High Temperature Phase Equilibria in the System Carbon-Oxygen-Uranium

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MUCH EFFORT is being made to develop uranium carbides, especially the monocarbide, for nuclear fuels. The more important properties of these fuels include a high and uniform uranium density, mechanical and chemical stability, and low cost. The carbides can be made by reaction of the elements or by reaction of uranium oxides and carbon. These reactions proceed appreciably at temperatures well below the melting points of the carbides, but in excess of 1000° C.

Phase relations in the carbon-uranium system have been rather thoroughly established, but this is not the case for the ternary system carbon-oxygen-uranium. The objective of the work reported here was to establish phase relations involving uranium carbides, uranium dioxide, and graphite. Such relations describe necessary conditions for forming a particular carbide from graphite and uranium dioxide.

EQUIPMENT

The reaction vessel is shown in Figure 1. A graphite susceptor 6 inches long, 2 inches in diameter, and 1/16 inch thick was heated by induction. The charge was contained in a graphite crucible 2 inches high, 1 inch in diameter, centered in the susceptor. Graphite powder was used for insulation. The assembly above the susceptor containing a sight tube served to minimize vertical temperature gradients in the crucible. For temperatures above 1625° C. the vessel was modified since SiC forms at the silica-graphite interface and interferes with the equilibria being studied. The susceptor was replaced by one 3/4 inch in diameter, and graphite powder by high purity graphite felt and batting.

The vessel along with an open end manometer, thermocouple gage, McLeod gage, cold traps, three gas sample tubes, and a mechanical pump comprised the static vacuum system. Dry ice and 1-propanol were used in the traps. O rings were used at the vessel lid to facilitate access between runs. The lid was water cooled and a short length of flexible copper tubing led from it to the rest of the system.

High frequency current for induction heating was provided by a 20-kw., 375-kc., tube generator. The work coil consisted of 13 equi-spaced turns of 3/8-inch copper tubing with a 4-inch inside diameter and 6 1/2-inch wound height. A 4.4 to 1 voltage reducing transformer was used between the generator and the coil. Power was manually controlled by a variable resistor in the grid circuit; in this fashion the charge temperature could be held within 5° C. of desired values.

An optical pyrometer of the disappearing filament type was used for temperature measurements. Radiation from the charge passed through the sight glass and was directed to the pyrometer by a prism. Corrections for adsorption by glass traversed were made by measuring apparent temperatures of a flat filament lamp both with and without the sight glass and prism interposed. The pyrometer was calibrated at the National Bureau of Standards.

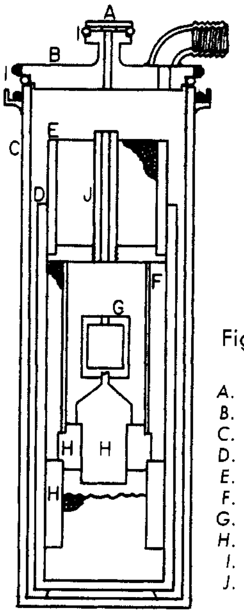

Figure 1. Cross section of reaction vessel

A. Sight glass and iron shutter
B. Brass lid
C. Outer silica tube
D. Inner silica tube
E. Insulating plug with sight tube
F. Graphite susceptor
G. Graphite crucible
H. Carbon support and centering pieces
I. O rings
J. Graphite particles

PROCEDURE

The starting materials consisted of reagent-grade depleted uranium dioxide (99.9% UO_2), reagent-grade carbon monoxide, and Ceylon graphite (0.2 ± 0.1% ash). Carbides used in charges were made from the uranium dioxide and graphite.

Finely ground and mixed powders were pressed into 3/8-inch diameter pellets. From 1 to 5 grams of powder were used per charge, and paraffin in toluene was used as a binder for some of the tablets. The charge was placed in the previously outgassed vessel and the system pumped down. The charge was then heated to about 1200° C. to volatilize and exhaust binder material and adsorbed gases. Then the system was heated to the temperature of equilibration and the pump closed off. Equilibrium was approached until the rate of change of pressure had fallen to 0.5 mm. per hour or less. The four-phase equilibria were approached in directions of both increasing and decreasing carbon monoxide pressures, and the time required was of the order of 2 to 4 hours. Upon reaching equilibrium a gas sample was taken, the power was turned off, and exhausting of gases was begun. Five minutes later the charge temperature had dropped about 500° C. and the gas pressure was less than 100 microns. At this time the barometric pressure was read from the manometer. The solid residue at room temperature was reduced to powder and analyzed by x-ray diffraction to determine phases present. The gas sample was analyzed in the mass spectrometer to determine the equilibrium carbon monoxide pressures.

A special series of equilibrations was carried out at 1605° C. to study the effect of nitrogen on the carbide-oxide equilibria. In these tests varying amounts of gaseous nitrogen were introduced into the system during the tests, and equilibration was allowed to proceed.

While carbon monoxide was the major constituent in the gas phase, hydrogen, nitrogen, carbon dioxide, oxygen, and argon were also detected. A correction was applied to the gas analyses because of the gas concentration gradient that exists due to thermal diffusion. The hydrogen atoms tend

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to concentrate in the high temperature portion of the system. To calculate the extent of this demixing, the following equation was used:

$$\Delta N_{H_2} = 0.416(N_{H_2})_{av}\log_{10}(T_h/T_c) \qquad (1)$$

where N is the mole fraction and T_h and T_c are the absolute temperatures of the hot and cool regions, respectively. This equation is based on the work of Ibbs and Underwood (7) who measured the extent of demixing in a carbon monoxide–hydrogen system in a thermal gradient. In deriving the above equation the separation in a given gas mixture was assumed to be proportional to $\log_{10}(T_h/T_c)$ since this proportionality has been observed in many binary gas mixtures. Average gas composition in the system was assumed to be the arithmetic mean of those at the two extreme temperatures. Corrections were calculated from the derived equation using a method of successive approximations. The above assumptions are considered to be valid since the magnitude of the correction is small compared to the carbon monoxide pressure in the system. For example, in a sample containing 15 mole % hydrogen ΔN_{H_2} is 0.05.

A Norelco diffraction unit with a wide angle goniometer using a Geiger counter detector was used to obtain diffraction patterns. For precision lattice parameter measurements, a symmetrical back-reflection focusing camera 12.0 cm. in diameter and an 11.46-cm. Debye-Scherrer camera were used. Film measurements were made to ±0.025 mm.

Accurate and precise lattice parameters for the uranium dioxide and uranium monocarbide phases were obtained by detecting high angle diffracted radiation and by using a mathematical extrapolation technique. The values of the lattice parameters as calculated from the various lines that occurred on the diffraction film at $\theta > 60°$ were plotted *vs.* the function $\phi \tan \phi$ where ϕ is the complement of the diffraction angle, θ. The best straight line plotted through these points was determined by the method of least squares, and its intersection at θ equal to 90° gave the precision lattice parameter. An IBM 704 computer program was prepared and used for the least squares analyses and for determining standard deviations of parameter values.

RESULTS

Univariant Equilibria. Two univariant equilibria were found in the temperature range investigated. They are:

$$UO_2 + 4C = \text{'}UC_2\text{'} + 2CO \qquad (2)$$

and

$$UO_2 + 3\text{'}UC_2\text{'} = 4\text{'}UC\text{'} + 2CO \qquad (3)$$

Diacritical marks indicate that the compositions of the designated phases differ slightly from the stoichiometric compositions of the compounds in question. At a given temperature the equilibrium pressure for the equilibrium of Equation 3 is lower than that of Equation 2. The equilibria were approached in the direction of increasing and decreasing carbon monoxide pressure, but this procedure was found unnecessary at temperatures above 1575° C. because the equilibria could be closely approached in the direction of increasing pressure. This was demonstrated in run 62 of Table I by reacting uranium dioxide and graphite at 1596° C. until the carbon monoxide pressure reached a steady value, then adding carbon monoxide to reverse the reaction. After the addition, the reverse reaction occurred until the system pressure fell to a steady value which was the same as measured previously.

Equilibrium Pressures for Univariant Equilibria. The results of the determinations of carbon monoxide equilibrium pressures for the equilibria of Equation 2 and 3 are summarized in Tables I and II. Listed as reactants are the phases that were consumed as the equilibrium was

Table I. Results of Carbon Monoxide Equilibrium Pressure Determinations for the Equilibria $UO_2 + 4C = \text{'}UC_2\text{'} + 2CO$

Run	Reactants	Temp., ° K.	Pressure, Mm. Hg	Gas Phase Compn., %							CO Equilibruim Press., Mm. Hg
				CO, %	H_2	N_2	O_2	A	CO_2	CO Corr.	
30	UO_2 C	1714	$3\frac{3}{4}$	83.48	15.03	1.02	0.04	0.00	0.42	77.9	3
42	UO_2 C	1780	$10\frac{1}{2}$	84.91	13.65	0.84	0.07	0.04	0.48	79.7	$8\frac{1}{2}$
41	'UC_2'. Co	1786	$11\frac{3}{4}$	93.89	4.80	1.00	0.10	0.01	0.20	92.1	$10\frac{3}{4}$
12	UO_2, C	1817	18	90.89	8.46	0.39	0.10	0.01	0.15	86.0	$15\frac{1}{2}$
49	UO_2, C	1845	22	89.43	7.87	2.49	0.00	0.00	0.20	86.4	19
39	'UC_2', CO	1839	$26\frac{3}{4}$	94.64	3.55	1.36	0.20	0.02	0.23	93.3	25
11	UO_2, C	1853	25	91.83	5.57	1.85	0.33	0.06	0.36	89.9	$22\frac{1}{2}$
62	UO_2, C	1869	$38\frac{1}{2}$	89.57	9.16	1.04	0.10	0.02	0.10	86.0	33
62	'UC_2', CO	1869	$38\frac{1}{2}$	88.77	10.01	0.94	0.12	0.02	0.13	84.8	$32\frac{3}{4}$
61	UO_2, C	1892	45	90.83	8.97	0.16	0.00	0.00	0.04	87.2	$39\frac{1}{4}$
60	UO_2, C	1922	$62\frac{3}{4}$	92.17	7.20	0.55	0.00	0.01	0.07	89.3	56

Table II. Results of Carbon Monoxide Equilibrium Pressure Determinations for the Equilibria $UO_2 + 3\text{'}UC_2\text{'} = 4\text{'}UC\text{'} + 2CO$

Run	Reactants	Temp., ° K.	Pressure, Mm. Hg	Gas Phase Compn., %[a]							CO Equilibrium Pres., Mm. Hg
				CO	H_2	N_2	O_2	A	CO_2	CO	
23	'UC', CO	1761	$6\frac{1}{4}$	94.88	4.74	0.06	0.09	0.01	0.23	93.1	$5\frac{3}{4}$
45	UO_2,'UC_2'	1778	$6\frac{1}{4}$	90.57	9.43	0.00	0.00	0.00	0.00	87.0	$5\frac{1}{2}$
29	'UC', CO	1822	13	93.74	5.42	0.44	0.15	0.02	0.23	91.7	12
40	UO_2, 'UC_2'	1847	$15\frac{1}{2}$	86.88	11.85	0.96	0.06	0.02	0.24	82.3	$12\frac{3}{4}$
105	UO_2, 'UC_2'	1878	$21\frac{1}{2}$	89.82	9.88	0.20	0.00	0.00	0.10	85.9	$18\frac{1}{2}$
44	UO_2, 'UC_2'	1914	$28\frac{1}{2}$	93.42	6.11	0.20	0.00	0.00	0.27	91.0	26
34	'UC', CO	1911	$31\frac{3}{4}$	94.75	4.41	0.52	0.06	0.00	0.26	93.0	$29\frac{1}{2}$
57	UO_2, 'UC_2'	1939	$38\frac{3}{4}$	91.31	8.29	0.27	0.00	0.00	0.13	87.9	34
52	'UC', CO	1953	$52\frac{1}{4}$	87.83	7.11	3.42	0.18	0.07	0.25	84.9	$44\frac{1}{4}$

[a] The gas phase of run 52 contained 1.14% helium in addition to the gases listed.

approached. For every run, the solid phases involved in the associated equilibrium were determined by x-ray diffractions analyses of the solid residue. Total gas pressures and the gas analyses of samples from each equilibrium are listed. The corrected values of per cent carbon monoxide represent the calculated amounts of carbon monoxide in the hot gas. These values were calculated as previously described.

The pressure-temperature data for both equilibria were plotted in the form of the common logarithm of carbon monoxide pressure *vs.* the reciprocal of the absolute temperature, and these graphs were observed to be linear. A least squares analysis was used to obtain expressions to represent the data and a statistical analysis was carried out to evaluate the size of the random errors of the parameters and of calculated values of $\log_{10} p_{CO}$. The expressions are as follows:

$$\log_{10} p_{CO} = -18{,}000/T + 8.23 \qquad (4)$$

$$\log_{10} p_{CO} = -16{,}000/T + 7.26 \qquad (5)$$

Equation 4 is for the equilibria of Equation 2 and Equation 5 is for the equilibria of Equation 3. In these expressions T is temperature in degrees Kelvin and p is the pressure in atmospheres. The experimental data and the calculated lines are shown in Figure 2 along with the values of two standard deviations of calculated values of pressure for selected values of temperature as indicated.

Divariant Equilibria with Nitrogen. The results of equilibrations involving nitrogen are summarized in Table III. The results of runs 8, 50, and 57 are included because the lattice parameters of the monocarbide phases in residue of these runs were measured.

Lattice Parameter Measurements. The lattice parameters measured for monocarbide-rich phases have been tabulated in Table III. Values for which the uncertainty is expressed as ±0.001 A. units were calculated from measured values of the (620) reflections. These reflections occurred at diffraction angles of greater than 80 degrees and the corresponding precision and accuracy in the calculated values of the lattice parameter are better than ±0.001 A. Values for the lattice parameters of the uranium dioxide phases are listed in Table IV. In run 7 the uranium dioxide was equilibrated with uranium dicarbide, graphite, and carbon monoxide but the run was interrupted before the rate of pressure increase fell to 0.5 mm. per hour.

ANALYSIS OF RESULTS

Estimation of Activity Values. The activity of the graphite used is assumed to be unity. The activity of the uranium monocarbide could, however, have been less than unity due to one or more of these causes: The carbon content of this phase could have been in excess of the stoichiometric amount. It could have contained some oxygen which had substituted for the carbon. It could have contained some nitrogen which had substituted for carbon. All three of these factors would involve variation in the lattice parameter of the monocarbide phase.

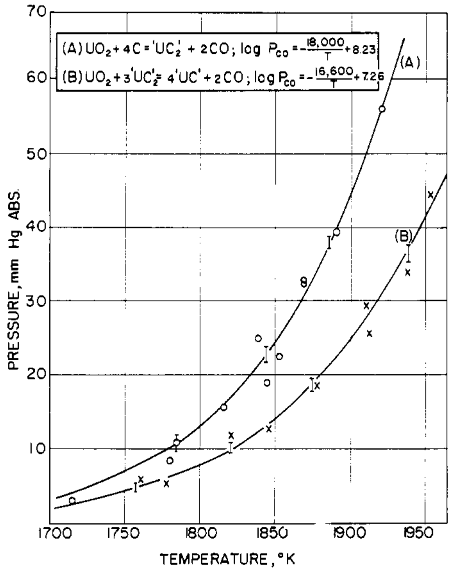

Figure 2. Carbon moxoxide equilibrium pressure *vs.* absolute temperature for the equilibria indicated

Williams and coworkers (*14*) have found that the lattice parameter of uranium monocarbide decreases with carbon content from 4.960 ± 0.0005 A. at 50.3 atomic % to 4.9520 ± 0.0005 A. at some undetermined carbon content below 50.3 atomic %. The monocarbide phases involved in equilibria of Equation 3 are to be expected to be carbon rich because they were in equilibrium with uranium dicarbide. Moreover the solubility of carbon in uranium monocarbide has been found to be small in the temperature range of this investigation. Wilson (*15*) has found the compositions of uranium monocarbide saturated with carbon to be about 51 atomic % carbon at 1950° K. and only slightly over 50 atomic % at 1878° K. Consequently, the lattice parameter and the activity of the monocarbide phase at the latter temperature should be appreciably affected only by the presence of oxygen or nitrogen.

Data for the lattice parameters *vs.* compositions for solid solutions of uranium monocarbide and uranium mononitride have been reported by Williams and Sambell (*13*). These investigators found the lattice parameter to vary linearly with per cent uranium monocarbide from 4.8898 ± 0.0004 A. for the mononitride to 4.9605 ± 0.0004 A. for the monocarbide. Their value for the monocarbide parameter is consistent with the value 4.9614 ± 0.0005 reported by Wilson (*15*). The existence of pure uranium monoxide has not been reported but Rundle (*10*) has reported obtaining this phase in solid solution with uranium monocarbide. Based on his observations he estimated the lattice parameter of pure uranium monoxide as 4.93 ± 0.01 A. The findings of Vaughn (*12*) and coworkers are consistent with this value.

Table III. Summary of Equilibrations Involving Nitrogen as a Component

Run	Charge	Temp. ° K.	Pressure, Mm. Hg. CO	Pressure, Mm. Hg. N_2	Solid Phases in Residue	Monocarbide Phase Lattice Parameter, A.
101	$UO_2 + C$	1875	21.66	31.31	UO_2, C, U(C, N)	4.935 ± 0.001
102	$UO_2 + C$	1878	22.86	63.17	UO_2, C, U(C, N)	4.9214 ± 0.0003
103	$UO_2 + C$	1878	24.54	15.05	UO_2, C, U(C, N)	4.938 ± 0.001
104	$UO_2 + UC_2$	1878	19.43	3.13	UO_2, UC_2, U(C, N)	4.953 ± 0.001
105	$UO_2 + UC_2$	1878	18.47	0.04	UO_2, UC_2, U(C, N)	4.9608 ± 0.0003
57	$UO_2 + UC_2$	1939	34	0.10	UO_2, UC_2, U(C, N)	4.9616 ± 0.0003
50	$UO_2 + UC_2$	1892	21	0.01	UO_2, UC_2, U(C, N)	4.9573 ± 0.0006
9	$UO_2 + C$	1795	4	0.03	UC_2, U(C, N)	4.9582 ± 0.0002

Table IV. Measured Lattice Parameters for Indicated Uranium Dioxide Phases

Phase Source	Lattice Parameter, A.
Reagent Grade UO_2	5.4685 ± 0.0001
Residue from run 7 at 1936° K.	5.4707 ± 0.0003
Residue from run 45 at 1778° K.	5.4704 ± 0.0005

The results of run 105, given in Table III, show that the lattice parameter of the monocarbide phase after equilibrating at 1878° K. with 0.2% nitrogen in the gas phase was 4.9608 ± 0.0003 A. This value is close to the values cited for oxygen- and nitrogen-free uranium monocarbide. Thus, the uranium monoxide content of the monocarbide phases involved in the equilibria achieved is of the order of 2 or 3 mole % or less and the monocarbide phases of runs 101 through 105 can be considered to be binary solid solutions of uranium monocarbide and uranium mononitride. Figure 3 has been prepared on this basis using the data of Williams and Sambell (*13*) to convert lattice parameters to mole per cent.

Figure 3 can be used to estimate the order of magnitude of the uranium mononitride content of the equilibrium uranium monocarbide phases above and below 1878° K. by considering the effect of temperature on the equilibria.

$$2\,UC + \tfrac{1}{2}\,N_2 = UN + UC_2 \qquad (6)$$

The equilibrium constant for this reaction is given by

$$K_T = a_{UN}\,a_{UC_2}/a^2_{UC}\,p^{0.5}_{N_2} \qquad (7)$$

Raising the temperature favors the formation of nitrogen and uranium monocarbide. Thus K_T decreases with increasing temperature and the activity of the mononitride corresponding to a given nitrogen equilibrium pressure would be smaller above 1878° K. than at that temperature.

Data of nitrogen pressures in equilibrium with uranium monocarbide phases have been listed in Table V. Utilizing these data, Figure 3, and the lattice parameter data of Table III, it is concluded that the concentrations of uranium mononitride were of the order of 5 mole % or less.

Based on the estimated levels of excess carbon, nitrogen, and oxygen in the monocarbide phases, the activity of uranium monocarbide is assessed as 0.95 ± 0.05. The question of error in observed carbon monoxide equilibrium pressures due to the presence of nitrogen will be taken up in the subsection on interpretations of the observed phase equilibria.

The effect of excess oxygen on the uranium dioxide lattice parameter has been studied by Hering and Perio (*6*) who report values of 5.468 A. for $UO_{2.00}$ and 5.427 A. for $UO_{2.35}$. Between these values they found the lattice parameter to vary linearly with the atom ratio. More recently, Gronvold (*5*) has reported the lattice parameter of $UO_{2.00}$ as 5.472 A. From these data and the observed uranium dioxide lattice parameters listed in Table IV, it is concluded that the composition of the equilibrium dioxide phases is $UO_{2.01 \pm 0.01}$. Hence the UO_2 activity is essentially unity.

Table V. Partial Pressures of Nitrogen in Equilibrium with Uranium Dicarbide and Solid Solutions of Uranium Monocarbide and Uranium Mononitride

Run	Temp., ° K.	Total Pressure, Mm. Hg.	$\%N_2$	N_2 Pressure, Mm. Hg.
23	1761	6¼	0.06	0.00375
45	1778	6¼	. . .	. . .
29	1822	13¼	0.44	0.0572
40	1847	15½	0.96	0.1488
105	1878	21½	0.20	0.0430
50	1892	26½	0.05	0.0130
44	1914	28½	0.20	0.0570
34	1911	31¾	0.52	0.1651
57	1939	38¾	0.27	0.1046
52	1952	52¼	3.42	1.787

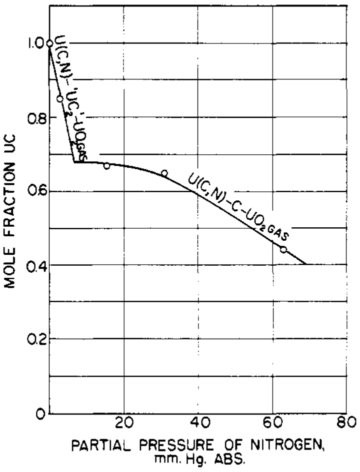

Figure 3. Composition of the U(C,N) phase *vs*. the partial pressure of nitrogen at 1878° K.

In their study of the carbon-nitrogen-uranium system, Austin and Gerds (*1*) found that the solubility of nitrogen in uranium dicarbide is negligible. One would, therefore, expect the solubility of oxygen to also be small. This phase can, however, contain excess uranium. Wilson (*15*) indicates that the composition of the dicarbide phase saturated with uranium at 1800° C. is 65 atom % carbon. In view of this the activity of the dicarbide phase was taken as 0.95 ± 0.05 throughout the region investigated. This procedure does not reflect the increasing uranium accommodation with temperature, but this omission does not affect appreciably the calculated values of the thermodynamic functions reported in the next subsection.

Determination of Gibbs Free Energies of Reaction. Utilizing the expressions for carbon monoxide equilibrium pressures of Equations 4 and 5 and the activity values estimated in the previous subsection, analytical expressions were formulated for the standard Gibbs free energies of reaction for

$$UO_2 + 4C \rightarrow UC_2 + 2CO \qquad (8)$$

$$UO_2 + 3UC_2 \rightarrow 4UC = 2CO \qquad (9)$$

These expressions are:

$$\Delta G^\circ_T = 164{,}500 - 74.23T \pm 1{,}200 \text{ cal./gram mole} \qquad (10)$$

$$\Delta G^\circ_T = 152{,}200 - 65.42T \pm 1{,}500 \text{ cal./gram mole} \qquad (11)$$

These expressions are valid over the range of temperatures studied in this work. The uncertainties in the values of free energies of reaction are based on calculated values of twice the standard deviation of free energy values at selected temperatures in the range studied. The standard deviations were calculated from previously determined values of standard deviations in $\log_{10} p_{CO}$ and estimated standard deviations in activity values using the equation for propagation of error:

$$R^2 = \sum^{i} (\partial Q/\partial q_i)^2 r_i \qquad (12)$$

In this expressions, Q is a function of independently measured variables of which q_i is the ith. R and r_i are the probable errors of Q and q_i, respectively.

Twice the standard deviation of the carbide activity values was assumed to be 0.05. Standard deviations of selected values of $\log_{10} p_{CO}$ were calculated in a manner analogous to that outlined bv Beers (*2*), modified to take into account unequal weights assigned to the measured values of $\log_{10} p_{CO}$. Weighting of these values was done on the basis that equal precisions in p_{CO} correspond to precisions in $\log_{10} p_{CO}$ varying with p_{CO}. The proper criterion for weighting of measured values is that the weights be inversely proportional to the squares of the probable errors (*11*). Using this criterion and Equation 12 it follows the weight factor, w, to be assigned to measured values in $\log_{10} p_{CO}$ is

$$w(\log_{10} p_{CO}) = K p_{CO}^2 \qquad (13)$$

K is a proportionality constant.

Utilizing Equations 10 and 11, similar expressions were calculated for the reactions

$$UO_2 + 3C \rightarrow UC + 2CO \qquad (14)$$

$$UC + C \rightarrow UC_2 \qquad (15)$$

These expressions are:

$$\Delta G_T^\circ = 161{,}400 - 72.03T \pm 900 \text{ cal./gram mole} \qquad (16)$$

$$\Delta G_T^\circ = 3100 - 2.20T \pm 1350 \text{ cal./gram mole} \qquad (17)$$

Utilizing expressions for the standard Gibbs free energies of formation of carbon monoxide and uranium dioxide along with Equations 10 and 16 one can formulate expressions for the free energies of formation of uranium monocarbide and uranium dicarbide.

For the reaction

$$2C + O_2 \rightarrow 2CO \qquad (18)$$

Kubaschewski and Evans (*8*) give the free energy of formation as

$$\Delta G_T^\circ = -53{,}400 - 41{,}90T \pm 2{,}000 \text{ cal.} (298 - 2500^\circ \text{ K.}) \qquad (19)$$

For the reaction

$$U(\alpha, \beta, \gamma, \lambda) + O_2(g) \rightarrow UO_2 \qquad (20)$$

Coughlin (*3*) expresses the free energy of formation as

$$\Delta G_T^\circ = -258{,}650 + 40.64T \pm 600 \text{ cal./gram} (298 - 1500^\circ \text{ K.}) \qquad (21)$$

Since the expression of Equation 21 gives values of the free energy of formation of uranium dioxide within 600 calories of the experimentally determined values below 1500° K., it is considered sound to use the expression at temperatures up to 2000° K. to give values accurate to 1000 calories.

Utilizing Equations 10, 16, 19, and 21, expressions were calculated for the standard Gibbs free energies of formation of uranium monocarbide and uranium dicarbide. For the reactions:

$$U(l) + C \rightarrow UC \qquad (22)$$

$$U(l) + 2C \rightarrow UC_2 \qquad (23)$$

the calculated free energies of formation are:

$$\Delta G_T^\circ = -43{,}850 + 10.51T \pm 2{,}400 \text{ cal./gram mole} (1700 - 1950^\circ \text{ K.}) \qquad (24)$$

$$\Delta G_T^\circ = -40{,}705 + 8.31T \pm 2{,}400 \text{ cal./gram mole} (1700 - 1950^\circ \text{ K.}) \qquad (25)$$

These expressions should be compared with those reported by Grieveson (*4*).

$$\Delta G_T^\circ = -25{,}200 + 3.6T (1723 - 1823^\circ \text{ K.}) \qquad (26)$$

$$\Delta G_T^\circ = -32{,}610 + 3.6T (2001 - 2071^\circ \text{ K.}) \qquad (27)$$

Grieveson obtained Equation 27 by measuring the effusion of uranium vapor from a graphite Knudsen cell containing solid uranium dicarbide. He obtained Equation 26 by equilibrating monocarbide-dicarbide mixtures with gold-uranium alloy beads, measuring the effusion of gold vapor from a graphite Knudsen cell, then integrating the Gibbs-Duhem equation to obtain the activity of solid uranium in equilibrium with the carbide mixture. The linear expressions of Grieveson (Equations 26 and 27) have been plotted in Figure 4 along with the expressions formulated in this work, Equations 24 and 25. Agreement of values for the free energy of formation of uranium dicarbide is fairly good. The expressions for the free energy of formation of uranium monocarbide yield values that differ by over 5000 cal. per gram mole between 1700° and 1900° K. Grieveson's results indicate that the free energy of reaction for Equation 15 is −7410 cal. per gram mole throughout the temperature range of 1700° to 1900° K. Based on this figure it would be necessary to reduce the activity of the monocarbide to the value of 0.13 equilibrate the monocarbide and the graphite with the uranium dicarbide. On the other hand, using Equation 17 the activity of the monocarbide in equilibrium with graphite and uranium dicarbide at 1875° K. would be 0.76. This value is more in line with the results of runs 101 to 105, shown in Table III and Figure 3.

The data of Table III were used to evaluate the free energy of formation of uranium mononitride at 1878° K. This was accomplished by determining the free energy of reaction for

$$UC + 0.5N_2 \rightarrow UN + C \qquad (28)$$

$$2UC + 0.5N_2 \rightarrow UN + UC_2 \qquad (29)$$

using the relations:

$$\Delta G_{1878}^\circ = -RT \ln(a_{UN}/a_{UC} p_{N_2}^{0.5}) \qquad (30)$$

$$\Delta G_{1878}^\circ = -RT \ln(a_{UN} a_{UC_2}/a_{UC_2} p_{N_2}^{0.5}) \qquad (31)$$

In using Equations 30 and 31 the activity was taken to be the mole fraction. Estimated uncertainties in the various measured quantities were used in Equation 12 to calculate the propagation of error in the free energies of reaction. The value determined for the free energy of formation of the mononitride from nitrogen gas and liquid uranium at 1878° K. was −28,200 ± 2500 cal. The determination of this figure is summarized in Table VI. The final figure is the average of the values from runs 101, 102, and 103.

PHASE EQUILIBRIA INTERPRETATIONS

Effect of Nitrogen. Small amounts of uranium mononitride were present in uranium monocarbide equilibrium phases due to the presence of nitrogen in the gas phase. This condition is a source of error in carbon monoxide equilibrium pressures measured for equilibria in the ternary system involving uranium monocarbide, because of the lowering of the monocarbide activity due to the presence of nitrogen in that phase. For the equilibria

$$UO_2 + 3UC_2 = 4UC + 2CO \qquad (32)$$

the equilibrium constant K_T is

$$K_T = (a_{UC}^4 p_{CO_2}/a_{UC_2}^3) \qquad (33)$$

Consequently the carbon monoxide equilibrium pressure is very sensitive to the presence of nitrogen in the monocarbide phase; the presence of 5 mole % uranium mononitride in this phase would result in an error in the observed carbon monoxide equilibrium pressure of about 10%. Based on considerations developed earlier it is concluded that the presence of nitrogen in the gas phase could have caused the carbon monoxide equilibrium pressures measured in runs 23, 45, 29, 40, and 52 to be in error by as much as 10% and other runs involving the monocarbide phase to be in error by as much as 5%.

No appreciable error is considered to have occurred in the equilibria of Equation 2 due to the presence of nitrogen in the gas phase. This contention is based on the

Table VI. Summary of Calculations Made to Determine Free Energy of Formation of Uranium Mononitride at 1878° K.

Run	a_{UC}	a_{UN}	p_{N_2} Atm.	K_{1878}	ΔG^0_{1878}
101	0.65 ± 0.05	0.35 ± 0.05	0.0412 ± 0.002	2.65 ± 0.44	−3,635 ± 619
102	0.45 ± 0.05	0.55 ± 0.05	0.0831 ± 0.002	2.84 ± 0.41	−3,894 ± 538
103	0.67 ± 0.05	0.33 ± 0.05	0.0198 ± 0.002	3.49 ± 0.61	−4,663 ± 652
104	0.85 ± 0.05	0.15 ± 0.05	0.0041 ± 0.001	3.08 ± 1.16	−4,197 ± 1405

Run	ΔG^0_{1878} for $U(l) + \frac{1}{2} N_2 = UN$
101	−27,800 ± 2,500
102	−28,000 ± 2,500
103	−28,800 ± 2,500
104	−27,300 ± 4,400

For $U\ (1) + C = UC$; $\Delta G_{1878} = -24{,}150 \pm 2400$ cal.
For $U\ (1) + UC_2 = 2UC$: $\Delta G_{1878} = -23{,}130 \pm 4150$ cal.

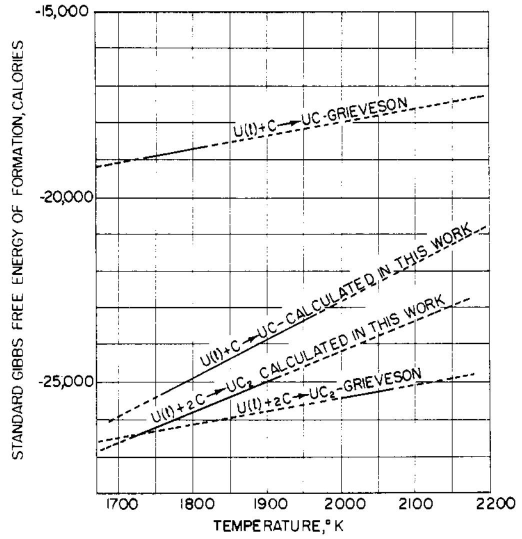

Figure 4. Standard Gibbs free energies of formation of uranium monocarbide and uranium dicarbide as a function of temperature

findings of Austin and Gerds (*1*) that the solubility of nitrogen in uranium dicarbide is negligible. The data of Table III indicate, however, that when large amounts, greater than 30% of nitrogen, are present in equilibrium with the gas phase, the monocarbide phase rather than the dicarbide phase exists in equilibrium with mixtures of uranium dioxide and graphite. This is a result of the lowering of the monocarbide activity, and the observed data of runs 101, 102, and 103 are consistent with Equation 17 in this respect.

Compatibility of Observations. Mallett, Gerds, and Vaughn (*9*) and Wilson (*15*) have reported that subjecting mixtures of uranium monocarbide and uranium dicarbide to stress causes uranium sesquicarbide to form. No attempt was made in this study to stress the solid phases involved. Consequently the equilibrium:

$$UO_2 + 3'UC_2' = 4'UC' + 2CO \qquad (3)$$

can be considered as quasistable even though it appears plausible that the equilibria:

$$UO_2 + 7UC_2 = 4U_2C_3 + 2CO \qquad (34)$$

$$UO_2 + 3U_2C_3 = 7UC + 2CO \qquad (35)$$

may be stable univariant equilibria in the system carbon-oxygen-uranium.

Other Phase Relations. The data of the common logarithm of the carbon monoxide equilibrium pressure *vs.* the reciprocal of the absolute temperature for Equations 2 and 3 indicate the existence of an invariant equilibrium among the five phases involved in these equilibria. The temperature and pressure of this equilibrium predicted by extrapolating the linear relations in log p_{CO} and $1/T$ are 1445° and 0.045 mm. of mercury absolute. Associated with this invariant equilibrium are five univariant equilibria among the five possible sets of four of the five phases: uranium dioxide, graphite, uranium dicarbide, uranium monocarbide, and carbon monoxide.

From this study certain features of the carbon-nitrogen-oxygen-uranium phase diagram can also be predicted. These features involve four phase equilibria among uranium dioxide, graphite, uranium dicarbide, solid solutions of uranium monocarbide and uranium mononitride, and a gas phase of nitrogen and carbon monoxide. Since four components are involved, these four phase equilibria are divariant. The nature of these divariant equilibria are shown in Figure 5, a three-dimensional graph qualitatively relating pressure, temperature, and composition of the gas phase. The divariant equilibria appear as surfaces that have a common intersection which is a space curve representing the univariant equilibria among the five phases in question. One of the termini of this curve is the invariant equilibrium among the five phases in the ternary system carbon-oxygen-uranium. This terminus lies on the face for which the per cent nitrogen in the gas phase is zero. This face is the *p*-*T* diagram for the carbon-oxygen-uranium system.

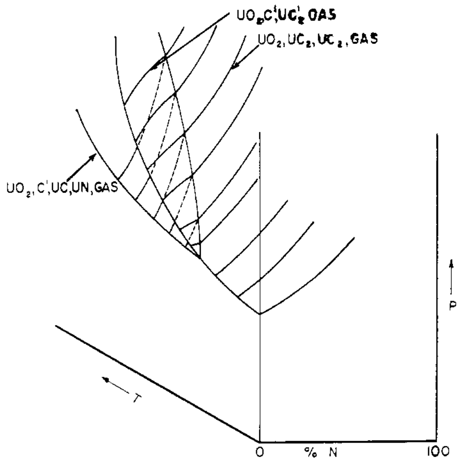

Figure 5. Composition of the gas phase involved in various equilibria in the system carbon-oxygen-nitrogen-uranium as function of temperature and pressure

NOMENCLATURE

a = thermodynamic activity
K = equilibrium constant
N = mole fraction
Q = independently measured variable
p = pressure, atm.
q_i = ith measured independent variable
R = probable error in Q
r_i = probable error in q_i measurement
T = temperature, Kelvin
w = weight factor
ΔG° = Gibbs free energy change, cal./gram mole
θ = Bragg diffraction angle
ϕ = complement of Bragg diffraction angle

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Solubility and Equilibrium Data of Phenol–Water–Isoamyl Acetate and Phenol–Water–Methyl Isobutyl Ketone Systems at 30° C.

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SOLUBILITY and equilibrium data for the system phenol-water-*n*-butyl acetate (system 1) at 30° C. were reported in a previous communication (*4*). The present article deals with the systems phenol-water-isoamyl acetate and phenol-water-methyl isobutyl ketone at 30° C. As in the previous system, the solubility data of the ternary systems were determined first, followed by the determination of the equilibrium data.

MATERIALS

Phenol. Phenol was distilled in a glass Quick-fit distillation apparatus. The fraction obtained at the boiling point corresponding to 181.7° C. at 760 mm. having a purity of 99.93% was used.

Water. Pure distilled water was used.

Isoamyl Acetate. Isoamyl acetate was fractionated twice in Tower's fractionating column and the fraction within 2° C, of the boiling point corresponding to 140.1 - 42.1° C. at 760 mm. was used.

Methyl Isobutyl Ketone (MIBK). Commercial methyl isobutyl ketone was similarly fractionated and the fraction corresponding to 113.9 - 15.5° C. at 760 mm. was used.

Solvents Used

	Purified Sample	Lit. Value	Ref.
Isoamyl acetate			
Ester content, %	100	...	...
Specific gravity, 24/4° C.	0.8670	0.8664	(*3*)
Refractive index, 20° C.	1.4005	1.4005	(*3*)
Methyl isobutyl ketone			
Ketone content, %	99.1–99.5	...	...
Specific gravity, 20/20° C.	0.7973	0.8042	(*3*)
Refractive index, 20° C.	1.3960	1.3958	(*3*)

EXPERIMENTAL PROCEDURE

Solubility data were obtained by the turbidity end point method as described by Othmer, White, and Trueger (*6*). The experimental details were similar to those of the earlier system (*4*). Tables I and II give the solubility data in weight fractions for systems phenol-water-isoamyl acetate (system 2) and phenol-water-methyl isobutyl ketone (system 3), respectively. Mutual solubilities of