

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 η_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_2 = association parameter in eq 7
 D_{12}° = interdiffusion coefficient, $\text{cm}^2 \text{s}^{-1}$
 D_{12} = diffusion coefficient at infinite dilution, $\text{cm}^2 \text{s}^{-1}$
 D_{self} = self-diffusion coefficient, $\text{cm}^2 \text{s}^{-1}$
 I_1 = interaction parameter in eq 7
 K_1 and K_2 = constants in eq 4 to 6
 k = Boltzmann constant
 n = number of carbon atoms in paraffin hydrocarbons
 N_{av} = Avogadro number
 Q_1 = 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, $\text{cm}^3 \text{mol}^{-1}$
 V_2 = molar volume of solvent, $\text{cm}^3 \text{mol}^{-1}$

Greek Letters

- Λ^* = de Boer parameter for quantum correction
 η_2 = viscosity of solvent, cP

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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.

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_5 , UF_4 , C_1 , C_2 , C_3 , C_4 , C_5 , F, F_2 , CF, CF_2 , CF_3 , CF_4 , C_2F_2 , C_2F_4 , and C_2F_6 . Moreover, we investigated the condensation of U, UF_5 , UF_4 , UC, UC_2 , and U_2C_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

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

where G is the Gibbs free energy of the system, μ_i^α is the chemical potential of compound i in phase α ($i = 1, \dots, m$; $\alpha = 1, \dots, p$), n_i^α is the number of moles of compound i in phase α , λ_j is the Lagrangian multiplier of element j ($j = 1, \dots, r$), a_{ij} 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

$$\Gamma = \sum_{i=1}^m \sum_{\alpha=1}^p n_i (g_i^\alpha + \ln n_i^\alpha - \ln n_{m+\alpha}^\alpha) + \sum_{j=1}^r \lambda_j \left(\sum_{i=1}^m \sum_{\alpha=1}^p a_{ij} n_i^\alpha - b_j \right) + \sum_{\alpha=1}^p \lambda_{r+\alpha} \left(\sum_{i=1}^m n_i^\alpha - n_{m+\alpha}^\alpha \right) \quad (2)$$

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

R is the gas constant, n_{m+1}^α is the total number of moles in phase α , and $\lambda_{r+\alpha}$ is the Lagrangian multiplier for phase α , numbered from $(r + 1)$ onward to avoid double parameters λ_j . The equilibrium condition is $\delta\Gamma = 0$, which can be converted to the following equations (since the variations of δn_i and $\delta \lambda_j$ are independent)

$$g_i^\alpha + 1 + \ln n_i^\alpha + \sum_{j=1}^r \lambda_j a_{ij} + \lambda_{r+\alpha} = 0$$

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

$$\sum_{i=1}^m \sum_{\alpha=1}^p a_{ij} n_i^\alpha - b_j = 0 \quad j = 1, \dots, r \quad (3)$$

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

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

$$\sum_{j=1}^r a_{ij} (\mu_j^g(p, T) + RT \ln n_j^g - RT \ln n_{m+1}^g) - \mu_i^c(p, T) \geq 0 \quad (4)$$

where μ_i^c is the chemical potential of the condensed compound i , μ_j^g 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}^g 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 UF_6 we employed the data calculated by Hassan and Deese (1974). Data for UF_5 and UF_4 , however, are uncertain. The temperature dependency is calculated by Hassan and Deese (1974) from estimations based upon a semiempirical method developed by Tumanov et al. (1968, 1970). The largest uncertainty is introduced by the enthalpies of formation at 298 K (−366 and −440 kcal/mol for UF_4 and UF_5 , 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 UF_4 and UF_5 , respectively (data set II). Table I indicates that the latter set agrees better with recent results of Hildenbrand (1977). For the U-F compounds UF_3 , UF_2 , and UF , no data are available.

Condensed Species. The Gibbs free energies of condensed UF_4 and UF_5 can be calculated from the Gibbs free energies of gaseous UF_4 and UF_5 and the vapor pressure formulas. Concerning UF_4 (both solid and liquid)

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

		$\text{UF}_6(\text{g})$	$\text{UF}_5(\text{g})$	$\text{UF}_4(\text{g})$
ΔH°_{298}	Set I	−505	−440	−366
	Set II	−505	−460	−386
	Hildenbrand (1977)	$−410.8 \pm 0.4$	$−460.6 \pm 3.4$	$−377.8 \pm 0.6$
ΔG°_{298}	Set I	−485	−420	−354
	Set II	−485	−440	−374

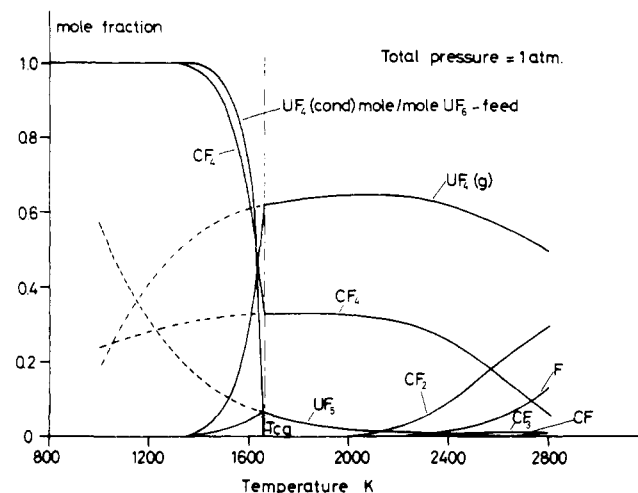


Figure 1. The equilibrium of UF_6 with graphite at 1 atm, using data set II. The dotted lines represent data calculated assuming a homogeneous gas phase at $T < T_{cg}$; then the pressure of UF_4 exceeds the vapor pressure of condensed UF_4 . All compounds having a mole fraction below 10^{-3} are omitted.

we used the vapor pressure formula from Rand and Kubaschewski (1963), and for UF_5 the vapor pressure measurements of Wolf et al. (1965). For UC and UC_2 , data are taken from Storms (1967); for U_2C_3 , from Holley and Storms (1967).

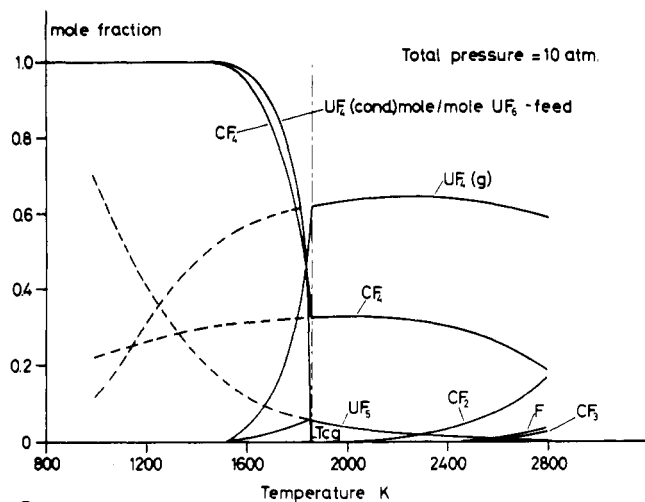
Results

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 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 at 298 K of gaseous UF_4 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_4 exceeds the vapor pressure of condensed UF_4 (dotted lines), so the calculation is repeated allowing for condensed UF_4 , assuming thermodynamic equilibrium between condensed and gaseous UF_4 . Condensed UF_4 and graphite are considered to be pure phases (solid lines).

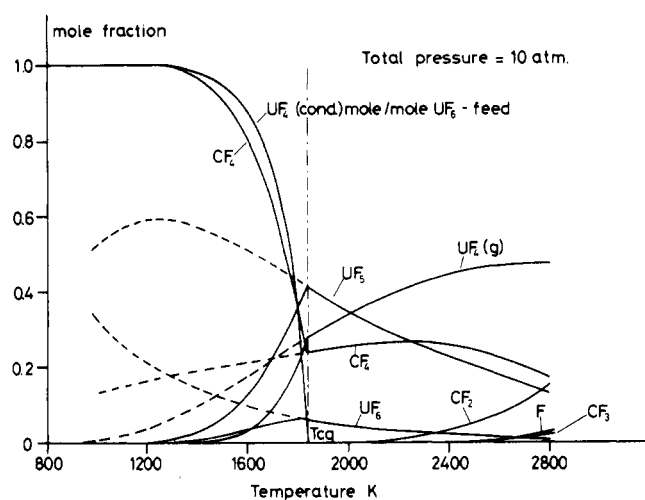
It is obvious that at high temperatures all UF_6 is converted and that graphite reacts with the fluorine liberated. If, however, the feed consists of UF_4 the graphite wall may be stable, provided that no lower U-F compound (e.g., UF_3) is formed.

In order to check whether the graphite wall might be stabilized by introducing a feed consisting of UF_6 and CF_4 , C_2F_2 , or C_2F_4 , 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



a



b

Figure 2. a, The equilibrium of UF_6 with graphite at 10 atm, using data set II; b, the equilibrium of UF_6 with graphite at 10 atm, using data set I. See Figure 1 for the meaning of the dotted lines.

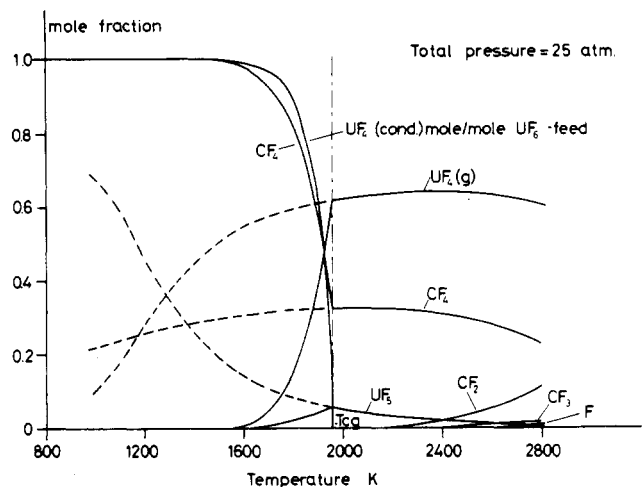


Figure 3. The equilibrium of UF_6 with graphite at 25 atm, using data set II. See Figure 1 for the meaning of the dotted lines.

only at the expense of converting an unsaturated carbon-fluorine compound into CF_4 . Moreover these unsaturated carbon-fluorine compounds are thermodynamically unstable.

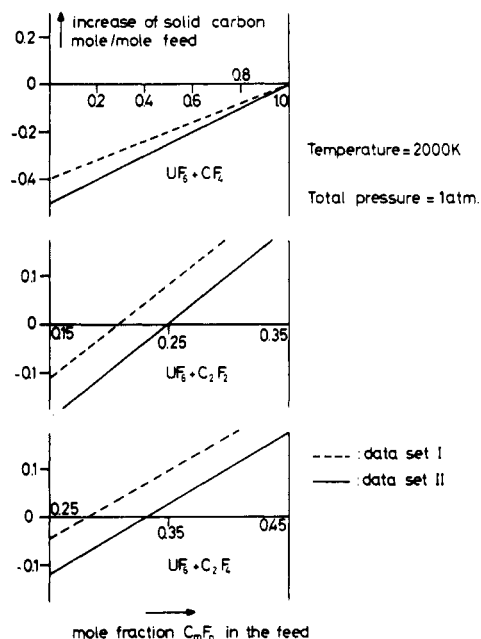


Figure 4. The stability of a graphite wall in equilibrium with a gas consisting of UF_6 and C_mF_n .

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, UC_2 , or U_2C_3 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 UF_5 exceed their respective vapor pressures.

Conclusion

UF_6 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 UF_4 , e.g., as an aerosol in CF_4 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

$$g_i + 1 + y_i + \sum_{j=1}^r a_{ij}\lambda_j + \lambda_{r+1} = 0 \quad (\text{A-1a})$$

$$1 + y_{m+1} + \lambda_{r+1} = 0 \quad i = 1, \dots, m$$

$$\sum_{i=1}^m a_{ij} \exp(y_i) - b_j = 0 \quad (\text{A-1b})$$

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

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

Let y° , λ° be an initial estimate. Using Newton's method, we obtain a correction on the initial estimate

$$\Delta y_i + \sum_{j=1}^r a_{ij}\Delta\lambda_j + \Delta\lambda_{r+1} = -\phi_i^\circ \quad (\text{A-2a})$$

$$\Delta y_{m+1} + \Delta\lambda_{r+1} = -\phi_{m+1}^\circ \quad i = 1, \dots, m$$

$$\sum_{i=1}^m a_{ij}n_i^\circ\Delta y_i = -\psi_j^\circ \quad (\text{A-2b})$$

$$\sum_{i=1}^m n_i^\circ\Delta y_i - n_{m+1}^\circ\Delta y_{m+1} = -\psi_{r+1}^\circ \quad j = 1, \dots, r$$

where $n_i^\circ = \exp(y_i^\circ)$, ϕ_i° and ψ_j° are the values of the left-hand side of eq A-1a and A-1b, respectively, substituting the initial estimate y° , λ° , and Δy_i and $\Delta\lambda_j$ are the corrections on the estimated values of y_i° and λ_j° , respectively. Using eq A-2a the Δy 's are expressed in the $\Delta\lambda$'s. Substituting the result in (A-2b) gives

$$R\Delta\lambda = q \quad (\text{A-3})$$

where

$$R_{kl} = \sum_{i=1}^m a_{ik}n_i^\circ a_{il} - \delta_k^{m+1} n_{m+1}^\circ$$

$$q_k = \psi_k^\circ - \sum_{i=1}^m a_{ik}n_i^\circ\phi_i^\circ + \delta_k^{m+1} n_{m+1}^\circ\phi_{m+1}^\circ$$

$$a_{k(m+1)} = 1$$

and δ_k^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 λ space than in the y space. In this way computer time is saved.

Appendix B

The thermodynamic functions of UF_5 and UF_4 as calculated from literature data are as follows.

UF₅. Using the data proposed by Rand and Kubaschewski (1963) ($\Delta H^\circ_{298}(\text{UF}_5(\text{cond})) \approx -488$ kcal/mol and $S^\circ_{298} = 45.0$ cal/mol K) and the vapor pressure measurements of Wolf et al. (1965), we obtain $\Delta H^\circ_{298}(\text{UF}_5(\text{g})) = -460$ kcal/mol.

UF₄. 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 $\Delta G^\circ_{873}(\text{UF}_4(\text{cond})) = -394.0$ kcal/mol (from emf measurements by Tanaka et al., 1971), we calculate $\Delta H^\circ_{298}(\text{UF}_4(\text{cond})) = -454$ kcal/mol, in good agreement with Rand and Kubaschewski (1963) (-450 ± 5 kcal/mol). Hence we obtain for $\text{UF}_4(\text{g})$: $\Delta H^\circ_{298} = -386$, $\Delta G^\circ_{298} = -374$ and $\Delta G^\circ_{1700} = -337$ kcal/mol (at the boiling point ≈ 1700 K). $\Delta G^\circ(\text{cond}) = \Delta G^\circ(\text{g})$ and $\Delta G^\circ(\text{cond})$ can be calculated from the data of Dworkin (1972) by extrapolation. To calculate the Gibbs free energy at other temperatures a linear relationship of ΔG vs. T is assumed.

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