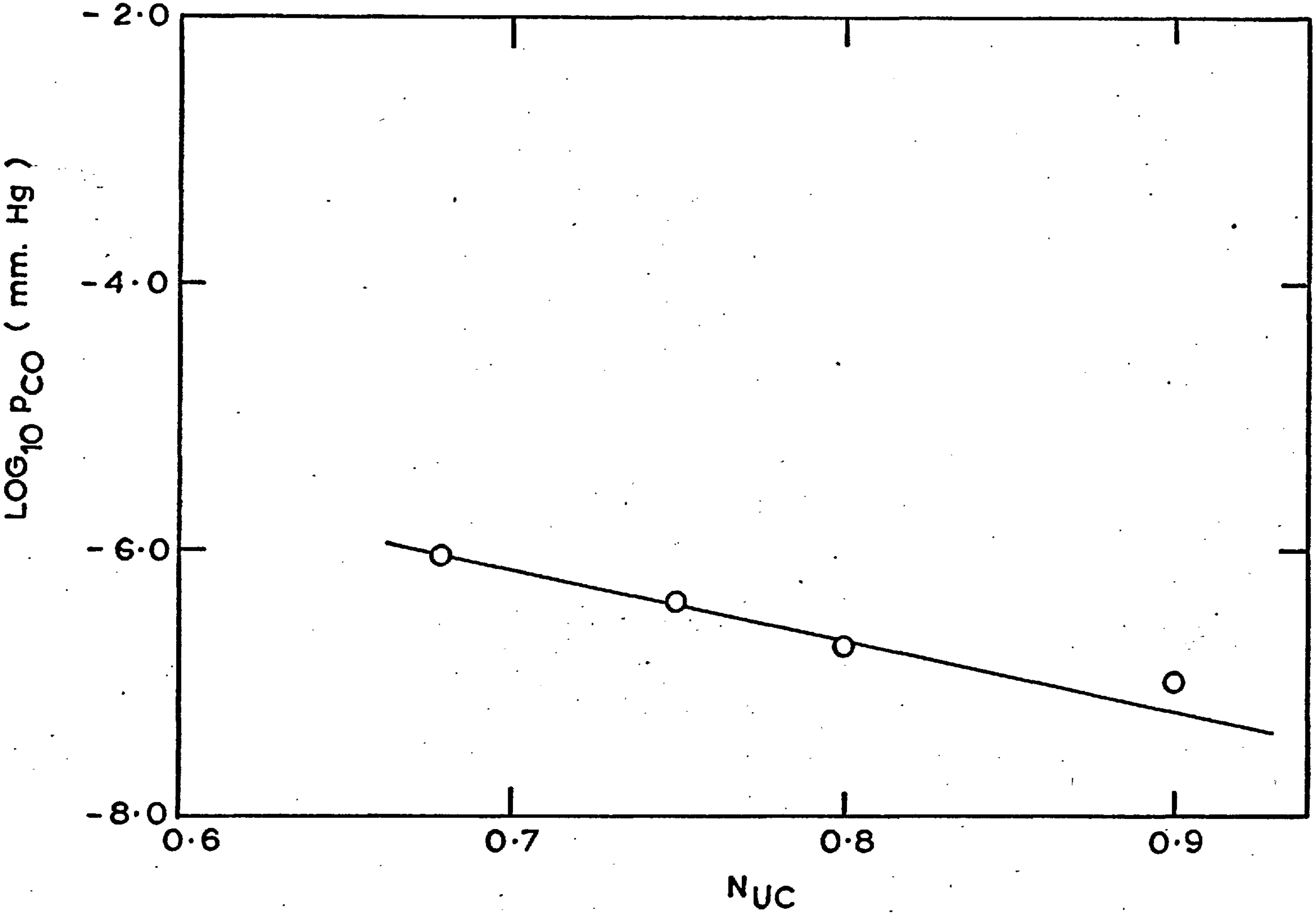

FIG.34 EQUILIBRIUM PARTIAL PRESSURE OF CO, AS A FUNCTION OF UC MOLE FRACTION IN U(C,O), AT 1573°K.

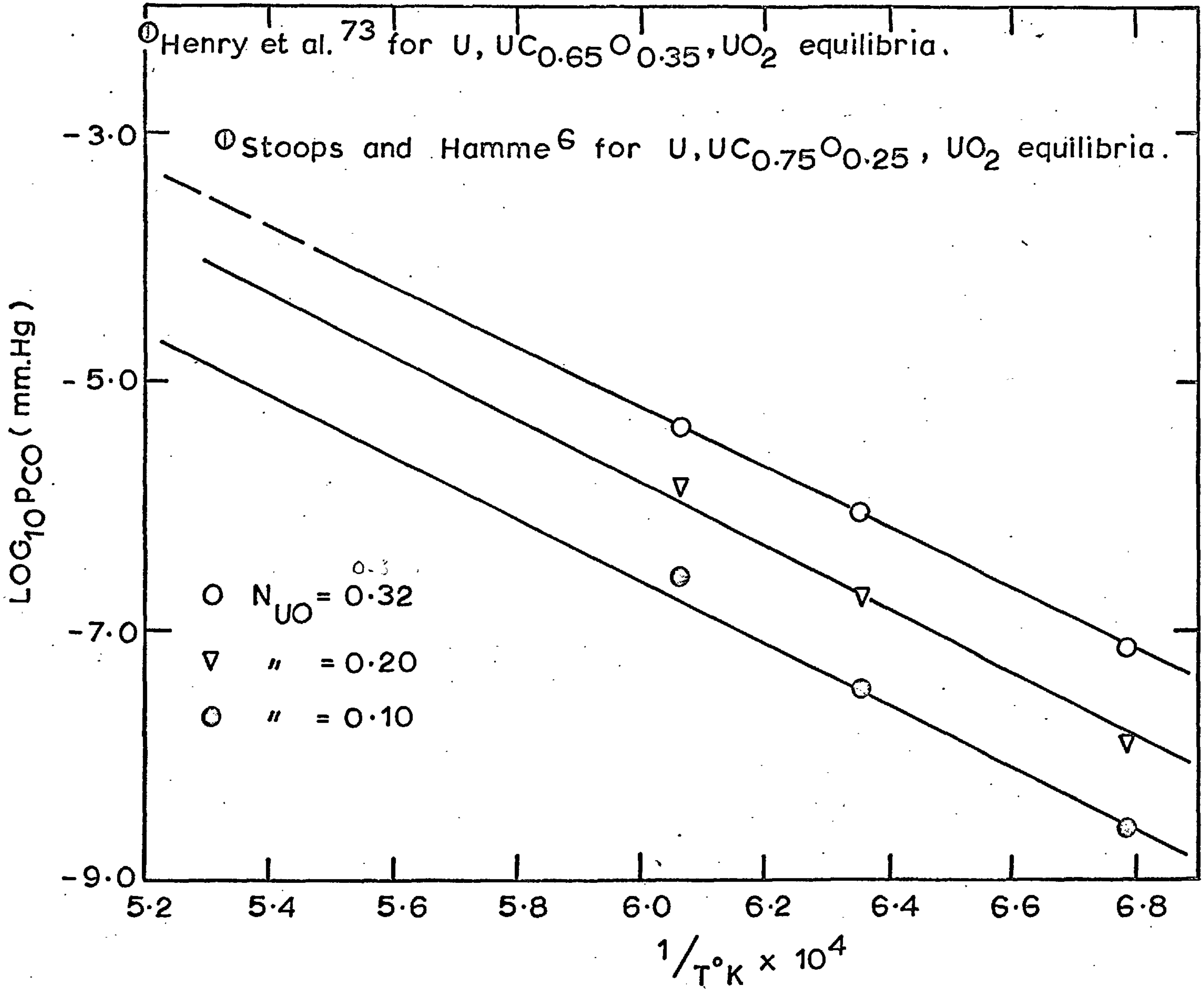

FIG.35 RELATIONSHIP BETWEEN LOG$_{10}$ P_{CO}, & $^1/T$°K FOR VARIOUS MOLE FRACTIONS OF UO IN U(C,O).

the total pressure and that the pressure was being recorded for a dynamic system, not one necessarily maintained under equilibrium conditions.

For a specified temperature, the following reaction can be formulated, for the uranium oxycarbide phase ($U(C_{0.68},O_{0.32})$), in equilibrium with uranium and uranium dioxide.

$$2.4 \ U(C_{0.68}, O_{0.32}) + 0.432 \ UO_2 = 2.832 \ U + 1.632 \ CO$$

Equilibrium CO, partial pressure for experiment 116A (reaction product C, and U_2C_3), was also calculated $p_{CO} = 2.74 \times 10^{-5}$ mm.Hg. for 1573°K, by taking $p_{O_2} = 3.4 \times 10^{-32}$ atm. (Ca/CaO equilibria) and activity of carbon as unity.

5.C.4. Single Phase U(C,O) Region

In order to study the thermodynamics inside the single phase region of U(C,O), the activity of uranium had to be less than unity and at the same time, the equilibrium oxygen partial pressure had to be low enough to avoid the formation of uranium dioxide as a separate phase. This made it essential to know the extent of calcium solubility in the uranium-gold alloy.

Preliminary experiments were carried out in which the solubility of calcium, in different compositions of uranium-gold alloys, was determined at unit activity of calcium. In this way the general shape of the iso-activity lines of calcium in the ternary uranium-gold-calcium alloy system was obtained. The results of these preliminary experiments are included in appendix D.

However, when U-AU, UC and Ca/CaO equilibration experiments were carried out for different uranium-gold compositions and at different activities of calcium, it was observed that most of the gold present as an alloy solution at 1573°K, had diffused through the calcia crucible. This was partly due to the porous nature of the calcia crucibles and partly due to long equilibration time (more than 100 hours). This reaction made it impossible to assess the true equilibrium composition of the uranium-gold-calcium alloy formed during the experiment. The presence of gold in large amounts in the calcia crucible after the equilibration was verified by examining under an electron microprobe analyser, a polished piece of the calcia crucible.

Two experiments were made in which single phase crystal calcia crucibles, were used. However, after the equilibration it was necessary to break the single crystal, to take out the specimen. Even by using a single crystal for the uranium-gold alloys, containing high gold content, there was a penetration of gold. However, the high cost of single crystal calcia crucibles, and lack of time prevented further experiments from being carried out.

However, the resulting uranium oxy-carbide phase for each experiment was subjected to chemical and X-ray analyses, even though the activity of uranium remained unknown.

These experiments were carried out primarily at 1573°K, so that the results could be helpful at least qualitatively, in order to construct a phase diagram for the U-C-O system at this temperature. Few such experiments were also carried out at 1648°K, while doing the experiments for the U-U(C,O) phase boundary.

The chemical and X-ray analyses of all such experiments are reported in tables 30 and 31.

Although it is difficult to draw any positive conclusions from the results reported in table 31, yet the results of experiments 203A and 204A could be significant. The high lattice parameters, i.e. 4.9625 Å and 4.9688 Å respectively, and a significant (7-10 mole % UO) amount of oxygen in the U(C,O) single phase, suggest that this phase may be hyperstoichiometric with repsect to carbon and oxygen, i.e. $\frac{O + C}{U} > 1$, and concequently deviation of stoichiometry of U(C,O) single phase could be greater at high carbon rich side of the U-C-O phase diagram (also see section 5.C.2.(i) a). This conclusion appears to be generally supported by the other experiments carried out at the low oxygen partial pressures. On the other hand at high oxygen partial pressures, the lattice parameter does not change very much with decrease in the uranium content.

Further speculation is not warranted and additional experiments should be performed to evaluate the thermodynamics and other properties of the U(C,O) single phase region.

TABLE 30

Equilibration Conditions For Experiments, For U(C,O) Single Phase Region.

Experiment Number	Starting materials for the equilibration	Temperature (K°)	Time for equilibration (hrs.)	Activity of Calcium (a_{Ca})	Oxygen partial pressure p_{O_2} (atm.)
201 A	10 mole % gold + 90 mole % uranium, UC, Ca/CaO	1573	101	1	3.43×10^{-32}
202 A	30 mole % gold + 70 mole % uranium, UC, Ca/CaO	"	102	"	"
203 A	50 mole % gold + 50 mole % uranium, UC, Ca/CaO*	"	112	"	"
204 A	90 mole % gold + 10 mole % uranium, UC, Ca/CaO*	"	97	"	"
205 A <u>a</u>	10 mole % gold + 90 mole % uranium, UC, Ca/CaO				
<u>b</u>	30 mole % gold + 70 mole % uranium, UC, Ca/CaO	1573	112	0.6	9.4×10^{-32}
<u>c</u>	50 mole % gold + 50 mole % uranium, UC, Ca/CaO				
<u>d</u>	90 mole % gold + 10 mole % uranium, UC, Ca/CaO				

* Single crystal calcia crucible

TABLE 30 continued

Experiment Number		Starting materials for the equilibration	Temperature (K^{o})	Time for equilibration (hrs.)	Activity of calcium (a_{Ca})	Oxygen partial pressure p_{O_2} (atm.)
206A	a	10 mole % gold + 90 mole % uranium, UC, $Ca/_{CaO}$	1573	106	0.2	8.9×10^{-31}
	b	30 mole % gold + 70 mole % uranium UC, $Ca/_{CaO}$				
	c	50 mole % gold + 50 mole % uranium, UC, $Ca/_{CaO}$				
	d	90 mole % gold + 10 mole % uranium, UC, $Ca/_{CaO}$				
207 A	a	10 mole % gold + 90 mole % uranium, UC, $Ca/_{CaO}$	"	"	0.08	5.54×10^{-30}
	b	30 mole % gold + 70 mole % uranium, UC, $Ca/_{CaO}$				
	c	50 mole % gold + 50 mole % uranium, UC, $Ca/_{CaO}$				
	d	90 mole % gold + 10 mole % uranium, UC, $Ca/_{CaO}$				
10 A	a	10 mole % gold + 90 mole % uranium, UC, $Ca/_{CaO}$	"	96	0.04	2.35×10^{-29}
	b	30 mole % gold + 70 mole % uranium, UC, $Ca/_{CaO}$				

TABLE 30 continued

Experiment Number		Starting materials for the equilibration	Temperature (K°)	Time for equilibration (hrs.)	Activity of calcium (a_{Ca})	Oxygen partial pressure p_{O_2} (atm.)
11 A	a	10 mole % gold + 90 mole % uranium, UC, Ca/CaO				
	b	30 mole % gold + 70 mole % uranium, UC, Ca/CaO	1573	100	0.098	3.55×10^{-30}
9 B	a	10 mole % gold + 90 mole % uranium, UC, Ca/CaO				
	b	30 mole % gold + 70 mole % uranium, UC, Ca/CaO	1648	105	0.16	1.12×10^{-28}
10 B	a	10 mole % gold + 9 mole % uranium, UC, Ca/CaO				
	b	30 mole % gold + 70 mole % uranium, UC, Ca/CaO	"	106	0.38	2.1×10^{-29}
11 B	a	10 mole % gold + 90 mole % uranium, UC, Ca/CaO				
	b	30 mole % gold + 70 mole % uranium, UC, Ca/CaO	"	110	0.42	1.7×10^{-29}
13 A	a	10 mole % gold + 90 mole % uranium, UC, Ca/CaO				
	b	30 mole % gold + 70 mole % uranium, UC, Ca/	1573	48	0.15	1.43×10^{-30}

TABLE 30. continued

Experiment Number		Starting materials for the equilibration	Temperature (K^o)	Time for equilibration (hrs.)	Activity of calcium (a_{Ca})	Oxygen partial pressure p_{O_2} (atm.)
14 A	a	10 mole % gold + 90 mole % uranium, UC, $Ca/_{CaO}$				
	b	30 mole % gold + 70 mole % uranium, UC, $Ca/_{CaO}$	1573	120	0.27	4.67×10^{-31}
15 A	a	10 mole % gold + 90 mole % uranium, UC, $Ca/_{CaO}$				
	b	30 mole % gold + 70 mole % uranium, UC, $Ca/_{CaO}$	"	98	0.28	4.35×10^{-31}
8 B	a	10 mole % gold + 90 mole % uranium, UC, $Ca/_{CaO}$	1648	110	0.11	2.31×10^{-28}
	b	30 mole % gold + 70 mole % uranium, UC, $Ca/_{CaO}$				

TABLE 31

X-Ray And Chemical Analyses Data About U(C,O) Phase Formed Under Conditions Mentioned In Table 30.

Experiment Number	Chemical Analysis (wt.%).				Phase identification by X-ray	Lattice parameter of U(C,O) (Å)
	Uranium	Carbon	Oxygen	Nitrogen		
201 A	95.18	4.36	0.4	0.2	U(C,O)	4.9615
202 A	-	4.32	0.35	0.08	"	4.9605
203 A	-	-	0.48	0.05	"	4.9625
204 A	95.19	4.37	0.7	-	"	4.9688
205 A						
a	95.21	4.42	0.51	0.05	"	4.9575
b	-	-	0.4	0.16	"	4.95835
c	-	-	0.4	-	"	4.9585
d	95.25	4.61	0.22	0.002	"	4.9616
206 A						
a	95.19	4.25	0.80	0.1	"	4.95725
b	-	-	0.64		"	4.9565
c	95.18	4.05	-	-	"	4.9589
d	95.16	4.15	0.60	-	"	4.9605
207 A						
a	95.18	3.92	1.2	0.2	"	4.95465
b	-	-	0.82	0.13	"	4.9551
c	-	-	-	-	"	4.9545
d	95.19	3.98	1.2	-	"	4.9545
10 A						
a	95.25	3.84	-	-	"	4.95375
b	-	3.89	-	-	"	4.9539
11 A						
a	95.2	4.05	-	-	"	4.95545
b	95.18	3.95	-	-	"	4.9548

TABLE 31 continued

Experiment	Chemical Analysis (wt.%).				Phase identification by X-ray	Lattice parameter of U(C,O) (Å)
Number	Uranium	Carbon	Oxygen	Nitrogen		
13 A						
a	95.19	4.61	-	-	U(C,O)	4.9596
b	-	4.57	-	-	"	4.95875
14 A						
a	95.25	4.15	0.56	0.19	"	4.9585
b	-	4.2	0.43	-	"	4.9596
15 A						
a	-	-	0.41	0.01	"	4.96051
b	-	-	0.53	0.02	"	4.9585
8 B						
a	95.31	4.27	0.7	-	"	4.95615
b	-	4.21	-	-	"	4.95755
9 B						
a	95.19	4.15	-	-	"	4.9576
b	95.18	4.2	0.82	0.13	"	4.9565
10 B						
a	95.18	4.61	-	-	"	4.9589
b	95.19	4.65	0.28	0.01	"	4.9605
11 B						
a	-	-	0.37	0.01	"	4.9595
b	95.18	4.56	0.4	-	"	4.9601

5.D. Phase Relationships In The U-C-O System

The data which have been presented, in determining the maximum carbon replacement by oxygen in the UC lattice, and for studying the thermodynamics of the uranium oxycarbide and oxygen stabilized uranium dicarbide, phases at 1573°K, have produced a considerable amount of information regarding the phase relationships in the U-C-O, system.

A ternary isothermal section is therefore, proposed for the phase equilibria existing at 1573°K and is shown in figure 36.

In this phase diagram a single phase $U(C_{1-x},O_x)$ region is shown having a lattice parameter range of 4.968-4.951 Å and a maximum value of x about 0.32. The upper boundary for this single condensed phase area is shown almost as a straight line, whereas the lower boundary runs parallel to the upper boundary when the oxygen content is relatively higher, i.e. more than 15 mole % UO in U(C,O); and diverges as the oxygen content decreases resulting into a relatively bigger stability region of single U(C,O) phase. The lattice parameter of the single U(C,O) phase in this region is in the range of 4.960-4.968 Å, and the U(C,O) is hyperstoichiometric with respect to carbon and oxygen.

Further, $U(C_{2-x},O_x)$ phase having the value of x about 0.08 is shown to co-exist with the U(C,O) phase having about 11 mole % UO, and the UO_2 phase. This is due to the reason that the standard free energy of formation of the oxygen stabilized UC_2 phase has

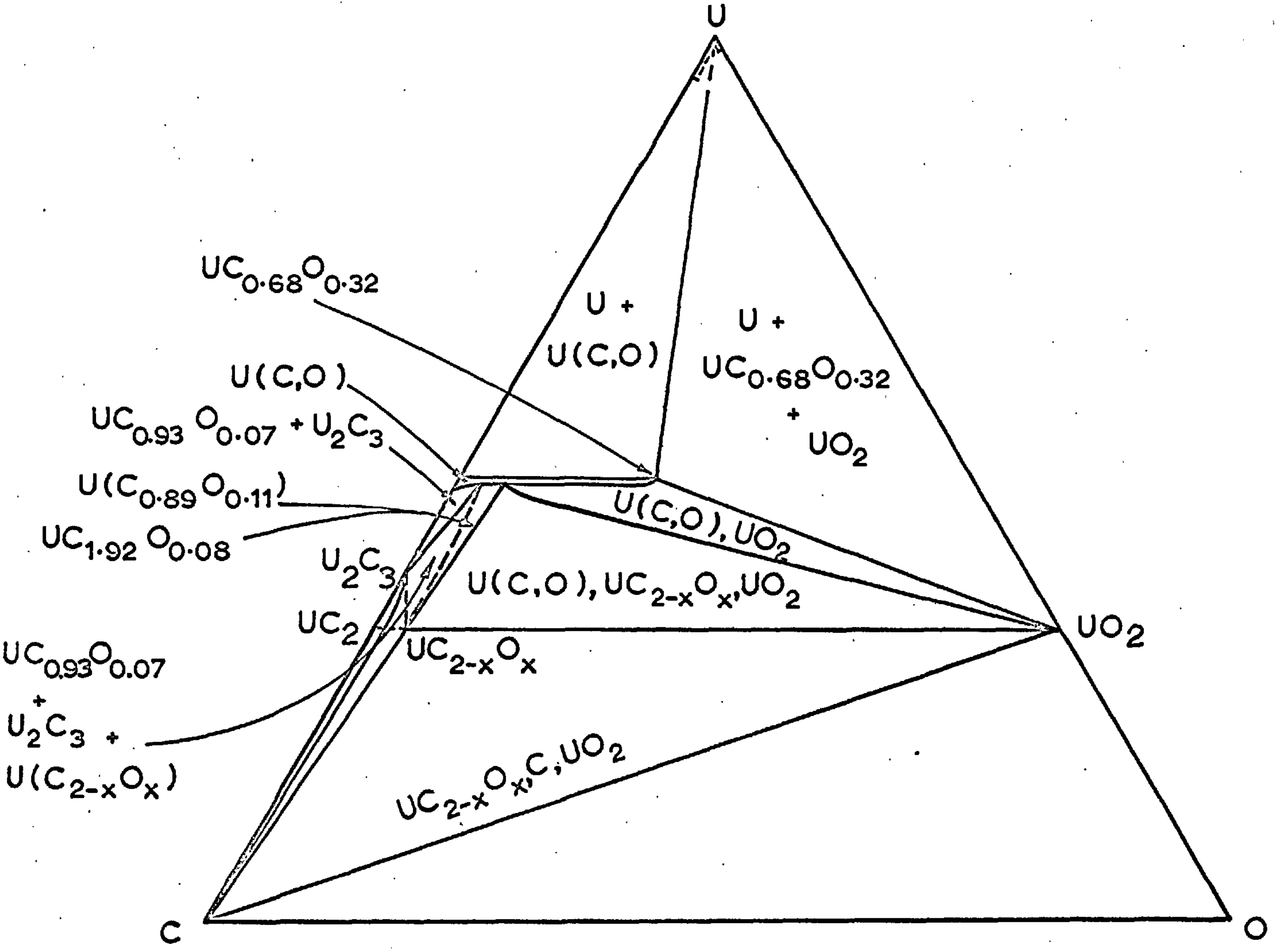

FIG.36 PROPOSED ISOTHERMAL SECTION OF THE U-C-O SYSTEM AT 1573°K

been found to be more negative than that of the pure U_2C_3 phase. Although, the U_2C_3 phase is found to co-exist with U(C,O) and UO_2 phase in one of the experiments, yet from the thermodynamic considerations its presence is attributed to metastability situation, due to kinetic reasons.

However, the U(C,O) phase having about 7 mole % UO, has been found to co-exist with almost pure U_2C_3 phase and is included in the phase-diagram. Similarly, it is shown that U_2C_3 could co-exist in equilibrium with carbon, at very low oxygen partial pressures, i.e. $< 10^{-32}$ atm. at 1573°K.

The other phase boundaries are drawn according to the experimental observations of Stoops and Hamme[6], and Henney[20], though the temperatures at which these investigators carried out their experiments are higher than 1573°K.

The same general phase relations probably also apply at temperatures higher than 1573°K, except that the U_2C_3 phase must disappear above 1973°K.

U-C-O, phase relations proposed by Stoops and Hamme[6], for the furnace cooled products at 2073-2123°K, are reproduced in figure 13, and do not differ much except that in the present proposed phase diagram, the presence of oxygen stabilized UC_2 phase is included. It is to be noted that Stoops and Hamme[6], did not do any experiments in which detailed study was made about the UC_2 phase.

Henney[20], **proposed** two phase diagrams for the U-C-O system, for

1773°K and 1973°K. In his phase diagram at 1773°K, Henney[20], suggested that U(C,O), U_2C_3 and UO_2 phases are compatible, but at 1973°K, the U(C,O) and the $U(C_{2-x}\ O_x)$, phases co-exist in the presence of UO_2. This investigator did not propose any separate field for the U(C,O) single phase. The phase diagrams proposed by Henney[20], are shown in figure 12. The phase diagram shown in figure 36, is more similar to the phase diagram proposed by Henney[20], at 1973°K.

An isothermal section for the uranium-carbon-uranium dioxide system has been drawn by Chiotti, et al.,[51], for a temperature below the melting point of uranium, i.e. 1133°C, and is reproduced as shown in figure 37. One of the main features of this phase diagram is that the uranium oxycarbide phase containing about 80 mole % UO, is found to co-exist with free carbon and the UO_2 phase. The field of single phase U(C,O) is also very large. The comparatively low temperatures involved have made it difficult to comment on the proposed extent of the U(C,O) phase field reported by Chiotti, et al[51]. However, these investigators do propose the existence of U(C,O) - U_2C_3, and U(C,O) - $U(C_{2-x}, O_x)$, binary phase regions, which is consistent with the phase diagram shown in figure 36.

Besson, Blum and Morlevat[76], have suggested a 2273°K isothermal section for the ternary system, uranium-uranium monocarbide-uranium dioxide, and have shown a single U(C,O) phase field having maximum oxygen solubility in the UC lattice corresponding to formula $U(C_{0.65}, O_{0.35})$. These investigators do suggest however, that this field gets

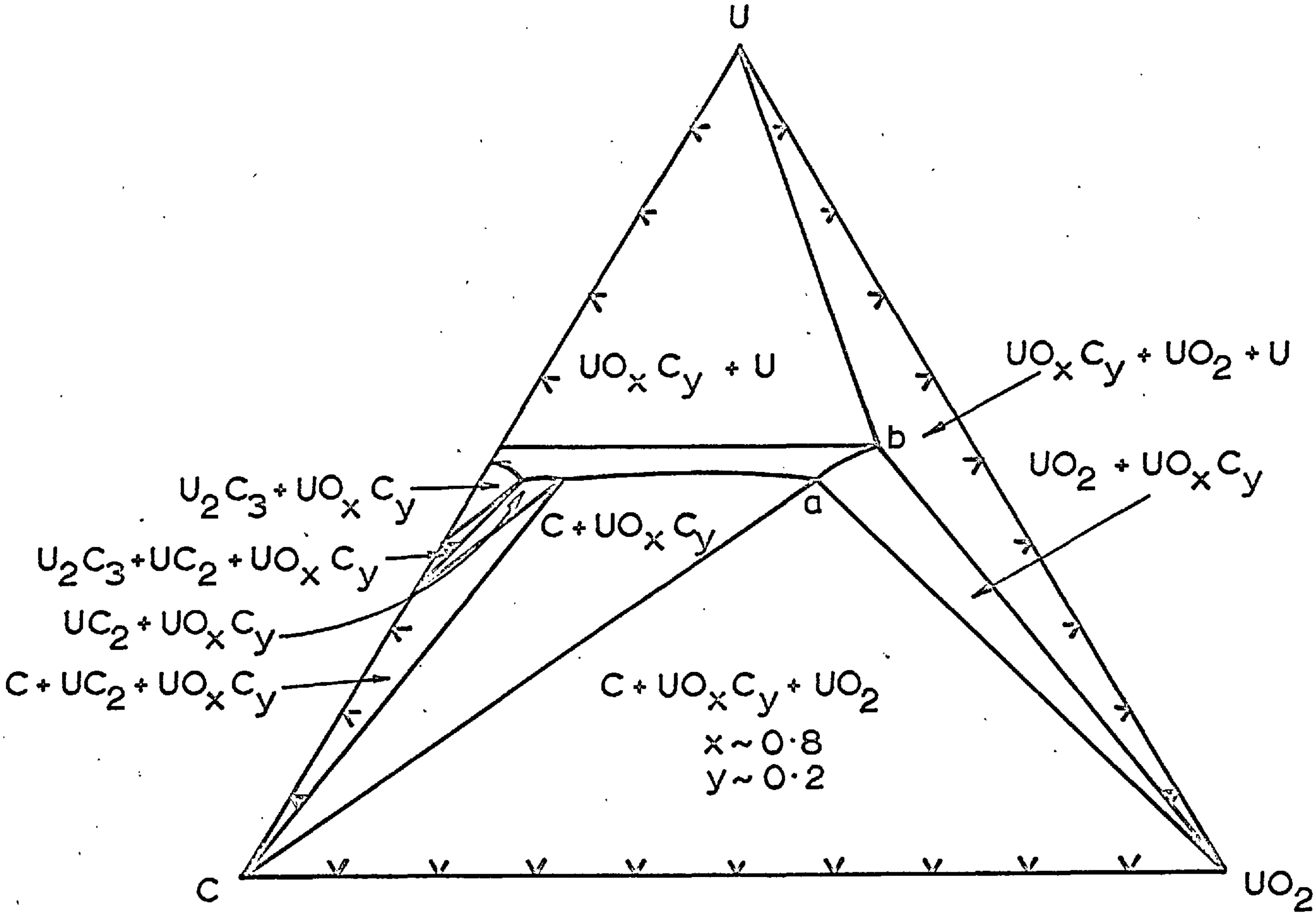

FIG. 37 ISOTHERMAL SECTION FOR THE U-C-UO_2 SYSTEM FOR A TEMPERATURE BELOW 1100°C AFTER CHIOTTI et al.[51]

smaller as the temperature is increased.

Thus, the results reported by Stoops and Hamme[6], Besson, et al.,[76], and in the present investigation, suggest that within broad limits, the extent of U(C,O) single phase field does not change greatly with temperature ,between the melting point of uranium (1410°K) and 2273°K, and probably gets smaller only at temperatures higher than 2273°K.

CHAPTER SIX

CONCLUSIONS

From this study of the U - C - O system, the following conclusions have been made.

1. In the temperature range of 1473°K to 1648°K, oxygen will replace carbon atoms in the uranium monocarbide lattice to the extent of thirty two per cent (± 1 atom per cent) of the carbon atoms.

2. The lattice parameter for the U(C,O) phases generally decreases, with the increasing oxygen content, when in equilibrium with uranium metal, and is independent of the temperature; provided equilibrium is attained. The lowest lattice parameter for the oxygen saturated UC, having the formula $U(C_{0.68},O_{0.32})$ is between 4.951-4.952Å.

3. The oxygen content in the U(C,O) phase increases with the increase of oxygen partial pressures between 1473°K to 1648°K at the U - U(C,O) phase boundary; but decreases with the increase of oxygen partial pressures at the UO_2 - U(C,O) phase boundary at 1573°K.

4. The U(C,O) phase may exist with the total carbon plus oxygen atoms slightly greater than fifty atomic per cent and this may probably be responsible for the high lattice parameter value, i.e. about 4.968 Å of such a phase.

5. Activities of uranium monocarbide in uranium oxycarbide solid solutions have been calculated by the use of a modified Gibbs-Duhem equation, by assuming that the uranium oxycarbide phase is a pseudo-binary solid solution of uranium monocarbide and that

of uranium monoxide.

6. The standard free energy of formation of the oxygen saturated uranium carbide phase, i.e. $U(C_{0.68},O_{0.32})$, is about -49 Kcals./mole, as compared with -23 Kcals./mole for pure uranium monocarbide. in the temperature range of 1473°K to 1648°K.

7. The oxygen saturated uranium dicarbide having the formula $U(C_{1.92},O_{0.08})$, is stable at 1573°K, when in equilibrium with the uranium oxycarbide phase having eleven mole per cent uranium monoxide in it, and the stoichiometric uranium dioxide. The standard free energy of formation for the oxygen saturated uranium dicarbide phase is about -35 Kcals./mole at 1573°K.

8. The lattice parameter of the oxygen saturated uranium dicarbide phase does not change very much, from the reported lattice parameter values of oxygen free uranium dicarbide. The lattice parameter values for the oxygen saturated stabilized phase are:

$a = 4.952 \pm 0.001$ Å

$c = 5.991 \pm 0.001$ Å

9. In the absence of uranium dioxide phase, uranium dicarbide transforms to uranium sesquicarbide at 1573°K.

10. The lattice parameter of uranium sesquicarbide does not change and remains constant, i.e. about 8.0889 ± 0.0005 Å, even when in equilibrium with different phases (e.g. U(C,O) and C, etc.). This suggests that the carbon content of uranium sesquicarbide is invariant.

11. At very low oxygen partial pressures, i.e. $\lesssim 10^{-32}$ atm. at 1573°K, uranium sesquicarbide is the stable phase, in equilibrium with carbon.

12. At the U - U(C,O) phase boundary, the equilibrium partial pressures of carbon monoxide increases with the increase of oxygen content of the U(C,O) phase, but at the UO_2 - U(C,O) phase, it decreases as the oxygen content of the U(C,O) phase increases. The equilibrium carbon monoxide partial pressure is as high as $\simeq 10^{-5}$ atm. at 1573°K, when the oxygen stabilized uranium dicarbide and the U(C,O) phase are in equilibrium with the stoichiometric uranium dioxide.

APPENDIX A

Oxygen Partial Pressures, For The Equilibria, 2 CO + O_2 = 2 CO_2 At Different Temperatures For Various CO/CO_2 Values.

Temperature (C^o)	CO/CO_2	Oxygen partial pressure in (atm.)
1200	1	$1.09x10^{-11}$
	10	$1.09x10^{-13}$
	10^2	$1.09x10^{-15}$
	10^3	$1.09x10^{-17}$
	10^4	$1.09x10^{-19}$
	10^5	$1.09x10^{-21}$
	10^6	$1.09x10^{-23}$
	10^7	$1.09x10^{-25}$
1300	1	$2.05x10^{-10}$
	10	$2.05x10^{-12}$
	10^2	$2.05x10^{-14}$
	10^3	$2.05x10^{-16}$
	10^4	$2.05x10^{-18}$
	10^5	$2.05x10^{-20}$
	10^6	$2.05x10^{-22}$
	10^7	$2.05x10^{-24}$
1400	1	$2.71x10^{-9}$
	10	$2.71x10^{-11}$
	10^2	$2.71x10^{-13}$
	10^3	$2.71x10^{-15}$
	10^4	$2.71x10^{-17}$
	10^5	$2.71x10^{-19}$
	10^6	$2.71x10^{-21}$
	10^7	$2.71x10^{-23}$

APPENDIX A continued

Temperature (C^o)	CO/CO_2	Oxygen partial pressure in (atm.)
1500	1	$2.67x10^{-8}$
	10	$2.67x10^{-10}$
	10^2	$2.67x10^{-12}$
	10^3	$2.67x10^{-14}$
	10^4	$2.67x10^{-16}$
	10^5	$2.67x10^{-18}$
	10^6	$2.67x10^{-20}$
	10^7	$2.67x10^{-22}$
1600	1	$2.07x10^{-7}$
	10	$2.07x10^{-9}$
	10^2	$2.07x10^{-11}$
	10^3	$2.07x10^{-13}$
	10^4	$2.07x10^{-15}$
	10^5	$2.07x10^{-17}$
	10^6	$2.07x10^{-19}$
	10^7	$2.07x10^{-21}$
1700	1	$1.3x10^{-6}$
	10	$1.3x10^{-8}$
	10^2	$1.3x10^{-10}$
	10^3	$1.3x10^{-12}$
	10^4	$1.3x10^{-14}$
	10^5	$1.3x10^{-16}$
	10^6	$1.3x10^{-18}$
	10^7	$1.3x10^{-20}$

APPENDIX B

The carbon activities are calculated, at different total pressures, different temperatures and different CO/CO_2 values, by using the standard free energy data for the equilibrium $CO_2 + C = 2\ CO$

	1400°C			1500°C	
CO/CO_2	$P_{(CO+CO_2)}$ mm Hg	Carbon Activity (a_c)	CO/CO_2	$P_{(CO+CO_2)}$ mm Hg	Carbon Activity (a_c)
10	760	1.48×10^{-3}	10	760	6.14×10^{-4}
10^2	"	1.6×10^{-2}	10^2	"	8.15×10^{-3}
10^3	"	1.61×10^{-1}	10^3	"	8.2×10^{-2}
10^4	"	1.63	10^4	"	8.25×10^{-1}
10	100	1.9×10^{-4}	10	100	9.8×10^{-5}
10^2	"	2.03×10^{-3}	10^2	"	1.07×10^{-3}
10^3	"	2.04×10^{-2}	10^3	"	1.08×10^{-2}
10^4	"	2.08×10^{-1}	10^4	"	1.085×10^{-1}
10	10^{-1}	1.9×10^{-7}	10	10^{-1}	9.9×10^{-8}
10^2	"	2.1×10^{-6}	10^2	"	1.07×10^{-6}
10^3	"	2.1×10^{-5}	10^3	"	1.8×10^{-5}
10^4	"	2.1×10^{-4}	10^4	"	1.8×10^{-4}
10	10^{-3}	1.9×10^{-9}	10	10^{-3}	9.9×10^{-10}
10^2	"	2.07×10^{-8}	10^2	"	1.07×10^{-8}
10^3	"	2.071×10^{-7}	10^3	"	1.08×10^{-7}
10^4	"	2.08×10^{-6}	10^4	"	1.8×10^{-6}

APPENDIX B continued

1600°C			1700°C		
CO/CO$_2$	$P_{(CO+CO_2)}$ mm Hg	Carbon Activity (a_c)	CO/CO$_2$	$P_{(CO+CO_2)}$ mm Hg	Carbon Activity (a_c)
10	760	4.06×10^{-4}	10	760	2.28×10^{-4}
10^2	"	4.42×10^{-3}	10^2	"	2.4×10^{-3}
10^3	"	4.46×10^{-2}	10^3	"	2.45×10^{-2}
10^4	"	4.47×10^{-1}	10^4	"	2.5×10^{-1}
10^5	"	4.46			
10^6	"	4.47×10			
10^7	"	4.46×10^2			
10	100	5.34×10^{-5}	10	100	3.005×10^{-5}
10^2	"	5.82×10^{-4}	10^2	"	3.27×10^{-4}
10^3	"	5.87×10^{-3}	10^3	"	3.3×10^{-3}
10^4	"	5.88×10^{-2}	10^4	"	3.31×10^{-2}
10^5	"	5.86×10^{-1}			
10^6	"	5.87			
10^7	"	58.8			
10	10^{-1}	5.3×10^{-8}	10	10^{-1}	3.0×10^{-8}
10^2	"	5.8×10^{-7}	10^2	"	3.27×10^{-7}
10^3	"	5.82×10^{-6}	10^3	"	3.3×10^{-6}
10^4	"	5.9×10^{-5}	10^4	"	3.31×10^{-5}
10^5	"	5.84×10^{-4}			
10^6	"	5.87×10^{-3}			
10^7	"	5.85×10^{-2}			
10	10^{-3}	5.3×10^{-10}	10	10^{-3}	3.0×10^{-10}
10^2	"	5.4×10^{-9}	10^2	"	3.23×10^{-9}
10^3	"	5.8×10^{-8}	10^3	"	3.3×10^{-8}
10^4	"	5.87×10^{-7}	10^4	"	3.32×10^{-7}
10^5	"	5.84×10^{-6}			
10^6	"	5.86×10^{-5}			
10^7	"	5.871×10^{-4}			

APPENDIX C

Activities of Uranium and Carbon in UC at Different Temperatures.

In order to obtain information regarding the variations of uranium activities with carbon activities in UC, reference was made to figure 6. Tangents were chosen through the minimum point on the free energy diagram which corresponded to the UC position, and the appropriate uranium and carbon activities are listed below.

Temperatures (C°)	Carbon activity (a_c)	Relative partial molar free energy of carbon ($\Delta\bar{G}_C$) Kcals./mole	Relative partial molar free energy of uranium ($\Delta\bar{G}_U$) Kcals./mole	Activity of uranium a_U
1200	0.6198	-1.4	-21.7	6.026×10^{-4}
	0.1	-6.739	-16.3	3.819×10^{-3}
	0.01	-13.477	- 8.8	4.945×10^{-2}
	0.001	-20.217	- 2.1	0.4887
	4.436×10^{-4}	-22.6	0	1.0
1300	0.639	-1.4	-21.7	9.661×10^{-4}
	10^{-1}	-7.196	-15.7	6.59×10^{-3}
	10^{-2}	-14.39	- 8.0	7.76×10^{-2}
	10^{-3}	-21.59	- 1.0	0.7413
	7.244×10^{-4}	-22.6	0	1
1400	0.656	-1.4	-21.7	1.462×10^{-3}
	10^{-1}	-7.654	-15.25	1.017×10^{-2}
	10^{-2}	-15.308	- 7.3	1.114×10^{-1}
	1.117×10^{-3}	-22.6	0	1

APPENDIX C continued

Temperatures (C^o)	Carbon activity (a_c)	Relative partial molar free energy of carbon, ($\Delta\bar{G}_C$) Kcals./mole	Relative partial molar free energy of uranium, ($\Delta\bar{G}_U$) Kcals./mole	Activity of uranium a_U
1600	0.687	-1.4	-21.7	2.938×10^{-3}
	10^{-1}	-8.569	-13.9	2.388×10^{-2}
	10^{-2}	-17.138	-5.3	0.241
	2.307×10^{-3}	-22.6	0	1

APPENDIX D

Application of Gibbs-Duhem Equation, to Uranium-Gold-Calcium Ternary Alloy System

D-1: Recently, Darken[92], Wagner[93] and Schuhmann[94], have clarified the treatment of ternary systems by showing that a molar thermodynamic property (and in turn the corresponding partial molar quantities) may be computed for the whole of an isobaric, isothermal single phase ternary system, if the partial molar property of one component is known over the ternary field. Schuhmann[94], checked the precision of his solution by applying to the data of Elliott and Chipman[106], on the Cd - Pb - Bi system, and the results seemed to be of the same precision as those Elliott and Chipman obtained, by the Darken integration.

However, it appears that the solution derived by Schuhmann[94] is somewhat simpler in form, from that of the previous solutions[92,93].

In the case of uranium-gold-calcium system, the activity data about the binary uranium-gold system are known[97], and if the activity data are available for calcium, over the entire composition range, then the integration derived by Schuhmann[94], can be written as:

$$\left[\bar{G}_{U(x)} = \bar{G}_{U(X)} - \int_{\bar{G}_{Ca(X)}}^{\bar{G}_{Ca(x)}} \left(\frac{\partial n_{Ca}}{\partial n_U}\right)_{\bar{G}_{Ca},\, n_{Au}} d\bar{G}_{Ca}\right]_{\frac{n_U}{n_{AU}}=\text{constant}}$$

In the previous equation X, is a composition on n_U/n_{AU} = constant, for which $\bar{G}_U$ is known, and x is the composition for which $\bar{G}U$ is desired. It is clear that the integration may be made, therefore, if the experimental data for $\bar{G}_{Ca}$ are adequate to enable the partial derivative $(\partial n_{Ca}/\partial n_U)_{\bar{G}_{Ca}, n_{AU}}$, to be evaluated, as a function of $\bar{G}_{Ca}$, along the integration path n_U/n_{AU} = constant, between the limits $\bar{G}_{Ca(X)}$ and $\bar{G}_{Ca(x)}$.

The partial derivative $(\partial n_{Ca}/\partial n_U)_{\bar{G}_{Ca}, n_{AU}}$, is the direction expressed in terms of composition, of the tangent to a curve, along which $\bar{G}_{Ca}$ is constant at a point which must also be on the integration path given by n_U/n_{AU} = constant. Thus, on the isothermal triangle, tangents to isoactivity curves at the points where the latter cut the integration path are extended to intersect the Ca-U side of the triangle. These points of intersection, expressed in terms of the mole ratio of calcium to uranium, yields values of $(\partial n_{Ca}/\partial n_U)$, corresponding to the values of $\bar{G}_{Ca}$, for the isoactivity curves.

This technique may, of course be applied equally readily to either activity or the activity coefficient data.

D.2: Results of Preliminary Uranium-Gold-Calcium, Equilibration Experiments

D.2.(i) Time for Equilibration

It was to be expected that an increase in the gold content of the uranium-gold alloy would be accompanied by an increase in the calcium solubility, and therefore, an alloy having composition, 90 mole% gold + 10 mole% uranium, was chosen for experiments. The equilibration procedure was the same as described in chapter 4 (section 4.C.1.i.). The equilibration time was varied between six and twenty four hours. The accompanying figure (D-1), indicates that at 1573°K, the equilibration was attained in 10 - 12 hours.

D.2.(ii) Solubility of Calcium in Uranium-Gold Alloys

The results obtained for the first equilibration experiments at 1623°K, for the solubility of calcium, at unit activity of calcium ($a_{Ca} = 1$), in 90 mole% gold + 10 mole% uranium are shown in table D-a. The time for equilibration was always six hours, as the equilibration curve was not constructed yet.

TABLE D-a

Experiment Number	Composition of the alloy, before equilibration (mole %)	Composition of the alloy, after equilibration (mole %)
1	gold = 90 uranium = 10	gold = 52.85 uranium = 10.93 calcium = 36.1
2	"	gold = 56.25 uranium = 11.1 calcium = 31.65
3	"	gold = 52.77 uranium = 11.95 calcium = 35.27

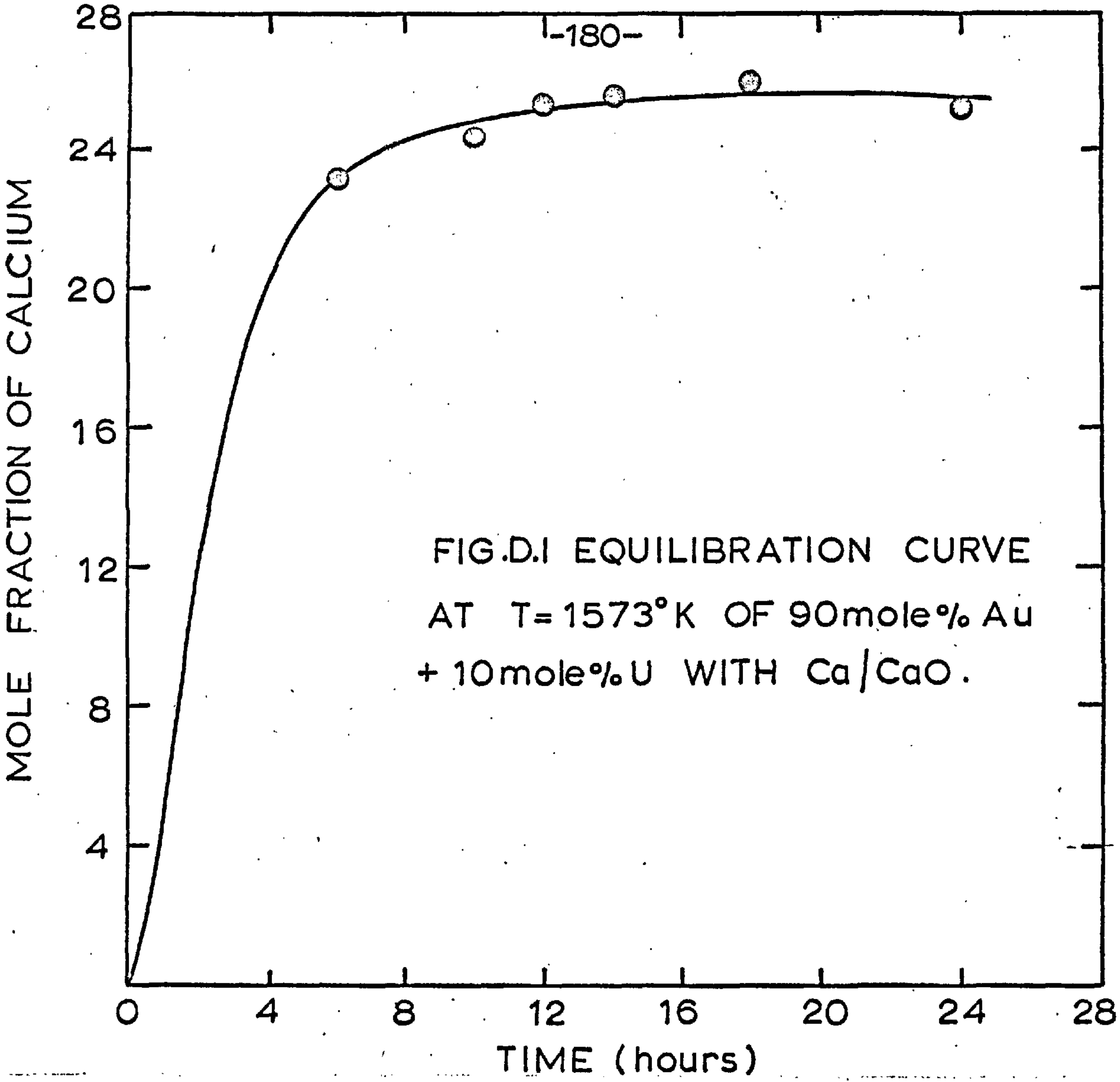

FIG.D.1 EQUILIBRATION CURVE AT T=1573°K OF 90mole% Au + 10mole% U WITH Ca/CaO.

The results shown in table D-a, indicate an extensive solubility of calcium in the liquid U-Au system. It is obvious therefore, that the solubility of calcium in the U-Au alloys cannot be neglected, while equilibrating U-Au, UC and Ca/CaO, for a thermodynamic study of U(C,O), inside the single phase region; and it will not be possible to use the uranium activity data, already available for the simple uranium-gold binary system[97]. However, the uranium activity in the U-Au-Ca alloy system, can be calculated by a ternary Gibbs-Duhem integration described in section D-1, of this appendix; provided the data about the activities of calcium are known for the whole range of composition.

Preliminary results obtained for the solubility of calcium (at unit activity) in the uranium-gold alloys of varying compositions, at 1573°K, are depicted in figure D-2. These results indicate the probable shape of the isoactivity lines of calcium (e.g. figure D.3.).

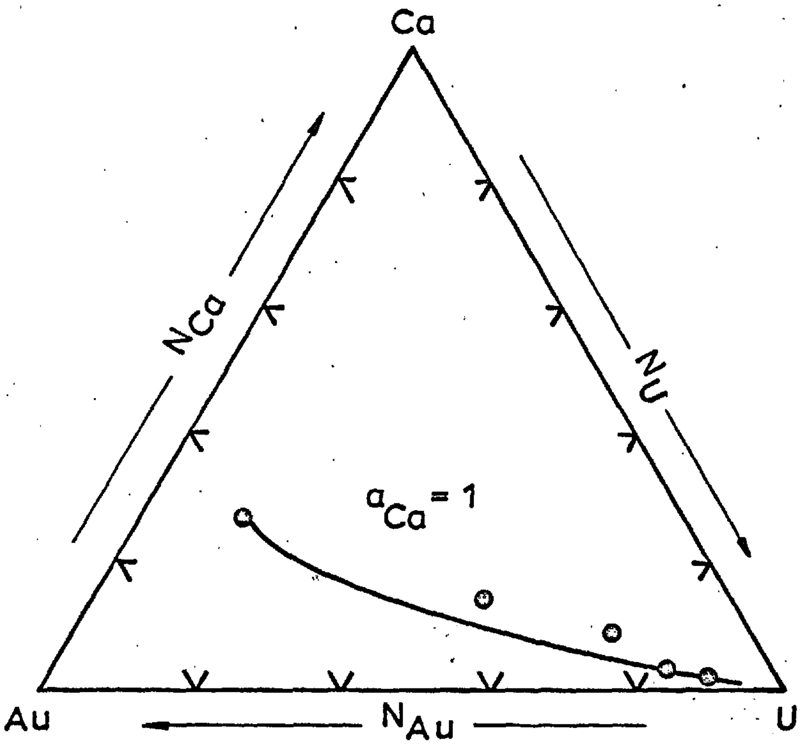

FIG. D.2 TERNARY SYSTEM U-Au-Ca AT 1648°K

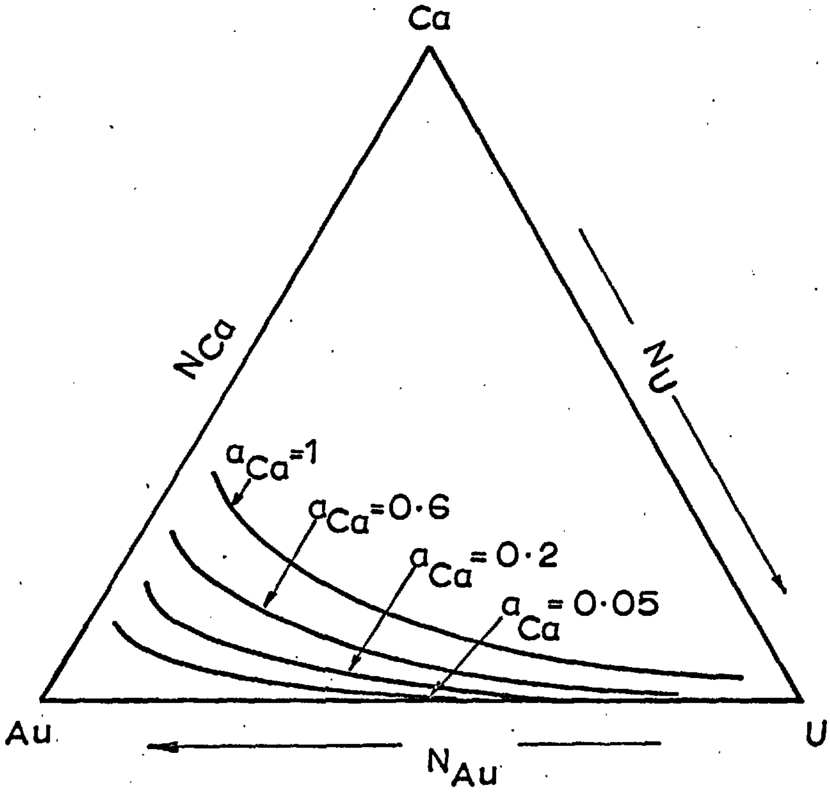

FIG.D.3 EXPECTED ISOACTIVITY LINES OF CALCIUM IN U-Au-Ca ALLOYS AT A CERTAIN TEMPERATURE

APPENDIX E

Calculations of Activities of Carbon in UC and CaC_2 at Different Activities of Uranium and Calcium Respectively.

The standard free energy data for UC and CaC_2 were taken from references 18 and 79 respectively. The calculated activities of carbon at different temperatures for various activities of uranium and calcium are listed below.

	$U_{(l)} + C_{(s)} = UC_{(s)}$ equilibria		$Ca_{(l)} + 2C_{(s)} = CaC_2$ equilibria	
Temperature (C°)	Activity of uranium (a_U)	Activity of carbon (a_C)	Activity of calcium (a_{Ca})	Activity of carbon (a_C)
1200	1	4.14×10^{-4}	1	1.739×10^{-2}
	0.1	4.14×10^{-3}	0.1	5.499×10^{-2}
	0.01	4.14×10^{-2}	0.01	0.1739
1300	1	6.79×10^{-4}	1	2.02×10^{-2}
	0.1	6.79×10^{-3}	0.1	6.38×10^{-2}
	0.01	6.79×10^{-2}	0.01	0.202
1375	1	1.006×10^{-3}	1	2.23×10^{-2}
	0.1	1.006×10^{-2}	0.1	7.05×10^{-2}
	0.01	0.1006	0.01	0.223

APPENDIX F

Determination of Nitrogen in Uranium Oxycarbide Samples

The determination of nitrogen in some of the equilibrated specimens of uranium oxycarbides was carried out with the co - operation of Analytical Services Laboratory of Imperial College.

Principle: When uranium oxycarbide containing nitrogen, is dissolved in acid, the nitrogen is converted to ammonium ion. Steam distillation of the solution, after making it alkaline, separates the ammonia for determination. Ammonia in the distillate reacts with Nessler's reagent to give a yellow colour, the intensity of which provides a measure of the amount of ammonia, and hence of nitrogen in the sample.

Procedure: The procedure adopted was the same as described by Milner, et al.[107].

APPENDIX G

Preparation of Urania (UO_2) Crucible.

The uranium dioxide powder supplied by A.E.R.E. Harwell., was finely ground in an agate mortar, and then mixed with 0.5 - 1.0% by weight of Cranko binder using toluene as solvent. The slurry was stirred so that the binder distributed thoroughly into the uranium dioxide particles. The slurry was then allowed to dry at room temperature until it formed a good powder.

A vinamould of the required dimensions was used for making the urania crucible and isostatically pressed with a pressure of 7 - 10 tons per square inch. The green urania crucible was carefully taken out from the vinamould and heated slowly to get rid of the binder, first at 500°C, and then at 1000°C in hydrogen atmosphere, in a specially made Kanthal wound furnace. The urania crucible was then placed in a platinum boat and sintered in a Pt - 10% Rh, resistance furnace in dry H_2 atmosphere at 1450°C for several hours. The stoichiometry of the sintered UO_2 crucible was checked by determining its lattice parameter.The value found, 5.4690 Å ±0.0005 Å agreed with the reported values of Rundle et al.[33] and Piazza[100], for stoichiometric urania.

APPENDIX H

Preparation of Calcia Crucible

The starting material (CaO powder) was obtained by heating Ca CO_3* powder for about 8 - 10 hours at 1000 - 1050°C, and then the powder was ground to very fine size in an agate mortar, 0.5 - 0.7% by weight Cranko binder was added with toluene as solvent. The binder was mixed thoroughly by stirring the slurry and toluene was removed by heating under infra-red lamp. The powdered calcia material was then ready for pressing.

A vinamould of the required dimensions was used for making the calcia crucibles. The crucibles were pressed using a pressure of 10 - 15 tons per square inch. The CaO crucible was then heated slowly to about 400 - 500°C to get rid of the binder and then sintered in a vacuum furnace or molybdenum resistance wound furnace (in air), at about 1550 - 1600°C. As the dissociation pressure of CaO is quite high at 1600°C ($\simeq 1.78\text{x}10^{-8}$ atm.)[80], the vacuum sintering time was kept relatively short i.e. (15 - 30 mins. at 1600°C, followed by 4 hours at 1500°C) thus improving the density of the crucible.

*Analar grade Ca CO_3 (Hopkins and Williams Ltd., England.)

APPENDIX I

Analytical Procedure For The Determination of Total Carbon and Uranium in Uranium-Carbides

The principle and the apparatus (figure 22), involved in the determination of carbon and uranium were outlined in chapter 4 of this thesis. However, the experimental details are described below.

The combustion furnace was heated to 900°C, while the temperatures of the furnaces containing platinized asbestos and CuO were 600°C and 410°C respectively. The absorption tube filled with carbest and magnesium perchlorate was weighed*, and then attached to the system. The oxygen flow rate was adjusted to $\simeq$ 100 ml. per minute and was allowed to flow for 45 minutes. The absorption tube was weighed again giving a blank "B".

Then the sample (e.g. U(C,O)) was taken out from the drybox in a weighed platinum boat ($1.0 \times 1.0 \times 1.5$ Cm^3), placed in an air-tight sample holder. After weighing accurately the platinum boat containing the sample was transferred quickly to the cold part 'X' of the combustion furnace, into the silica boat, which in turn was attached to the silica rod and iron piece. The system was made leak tight so that no CO_2 or CO gases produced even at room temperature, escaped from the system. With the weighed absorption tube in place in the train, purified oxygen was allowed to flow. The platinum boat

---

* All weighings were done by using a balance which could weigh up to 10^{-5} gm. accurately.

placed was pushed into the hot zone of the combustion furnace by using a magnet. The sample was ignited for 45 minutes in a stream of oxygen. After ignition the platinum boat was brought back into the cold zone by means of a magnet. Then the absorption tube and the platinum boat were weighed again, to determine the carbon and uranium contents respectively.

Calculation of the Percentage of Carbon

If,

W = weight of the sample

W_1 = initial weight of the absorption tube

W_2 = final weight of the absorption tube

B = blank

then the percentage of carbon in the sample is:

$$= \frac{W_2 - (W_1 + B) \times 0.27291}{W} \times 100$$

Calculation of the Percentage of Uranium

If,

W = weight of the sample

W_3 = initial weight of the platinum boat

W_4 = final wt. of the platinum boat + ignited sample i.e. $U_3 O_8$

then the percentage of uranium in the sample is:

$$= \frac{(W_4 - W_3) \times 0.848019}{W} \times 100$$

APPENDIX J

Analysis Procedure For Uranium-Gold-Calcium Ternary Alloys

A number of analytical methods were examined and the following procedure was eventually adopted as giving the most reproducible and reliable results.

The alloy bead was dissolved in aqua regia (1 part by volume conc. HNO_3 + 4 parts conc. HCl + 1 part by volume distilled water). The resulting solution was evaporated to dryness to remove nitrate ions. This procedure was repeated three to four times by adding concentrated HCl, until there were no nitrate ions present. Then the pH value of the solution containing U-Au-Ca in HCl was adjusted to a value between five and six. Gold was removed by means of H_2S, in the form of sulphide. After filtering, the gold sulphide was used for gold determination and the filtrate for uranium and calcium determinations.

In the determination of gold, the gold sulphide was again dissolved in aqua-regia and boiled to dryness. The residue was taken up with HCl, H_2SO_4 and H_2O, and to each 75 ml. of this solution 25 ml. of concentrated oxalic acid solution were added and the solution was digested for four hours. The precipitate was weighed as pure gold.

For the determinations of uranium and calcium from the filtrate; the chloride ions present in it were completely removed by evaporation. The residue was dissolved in 5 - 6 M HNO_3 and the uranium was extracted by means of 20% tributyl phosphate (TBP) - carbon tetrachloride mixture. The extraction was repeated from five to six times. The aqueous phase containing calcium was washed with pure C Cl_4 and filtered. This filtrate was evaporated to dryness and the residue was taken up in dilute HCl. Then calcium was determined gravimetrically as the oxalate.

Uranium was determined using a spectrophotometric technique by a complex formed with ammonium thiocyanate.

An error of 2 - 3% by weight was associated with this method, as can be seen from the following typical results in table J.

Table J

Experiment Number	weight of uranium, gold and calcium taken before analysis (gms.)	weight of uranium, gold and calcium obtained after analysis (gms.)
1	uranium = 0.1	uranium = 0.1005
	gold = 0.8	gold = 0.78
	calcium = 0.1	calcium = 0.098
2	"	uranium = 0.1095
		gold = 0.779
		calcium = 0.1027
3	"	uranium = 0.11
		gold = 0.81
		calcium = 0.1

APPENDIX K

Analysis of Errors

The main sources of errors associated with the experimental data reported in this thesis, using the equilibration techniques, are described below.

1: Chemical Analysis

The chemical analysis of carbon and oxygen is important so far as the stoichiometry of U(C,O) is concerned, and consequently to the assignment of formula to $U(C_{y-x},O_x)$. The errors involved in the chemical analysis of carbon and oxygen were about ± 0.02 wt.% and 0.2 wt.% respectively, which could alter the mole fractions of UC and UO, in the uranium oxycarbide phase, by ± 0.004 and ± 0.03 respectively.

Similarly, there is an error involved in the chemical analyses of uranium-gold alloys. Grieveson[97], found about one atomic per cent error, and attributed it to carbon and consequently he corrected the activity of uranium, using a ternary Gibbs-Duhem equation. During the present investigation it was observed, however, that the error is probably more than one atomic per cent (about two atomic per cent) as it is difficult to separate the carbide from the alloy hundred per cent. However, a polished specimen of uranium-gold alloy was examined under the electron-microprobe and no trace of any free or combined carbon was reported to be observed. Possibly, the presence of carbon in the alloy could have been below the detections limit of the microprobe, hence due to this uncertainty involved, no correction was made of the activity data of uranium.

2: Temperature Fluctuations and Position of Specimens

Uncertainty in the position of specimens of U and(UC) (± 2mm.) could cause an error of about ± 0.05 K.cal. in $\Delta\bar{G}_o$. Fluctuations of the temperature of the specimens and the temperature of the metal reservoir (about ± 2°C), could cause an error of 0.1 - 0.2 K.cal in $\Delta\bar{G}_o$.

3: Activity of Uranium

For the equilibration experiments at the U-U(C,O) phase boundary, the activity of uranium was maintained as unity, by placing an excess of uranium metal with UC. However, the activity of uranium may be lowered, due to the presence of impurities such as carbon, oxygen, iron and nickel. According to the U-C phase diagrams shown in figures 1 and 2, carbon dissolved in liquid uranium upto 2-5 atomic per cent, depending upon temperature (1473°K - 1648°K). However, when uranium metal is in equilibrium with U(C,O), the solubility of carbon is an unknown factor. One may expect it, lower than when uranium is in equilibrium with pure UC. A uranium metal piece was subjected to electron microprobe examination and no carbon was detected, which was probably below the detection limits of microprobe, i.e. $<$ two atomic per cent. Similarly, the solubility of oxygen in liquid uranium is about

0.05 atomic per cent, according to Katz and Rabinowitch[41A], and is negligible.

However, as all the equilibration experiments were carried out in sealed pure iron tubes, so at high temperatures iron from the vapour phase could dissolve in the liquid uranium, even though the vapour pressure of pure iron in the temperature range of this investigation is not very high, i.e. about 10^{-7} atm. Upon examination of a polished specimen of equilibrated uranium metal, under an electron microprobe it was reported to be present mainly in the grain boundaries, but the overall composition of uranium was about 99.7 wt.%.

The presence of nickel was also observed in the equilibrated uranium metal, and the nickel content reported to be less than 0.1 atomic per cent.

Calcium was also not observed in the equilibrated uranium metal. According to Ahmann[108], the calcium solubility in uranium is negligible.

It appears that the activity of uranium oould not have been less than 0.95, with all the impurities present. This would have consequently, affected the standard free energy of formation of oxygen saturated uranium oxycarbide phase by 0.1 - 0.2 K.cal./mole, in the temperature range of this investigation.

4: Activity of the U(C,O) Phase

All the possible impurities would react preferentially with uranium metal during the equilibration, as described earlier. Only nitrogen is likely to dissolve in U(C,O), to form a quarternary U(C,ON) solid solution phase. The presence of nitrogen as an impurity is described in Chapter 5.

5: Solubility of Calcium in Calcium Oxide

Bevan[99] found that calcium was soluble in solid lime of about 0.2 - 0.5 mole per cent at temperatures of 1223 - 1323°K, and a calcium activity of 0.75. However, later on he inferred that the apparent solubility of calcium in lime was due to the presence of calcium nitride as an impurity in solid solution in the lime. In its absence a negligible calcium solubility in solid lime was reported.

However, the activity of solid calcium oxide was always taken as unity, during all calculations.

6: Other Errors

All the equilibration experiments were terminated by quenching the specimen tube. During this period the specimens were subjected to uncontrolled conditions of temperature and metal vapour pressure. The time was however too short, i.e. it took about 3-5 minutes to cool from 1648°K to 323°K, to cause any significant changes.

During various graphical procedures, errors were introduced, but due to mutual cancellation, the errors are probably not very high.

APPENDIX L

Uranium Activity Data, of The Uranium-Gold Binary System

Grieveson[97], calculated the activities of uranium, from the vapour pressure measurements of uranium-gold liquid solutions of various compositions, for 1723°K, 1773°K and 1823°K. From these data, Rand and Kubaschewski[50], calculated the partial molar heats of uranium and gold, by assuming the uranium-gold solutions to be regular, and observed that the temperature variation of the free energies, was consistent with this assumption. However, although the uranium-gold solutions are **sub-regular**, yet for a fixed composition the quantity RT $\ln \gamma i$ does not change with temperature, and. the activities of uranium can be calculated, at 1573°K, for various compositions of uranium and gold alloys.

The calculated activity data of uranium, of various compositions of uranium in the uranium-gold binary alloy system, at 1573°K, from Grieveson's data at 1723°K, are shown in table L.1.

The calculated activities of uranium at 1573°K, are correct only if uranium and gold are liquid for all compositions at this temperature. However, using the phase diagram of uranium-gold system from Smithel[101], activity versus composition plot for uranium is drawn, as shown in figure L.1.

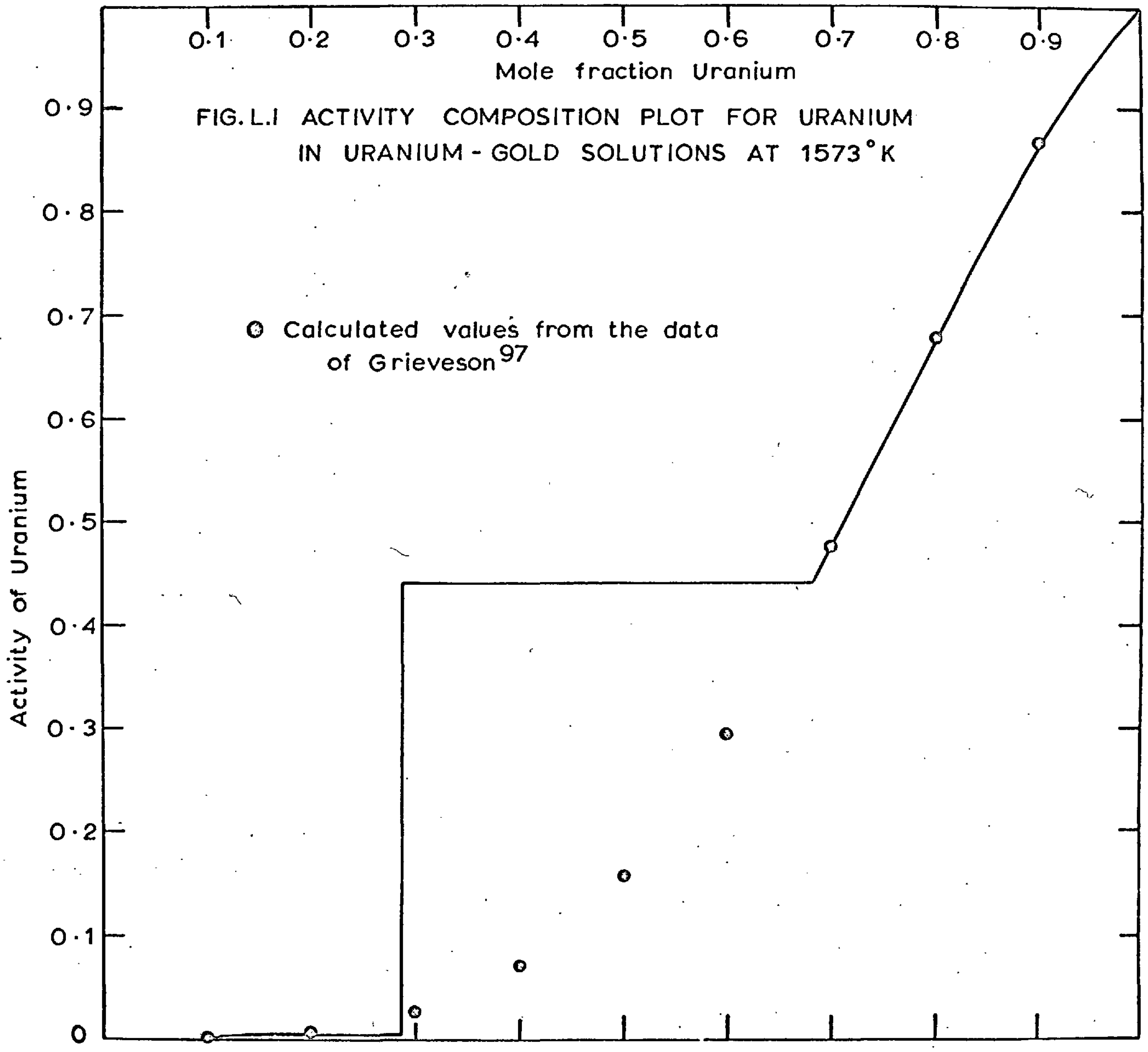

FIG. L.I ACTIVITY COMPOSITION PLOT FOR URANIUM IN URANIUM - GOLD SOLUTIONS AT 1573°K

TABLE L.1.

N_u	Activity data at 1723°K	Calculated activity data at 1573°K
0.1	2.09×10^{-3}	1.45×10^{-3}
0.2	1.03×10^{-2}	7.76×10^{-3}
0.3	3.30×10^{-2}	2.67×10^{-2}
0.4	8.35×10^{-2}	7.25×10^{-2}
0.5	0.174	0.157
0.6	0.313	0.294
0.7	0.492	0.476
0.8	0.688	0.678
0.9	0.868	0.865

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