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 $D_{12}$ may be calculated with fairly good accuracy.

**Nomenclature**

$A_s =$ association parameter in eq 7

$D_{12}$ = interdiffusion coefficient, cm$^2$ s$^{-1}$

$D_{12}^*$ = diffusion coefficient at infinite dilution, cm$^2$ s$^{-1}$

$D_{self}$ = self-diffusion coefficient, cm$^2$ s$^{-1}$

$I_1 =$ interaction parameter in eq 7

$k =$ Boltzmann constant

$n =$ number of carbon atoms in paraffin hydrocarbons

$N_m =$ Avogadro number

$q_2 =$ quantum correction factor in eq 7

$r_1 =$ molecular radius, cm

$S_1$ and $S_2 =$ shape factor in eq 7

$T =$ temperature, K

$V_1 =$ molar volume of solute, cm$^3$ mol$^{-1}$

$V_2 =$ molar volume of solvent, cm$^3$ mol$^{-1}$

**Greek Letters**

$\alpha =$ de Boer parameter for quantum correction

$\eta_2 =$ viscosity of solvent, cP

$A*$ = de Boer parameter for quantum correction

$\mu_i =$ chemical potential of compound $i$, and

$\lambda_i =$ Lagrangian multiplier of element $i$, and

$n_i =$ the number of atoms of the jth element in

$\rho =$ the number of moles of compound $i$ in phase $j$

$L = \text{total number of gram atoms of each element present.}$

**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 from the reactor 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$, UF_2$, UF$_3$, C$_4$, C$_5$, C$_6$, F$_2$, F$_3$, CF, CF$_2$, CF$_3$, CF$_4$, C$_2$F$_2$, C$_2$F$_3$, and C$_2$F$_6$. Moreover, we investigated the condensation of U, UF$_6$, UF$, UF_2$, UF$_3$, UC, UC$_2$, and U$_2$C$_3$.

**Theoretical**

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

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

where $G$ is the Gibbs free energy of the system, $\mu_i^a$ is the chemical potential of compound $i$ in phase $\alpha$ ($\alpha = 1, ..., m$; $\alpha = 1, ..., p$), $n_i^a$ 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

$$\Gamma = \sum_{j=1}^{r} \sum_{i=1}^{m} n_i (g_i^a + \ln n_i^a - \ln n_{m+1}^a) + \sum_{j=1}^{r} \lambda_j \sum_{i=1}^{m} a_j (n_i^a - b_j) + \sum_{i=1}^{m} \lambda_{i+1} (\sum_{j=1}^{r} n_i^a - n_{m+1}^a)$$

where $g_i^a = \mu_i^a(p,T)/RT$, $p =$ pressure, $T =$ temperature.

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**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.

**Literature Cited**


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**Supplementary Material Available**: Table II showing results of the experimental test of eq 7, Wilke-Chang and Tyn-Calus correlations and sample calculations illustrating each step of the calculation of $D_{12}$ with eq 7 (5 pages). Ordering information is given on any current masthead page.
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

\[
\sum_{j=1}^{r} a_{ij} \mu^f_i(p, T) + RT \ln n_j^g - RT \ln n_{m+1,j}^g - \mu^f_j(p, T) \geq 0
\]

where \(\mu^f_i\) is the chemical potential of the condensed compound \(i\), \(\mu^f_j\) is the chemical potential of element \(j\) in the gas phase, \(n_j^g\) is the number of gram atoms of element \(j\) in the gas phase, and \(n_{m+1,j}\) 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 data (1963) are used; for UF6 we employed the data calculated by Hassan and Deese (1974). Data for UF3 and UF4, however, are uncertain. The temperature dependency is calculated by Hassan and Deese (1974) from estimations based upon a semiempirical method developed by Tu-
manov et al. (1968, 1970). The largest uncertainty is introduced by the enthalpies of formation at 298 K (−366 and −440 kcal/mol for UF3 and UF4, respectively (Godnev and Sverdlin, 1966): data set I). These enthalpies are not very reliable. From other literature data (see Appendix B) we calculated −386 and −460 kcal/mol for UF4 and UF3, respectively (data set II). Table I indicates that the latter set agrees better with recent results of Hildenbrand (1977). For the U–F compounds UF3, UF2, and UF, no data are available.

Condensed Species. The Gibbs free energies of condensed UF3 and UF4 can be calculated from the Gibbs free energies of gaseous UF3 and UF4 and the vapor pressure formulas. Concerning UF4 (both solid and liquid)

\[
g_i^a = 1 + \ln n_i^a + \sum_{j=1}^{r} \lambda_i \alpha_j + \lambda_{r+1} = 0
\]

Figure 1. The equilibrium of UF4 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 UF4 exceeds the vapor pressure of condensed UF3. All compounds having a mole fraction below \(10^{-3}\) are omitted.

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

<table>
<thead>
<tr>
<th>Compound (g)</th>
<th>UF3(g)</th>
<th>UF4(g)</th>
<th>UF6(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta H_{298}^f)</td>
<td>-505</td>
<td>-440</td>
<td>-366</td>
</tr>
<tr>
<td>(\Delta G_{298}^f)</td>
<td>-410.8</td>
<td>-460.6</td>
<td>-377.8</td>
</tr>
</tbody>
</table>

Figure 2a and 2b is remarkable, although the enthalpies of formation at 298 K of gaseous UF4 and UF4 deviate only about 20 kcal/mol. UF6 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 UF4 exceeds the vapor pressure of condensed UF3 (dotted lines), so the calculation is repeated allowing for condensed UF3, assuming thermodynamic equilibrium between condensed and gaseous UF4.

Results

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 UF4 with graphite are shown in Figures 1 to 3. The difference between Figures 2a and 2b is remarkable, although the enthalpies of formation at 298 K of gaseous UF4 and UF4 deviate only about 20 kcal/mol. UF6 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 UF4 exceeds the vapor pressure of condensed UF3 (dotted lines), so the calculation is repeated allowing for condensed UF3, assuming thermodynamic equilibrium between condensed and gaseous UF4. Condensed UF4 and graphite are considered to be pure phases (solid lines).

It is obvious that at high temperatures all UF4 is converted and that graphite reacts with the fluorine liberated. If, however, the feed consists of UF4 the graphite wall may be stable, provided that no lower U–F compound (e.g., UF5) is formed.

In order to check whether the graphite wall might be stabilized by introducing a feed of UF6 and CF4, C2F2, or C3F2, 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 UF6, but
only at the expense of converting an unsaturated carbon–fluorine compound into CF₄. Moreover these unsaturated carbon–fluorine compounds are thermodynamically unstable.

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 UC₃ 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.

**Acknowledgment**

We thank Dr. A. J. H. Boerboom and Dr. H. A. G. Chermin for valuable discussions. This work is part of the research program of the Foundation for Fundamental Research on Matter (FOM) and was made possible by a special grant of the Dutch Organization for the Advancement of Pure Research (ZWO).

**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
\[ g_i + 1 + y_i + \sum_{j=1}^{r} a_{ij}\lambda_j + \lambda_{i+1} = 0 \]  \hspace{1cm} (A-1a)

\[ 1 + y_{m+1} + \lambda_{m+1} = 0 \quad i = 1, ..., m \]

\[ \sum_{i=1}^{m} a_{ij}\exp(y_i) - b_j = 0 \]  \hspace{1cm} (A-1b)

\[ \sum_{i=1}^{m} \exp(y_i) - \exp(y_{m+1}) = 0 \quad j = 1, ..., r \]

(Appendix B)

The thermodynamic functions of UF\(_3\) and UF\(_4\) as calculated from literature data are as follows.

UF\(_3\). Using the data proposed by Rand and Kubaschewski (1963) \((\Delta H_{298}^0(\text{UF}_3\text{cond})) = -488 \text{ kcal/mol}\) and \(S_{298}^0 = 45.0 \text{ cal/mol K}\) and the vapor pressure measurements of Wolf et al. (1965), we obtain \(\Delta H_{298}^0(\text{UF}_3\text{g})) = -460 \text{ kcal/mol}\).

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 \(\Delta C_{p,73}^0(\text{UF}_4\text{cond})) = -394.0 \text{ kcal/mol}\) (from emf measurements by Tanaka et al., 1971), we calculate \(\Delta H_{298}^0(\text{UF}_4\text{cond})) = -454 \text{ kcal/mol}\), in good agreement with Rand and Kubaschewski (1963) \((-450 \pm 5 \text{ kcal/mol}\)).

Hence we obtain for UF\(_4\)g): \(\Delta H_{298}^0 = -386, \Delta G_{298}^0 = -374\) and \(\Delta G_{1700}^r = -337 \text{ kcal/mol}\) (at the boiling point \(= 1700 \text{ K}\)). \(\Delta G_{298}^0(\text{cond}) = \Delta G_{298}^0(\text{g})\) and \(\Delta G_{298}^0(\text{cond})\) can be calculated from the data of Dworkin (1972) by extrapolation. To calculate the Gibbs free energy at other temperatures a linear relationship of \(\Delta G\) vs. \(T\) is assumed.

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Literature Cited


