Thermodynamic equilibrium calculations on the system uranium-carbon-fluorine

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Therefore, once we can estimate the values for $V_1$, $V_2$, and $\eta_2$ at the desired temperature by appropriate methods (see, e.g., Reid et al., 1976), the diffusion coefficient $D_{ij}$ may be calculated with fairly good accuracy.

### Nomenclature

- $A_i$ = association parameter in eq 7
- $D_{ij}$ = diffusion coefficient, cm$^2$ s$^{-1}$
- $D_{i}$ = diffusion coefficient at infinite dilution, cm$^2$ s$^{-1}$
- $I_1$ = interaction parameter in eq 7
- $K_1$ and $K_2$ = constants in eq 4 to 6
- $k$ = Boltzmann constant
- $n_i$ = number of carbon atoms in paraffin hydrocarbons
- $N_A$ = Avogadro number
- $Q_i$ = quantum correction factor in eq 7
- $r_i$ = molecular radius, cm
- $S_1$ and $S_2$ = shape factor in eq 7
- $T$ = temperature, K
- $V_i$ = molar volume of solute, cm$^3$ mol$^{-1}$
- $V_2$ = molar volume of solvent, cm$^3$ mol$^{-1}$

**Greek Letters**

- $\Lambda^e$ = de Boer parameter for quantum correction
- $\eta_2$ = viscosity of solvent, cP

### Thermodynamic Equilibrium Calculations on the System Uranium–Carbon–Fluorine

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The equilibrium composition of gaseous mixtures consisting of UF$_6$ and carbon–fluorine compounds in a graphite vessel is calculated for temperatures ranging from 800 to 2800 K and pressures from 1 to 25 atm. It appears that UF$_6$ is not compatible with graphite at high temperatures and produces large quantities of CF$_4$ in the nonequilibrium phase.

### Introduction

In order to increase the efficiency of our energy conversion systems, a higher reactor temperature is required (2000 to 2500 K). This temperature may be obtained in a gas-core nuclear reactor based on fission of UF$_6$*(Thom et al., 1974). The advantage of such a reactor, in comparison with other types, is that the fuel and the waste products can be recycled. The problem is, however, to design a reactor wall that remains stable in contact with UF$_6$ up to the temperatures concerned (Kistemaker and Nieskens, 1978).

The following calculations are carried out to check whether a graphite wall meets these requirements at temperatures from 800 to 2800 K at pressures from 1 to 25 atm. The gaseous species involved are U, UF$_6$, UF$_4$, UF$_3$, CF$_4$, UF$_2$, UF, UF$_2$, CF$_2$, CF, CF$_2$, and C$_2$F$_6$. Moreover, we investigated the condensation of U, UF$_6$, UF$_4$, UC, UC$_2$, and U$_2$C$_3$.

### Theoretical

To calculate the equilibrium composition, a computer program is developed whereby we used a variant of Eriksson’s SOLGAS MIX program (1975). Eriksson minimizes the function

$$G = \sum_{i=1}^{m} \sum_{j=1}^{p} \mu_i n_i^{\alpha} + \sum_{j=1}^{r} \lambda_j (a_j n_{j}^{\alpha} - b_j)$$

(1)

where $G$ is the Gibbs free energy of the system, $\mu_i^{\alpha}$ is the chemical potential of compound $i$ in phase $\alpha$ ($i = 1, ..., m; \alpha = 1, ..., p$), $n_i^{\alpha}$ is the number of moles of compound $i$ in phase $\alpha$, $\lambda_j$ is the Lagrangian multiplier of element $j$ ($j = 1, ..., r$), $a_j$ is the number of atoms of the $j$th element in compound $i$, and $b_j$ is the total number of gram atoms of element $j$ in the system. So the Gibbs free energy of the system is minimized under the restraint of conservation of mass of each element present.

In order to handle heterogeneous systems, a modification suggested by Chermin (1976) is used introducing also a Lagrangian multiplier for each phase. In this respect our method deviates from Eriksson’s program (1975). The function to be minimized is then

$$\Gamma = \sum_{i=1}^{m} \sum_{j=1}^{p} n_i(g_i^{\alpha} + \ln n_i^{\alpha} - \ln m_{j}^{n+i}) + \sum_{j=1}^{r} \lambda_j \sum_{j=1}^{m} a_j (n_j^{\alpha} - b_j) + \sum_{j=1}^{m} \lambda_j (\sum_{i=1}^{m} n_i^{\alpha} - m_{j}^{n+i})$$

(2)

where $g_i^{\alpha} = \mu_i^{\alpha}(p,T)/RT$, $p$ = pressure, $T$ = temperature,
$R$ is the gas constant, $n_{m+1}^{a}$ is the total number of moles in phase $\alpha$, and $\lambda_{r+1}$ is the Lagrangian multiplier for phase $\alpha$, numbered from ($r+1$) onward to avoid double parameters $\lambda_{j}$. The equilibrium condition is $\delta\Gamma = 0$, which can be converted to the following equations (since the variations of $\delta n_{i}$ and $\delta \lambda_{j}$ are independent)

$$g^{a} + 1 + \ln n_{i}^{a} + \sum_{j=1}^{r} \lambda_{aj} + \lambda_{r+1} = 0$$

$$1 + \ln n_{m+1}^{a} + \lambda_{r+1} = 0 \quad i = 1,...,m; \quad \alpha = 1,...,p \tag{3}$$

$$\sum_{i=1}^{m} \sum_{j=1}^{r} a_{ij}n_{i} - b_{j} = 0 \quad j = 1,...,r$$

$$\sum_{i=1}^{m} n_{i}^{a} - n_{m+1}^{a} = 0 \quad \alpha = 1,...,p$$

The solution of this set of equations is discussed in Appendix A. This method enables us to exclude kinetically hampered reactions—e.g., carbon formation in benzene containing systems—from the calculations, because we introduce only the total number of moles of each element; Eriksson (1975), on the other hand, introduces the elements as such in their chosen reference state.

It is assumed that the gas phase behaves ideally; deviations from ideal behavior are supposed to influence the results of the calculations only to a minor degree in the temperature and pressure ranges concerned. The condensed phases are considered to be mutually insoluble. Then the set of equations (3) becomes linearly dependent if too many pure phases are introduced (Okulov and Semanov, 1974). This problem is solved by applying the condensation criterion derived by Okulov and Semanov (1974) for substances capable of being condensed

$$\sum_{j=1}^{r} a_{ij}(\mu_{j}^{c}(p,T) + RT \ln n_{j} - RT \ln n_{m+1}^{c}) - \mu_{i}^{c}(p,T) \geq 0 \tag{4}$$

where $\mu_{i}^{c}$ is the chemical potential of the condensed compound, $\mu_{j}^{c}$ is the chemical potential of element $j$ in the gas phase, $n_{j}$ is the number of gram atoms of element $j$ in the gas phase, and $n_{m+1}^{c}$ is the total number of gram atoms in the gas phase. Since we are interested in the behavior of a graphite wall it is assumed that graphite is in equilibrium with gaseous carbon.

**Basic Data**

**Gaseous Species.** For the carbon, fluorine, and carbon-fluorine species, thermodynamic data are taken from the JANAF tables (1971). Concerning uranium, Hultgren's containing systems—from the calculations, because we

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_{298}^{o}$</th>
<th>$\Delta G_{298}^{o}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF$_{6}$</td>
<td>-505</td>
<td>-485</td>
</tr>
<tr>
<td>UF$_{5}$</td>
<td>-485</td>
<td>-460</td>
</tr>
<tr>
<td>Hildenbrand</td>
<td>-410.8</td>
<td>-436</td>
</tr>
</tbody>
</table>

Table I. Thermodynamic Data of U-F Compounds (kcal/mol)

Figure 1. The equilibrium of UF$_{6}$ with graphite at 1 atm, using data set II. The dotted lines represent data calculated assuming a homogeneous gas phase at $T < T_{cg}$; then the pressure of UF$_{6}$ exceeds the vapor pressure of condensed UF$_{6}$. All compounds having a mole fraction below 10$^{-4}$ are omitted.

Because we think data set II to be the more reliable one, we performed calculations using data set II. To show the dependency of the system with respect to changes in data, we also calculated one equilibrium composition employing data set I. The results for the equilibrium of UF$_{6}$ with graphite are shown in Figures 1 to 3. The difference between Figures 2a and 2b is remarkable, although the enthalpies of formation of 298 K of gaseous UF$_{6}$ and UF$_{5}$ deviate only about 20 kcal/mol. UF$_{6}$ disappears completely if data set II is used. At temperatures above $T_{cg}$ a homogeneous gas phase is in equilibrium with graphite. Assuming a homogeneous gas phase at temperatures below $T_{cg}$ the partial pressure of UF$_{6}$ exceeds the vapor pressure of condensed UF$_{6}$ (dotted lines), so the calculation is repeated allowing for condensed UF$_{6}$, assuming thermodynamic equilibrium between condensed and gaseous UF$_{6}$. Condensed UF$_{6}$ and graphite are considered to be pure phases (solid lines).

It is obvious that at high temperatures all UF$_{6}$ is converted and that graphite reacts with the fluorine liberated. If, however, the feed consists of UF$_{6}$ the graphite wall may be stable, provided that no lower U-F compound (e.g., UF$_{5}$) is formed.

In order to check whether the graphite wall might be stabilized by introducing a feed consisting of UF$_{6}$ and CF$_{4}$. C$_{2}$F$_{6}$ or C$_{3}$F$_{8}$, we calculated the equilibria for different feed concentrations, using both data sets. The results at $T = 2000$ K and $p = 1$ atm are shown in Figure 4.

It can be concluded that it is theoretically possible to stabilize graphite in contact with a gas containing UF$_{6}$ but
only at the expense of converting an unsaturated carbon–fluorine compound into CF₄. Moreover these unsaturated carbon–fluorine compounds are thermodynamically unstable.

Figure 2. a, The equilibrium of UF₆ with graphite at 10 atm, using data set II; b, the equilibrium of UF₆ with graphite at 10 atm, using data set I. See Figure 1 for the meaning of the dotted lines.

Figure 3. The equilibrium of UF₆ with graphite at 25 atm, using data set II. See Figure 1 for the meaning of the dotted lines.

Finally, we investigated the possibility of condensation of the uranium carbides. In the temperature range where data on the vapor pressures in the U–C system are available (2000–2500 K (Holley and Storms, 1967; and Storms, 1967)), the uranium partial pressures obtained in our calculations are several orders of magnitude lower than those corresponding to UC, UC₂, or U₂C₃ formation. (About one year after we had finished this paper we gained access to more complete data in a paper by Tetenbaum et al. (1975) and in a publication from IAEA, Vienna (1976). These data do not essentially change our results.) It should be noted that the carbon partial pressures are the highest possible ones, because we assumed that graphite is in equilibrium with gaseous carbon. Outside this temperature range (2000–2500 K) we employed the condensation criterion (4). Using the data mentioned above, it can be concluded that no uranium carbide condenses. However, we are not sure if these data are reliable, but even when the Gibbs free energies of these compounds are varied substantially (more than 100%), no uranium carbide condenses according to the condensation criterion.

Neither uranium nor UF₅ exceed their respective vapor pressures.

Conclusion

UF₆ as material for a gas-core reactor is not compatible with graphite as wall material at high temperatures. A stable graphite wall may be obtained if the uranium is introduced as UF₄, e.g., as an aerosol in CF₄ as a carrier gas.

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Appendix A

The Solution of Eq 3. In order to reduce the number of equations, the iteration process will be described for one phase. Substituting \( n_i = \exp(y_i) \) (Storey and Van Zeggeren 1964) we obtain
\[ g_i + 1 + y_i + \sum_{j=1}^m a_{ij} \lambda_j + \lambda_{m+1} = 0 \]  
\[ 1 + y_{m+1} + \lambda_{m+1} = 0 \quad i = 1, \ldots, m \]  
\[ m \sum_{i=1}^m a_{ij} \exp(y_i) - b_j = 0 \]  
\[ \sum_{i=1}^m \exp(y_i) - \exp(y_{m+1}) = 0 \quad j = 1, \ldots, r \]  

(In this way negative concentrations are avoided, which pose an additional problem in Eriksson’s (1973, 1975) program.)

Let \( y^o, \lambda^o \) be an initial estimate. Using Newton’s method, we obtain a correction on the initial estimate

\[ \Delta y_i + \sum_{j=1}^m a_{ij} \Delta \lambda_j + \Delta \lambda_{m+1} = -\phi^o_i \]  
\[ \Delta y_{m+1} + \Delta \lambda_{m+1} = -\phi^o_{m+1} \quad i = 1, \ldots, m \]  
\[ m \sum_{i=1}^m a_{ij} n_i^o \Delta y_i = -\psi^o_j \]  
\[ \sum_{i=1}^m n_i^o \Delta y_i - n_{m+1}^o \Delta y_{m+1} = -\psi^o_{m+1} \quad j = 1, \ldots, r \]

where \( n_i^o = \exp(y_i^o), \phi^o_i \) and \( \psi^o_j \) are the values of the left-hand side of eq A-1a and A-1b, respectively, substituting the initial estimate \( y^o, \lambda^o \), and \( \Delta y_i \) and \( \Delta \lambda_i \) are the corrections on the estimated values of \( y^o_i \) and \( \lambda^o_i \), respectively. Using eq A-2a the \( \Delta y_i \) are expressed in the \( \Delta \lambda_i \). Substituting the result in (A-2b) gives

\[ R \Delta \lambda = q \]

where

\[ R_{kl} = \sum_{i=1}^m a_{ik} n_i^o a_{jl} - \delta_{k}^{m+1} n_{m+1}^o \]

\[ q_k = \psi_k^o - \sum_{i=1}^m a_{ik} n_i^o \phi_i^o + \delta_{k}^{m+1} n_{m+1}^o \phi_{m+1}^o \]

\[ a_{ik}^{m+1} = 1 \]

and \( \delta_{k}^{m+1} \) is the Kronecker symbol.

From the corrections on the Lagrangian multipliers, the corrections on the concentration of each compound can be calculated. This iteration process can be continued until convergence is achieved.

In most cases the number of substances is larger than the number of elements (i.e., \( m > r + 2p \)). Thus the number of equations that have to be solved simultaneously is much smaller in the \( x \) space than in the \( y \) space. In this way computer time is saved.

**Appendix B**

The thermodynamic functions of UF\(_6\) and UF\(_4\) as calculated from literature data are as follows.

**UF\(_6\)** Using the data proposed by Rand and Kubaschewski (1963) \( (\Delta H^0_{\text{298}}(\text{UF}_6) \text{(cond)}) = -488 \text{kcal/mol and } S^0_{\text{298}} = 45.0 \text{ cal/mol K}) \) and the vapor pressure measurements of Wolf et al. (1965), we obtain \( \Delta H^0_{\text{298}}(\text{UF}_6) \text{(g)}) \)

\[ \text{= -460 kcal/mol}. \]

**UF\(_4\)** Dworkin (1972) has measured the specific heat of condensed UF\(_4\) from 298 to 1400 K and has calculated some thermodynamic functions. Using his data together with \( \Delta C^0_{\text{293}}(\text{UF}_4) \text{(cond)}) = -394.0 \text{kcal/mol} \) (from emf measurements by Tanaka et al., 1971), we calculate \( \Delta H^0_{\text{298}}(\text{UF}_4) \text{(cond)}) = -454 \text{kcal/mol, in good agreement with Rand and Kubaschewski (1963) (-450} \pm 5 \text{ kcal/mol). Hence we obtain for } \text{UF}_6 \text{(g}): \Delta H^0_{\text{298}} = -386, \Delta C^0_{\text{298}} = -374 \text{ and } \Delta C^0_{\text{1700}} = -337 \text{ kcal/mol} \text{ at the boiling point = 1700 K}. \Delta C^0_{\text{298}} \text{(cond)} = \Delta C^0_{\text{298}}(\text{g}) \text{ and } \Delta C^0_{\text{298}}(\text{cond}) \text{ can be calculated from the data of Dworkin (1972) by extrapolation. To calculate the Gibbs free energy at other temperatures a linear relationship of } \Delta G \text{ vs. } T \text{ is assumed.}

**Literature Cited**


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