Equation of state and specific heats of U–C–F gas mixtures

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Thermodynamic properties of a (U–C–F–e) gas mixture in a gas-core fission reactor have been investigated, especially the equation of state and the specific heats. A cooled graphite wall is maintained at a fixed temperature of 2000 K. The wall is in chemical equilibrium with the gas mixture. Depending on the energy produced, the gas temperature varies between 2000 and 10000 K. The pressure will increase from about 3 bar to 100 bar as a result of dissociation and temperature increase. The free electron concentration at 10000 K is between 4 and 8%, depending on the pressure. Below 5000 K this concentration is negligible. The value of C_p varies by a factor 4 due to dissociation processes. At 2000 K $C_p/C_v \approx 1.1$ and at 10000 K ≈ 1.5 . The influence of uncertainties in basic data has been discussed.

1. Introduction

The basic principles and operating conditions of a gas-core fission reactor consisting of a graphite vessel and containing uranium fluorides as a fuel have been treated previously [1,2]. It was shown that such a reactor, based on an energy production of 50 MW_{th}, can be operated at a pressure of 2.5 MPa, a wall temperature of about 2000 K and a total hold-up of 28 kg U (30% enriched). In the center of the reactor the temperature rises to about 12000 K.

The possibility of the applications of such a reactor for energy extraction by means of a “Nuclear Diesel Engine”, has been discussed by one of us [3]. For a correct description of the cyclic processes happening in such a fast running engine, one has to know the equation of state and the specific heats of the gaseous mixture as a function of temperature and pressure.

From previous work [4,5] we know that our gaseous system is rather complicated. It involves ~ 50 species of a great physical and chemical variety. From the point of view of molecular composition, we have a mixture of polyatomic gases (up to 12 atoms). The amount of various species present in the equilibrium composition

at different temperatures and pressures was calculated by applying Eriksson’s computer program “SOLGASMIX” [6], which is based on the minimization of the free energy of the system. The basic data to be inserted in the program are the standard entropies, the heats of formation and the $c_p(T)$ values of the various species. We considered a temperature range of 2000 to 10000 K and pressure ranges from 0.1 to 10 MPa. Recently many improved thermodynamic data came available [7]. Therefore the calculated equilibrium compositions in our present work differ from those published earlier [4,5].

At temperatures up to about 2500 K the main species present are UF_5 , UF_4 and CF_4 . With increasing temperature, these molecules dissociate into lower valent fluorides. Dissociation processes are pressure dependent, i.e. at higher pressures equilibrium compositions are shifted to higher temperatures. These dissociation processes will affect the equation of state as well as the specific heats of our system. A summary of various equations of state and their industrial applications has recently been given by T.I. Barry [8]. The properties of a mixture can always be written in terms of an ideal contribution, which is a function of temperature only, and a residual

or “excess” contribution, depending on the temperature, pressure and composition of the gas mixture.

The purpose of this work is to provide an explicit expression relating pressure, volume and temperature data for our dissociating system, and to investigate the influence of these dissociation processes on the specific heats of our system. They produce the “residual contributions” mentioned above. For the calculation of the specific heats we considered three total pressures, namely 0.1, 2.5 and 10 MPa for the same temperature range. These three pressures were chosen because of the wide range of possible operating conditions of the gas-core fission reactor [1,3,9]. Clearly, a higher pressure involves higher temperatures and more possibilities for energy extraction. On the other hand lower pressures are preferable from a point of view of construction materials. Values of c_p and c_p/c_v were calculated by applying standard thermodynamic relations.

We find that in the temperature regions where UF_5 , CF_4 and UF_4 dissociate, the residual contributions multiply the ideal c_p value with a factor four to five. The ratio c_p/c_v increases from a value of ~ 1.1 at 2000 K (polyatomic gas) to ~ 1.5 at 10000 K.

2. Phenomenological aspects

2.1. The initial composition of the gaseous U–C–F mixture

One of the characteristics of this reactor is that the wall is part of the chemical system. This means that the graphite wall is in thermodynamic chemical equilibrium with the gaseous mixture. For a fixed amount of uranium and fluorine, the amount of carbon in the “boundary gas layer” depends on the temperature of the reactor-wall and the operating pressure inside the reactor. This amount of carbon can be found by calculating the equilibrium composition of a system consisting of gaseous and condensed U–C–F components. The gaseous system will be discussed in details below. The condensed components included in our calculations are: C – graphite; UF_n , $n = 0, 3, 4, 5$ and 6; UC, $\text{UC}_{1.9}$ and U_2C_3 . In table 1 we give some typical quantities of carbon in the boundary gas layer, in equilibrium with the graphite wall and for various temperatures and pressures.

As the primary purpose of this work was to investigate the thermodynamic behaviour of the gaseous U–C–F system as a function of pressure and temperature, we did all our calculations for a constant overall, mean molar ratio F : U : C = 4.00 : 0.70 : 0.18. From table 1 we

Table 1

Equilibrium amounts of carbon in the boundary gas layer for various wall temperatures and operating pressures. The fixed amounts of uranium and fluorine were 0.70 mol U and 2.00 mol F_2

Temperature (K)	Pressure (MPa)	Carbon (mol)
1700	0.1	0.17
1800	0.1	0.19
2000	0.1	0.21
1900	2.5	0.17
2000	2.5	0.18
2100	2.5	0.19
2200	10	0.18
2300	10	0.19
2500	10	0.22

see that this specific ratio corresponds with chemical equilibrium at a graphite wall at 2000 K, 2.5 MPa. *These are the assumed operating conditions of our reactor* [4]. Different wall temperatures or gas pressures will cause corrosion of the walls or deposition of carbon, as we have discussed in a recent publication [10]. Table 1 gives some indications in this direction.

2.2. Influence of temperature and pressure on the dissociation and ionization processes

Applying the computer program SOLGASMIX, we calculated equilibrium compositions in the temperature range from 2000 to 10000 K and in the pressure range from 0.1 to 10 MPa (1 to 100 bars). In these calculations we included 49 gaseous species, which are given in table 2. Equilibrium compositions at pressures of 0.1 MPa and 10 MPa are given in figures 1 and 2. For 2.5 MPa these compositions have been given elsewhere [11]. We present the molefractions of the various species as a function of temperature. Fig. 1 gives the main dissociat-

Table 2

Species included in the calculation of the equilibrium compositions of the gaseous system U–C–F–e–ions

C_n	$n = 1, \dots, 7$	CF_n^+	$n = 0, \dots, 3$
F_n	$n = 1, 2$	C_2^+	
CF_n	$n = 1, \dots, 4$	$\text{C}^-, \text{C}_2^-, \text{F}^-$	
C_2F_n	$n = 1, \dots, 6$	UF_n^+	$n = 0, \dots, 5$
UF_n	$n = 0, \dots, 6$	UF_n^-	$n = 1, \dots, 6$
UC_2		e^-	
U_2F_{10}

Fig. 1. Equilibrium compositions of the gaseous system U-C-F-e-ions. Major components. Number of moles available: F:U:C are 4.00:0.70:0.18. (—) $P = 0.1$ MPa, (---) $P = 10$ MPa.

Fig. 2. Equilibrium compositions of the gaseous system U-C-F-e-ions. Main minor components. Number of moles available: F:U:C are 4.00:0.70:0.18. (a) $P = 0.1$ MPa, (b) $P = 10$ MPa.

Fig. 3. Total number of moles as a function of temperature. Parameter: pressure in MPa. Number of molecules available: F : U : C = 4.00 : 0.70 : 0.18.

ing species for both pressures whereas figs. 2a and 2b show some minor species.

From these equilibrium calculations we find the total number of moles and the corresponding volume occupied by the gas mixture at every temperature and pressure on the assumption of ideal gas behaviour. Results are given in table 3 and fig. 3. The total number of moles increases especially:

- for 0.1 MPa, between 2400 and 3000 K, where the dissociation of UF_5 and CF_4 takes place,

Table 4

Equilibrium amounts of higher valent carbon and uranium fluorides and of fluorine for certain temperatures and pressure

Temperature (K)	Total pressure (MPa)	Species (mol)			
		UF_5	UF_4	CF_4	F
2000	0.1	0.49	0.21	0.18	0.00
3000	0.1	0.12	0.58	0.02	0.69
4000	0.1	0.00	0.61	0.00	1.15
6000	0.1	0.00	0.00	0.00	3.72
2000	10	0.49	0.20	0.17	0.00
3000	10	0.47	0.22	0.16	0.04
4000	10	0.18	0.51	0.02	0.62
5000	10	0.03	0.64	0.00	0.99
8000	10	0.00	0.00	0.00	3.23

and between 4000 and 6000 K, where UF_4 and lower valent uranium and carbon fluorides dissociate;

- for 10 MPa, between 3000 and 4400 K, and between 5500 and 8500 K, because of the same reasons.

The dissociation processes result in a large amount of monatomic fluorine-gas, as shown explicitly in table 4. Ionization of monatomic uranium-gas starts above 5000 K for 0.1 MPa and above 7000 K for 10 MPa. However, because of the enormous increase in the amount of free fluorine the relative contribution of the free electrons to the total number of moles is small, below 10000 K. This becomes quite different in the trajectory between 10000 and 15000 K, where the degree of ionization of uranium and carbon atoms tends to hundred percent. From figs. 2a and 2b we see that in the temperature ranges of

Table 3

Total number of moles as a function of temperature and pressure

Temperature (K)	Pressure (MPa)						
	0.10	0.25	0.50	1.00	2.50	5.0	10.0
2000	0.879	0.878	0.877	0.877	0.876	0.875	0.873
3000	1.563	1.367	1.219	1.102	0.998	0.949	0.917
4000	2.011	1.909	1.850	1.795	1.708	1.619	1.494
5000	3.553	3.046	2.649	2.326	2.062	1.947	1.862
6000	4.761	4.396	4.031	3.639	3.099	2.691	2.354
7000	5.173	5.016	4.862	4.638	4.182	3.752	3.308
8000	5.376	5.253	5.148	5.031	4.827	4.580	4.209
9000	5.488	5.402	5.315	5.216	5.072	4.942	4.758
10000	5.547	5.492	5.429	5.347	5.218	5.111	4.991

Fig. 4. Total number of moles as a function of the pressure. Parameter: temperature in K. Number of moles available: F : U : C = 4.00 : 0.70 : 0.18.

~ 4000–6500 K ($P = 0.1$ MPa) and ~ 5500–10000 K ($P = 10$ MPa) the concentration of positive ions is higher than the concentration of free electrons, owing to the formation of F^- ions. Formation of F^- is enhanced at higher pressures. All negative ions are thermally destroyed between 8000 and 10000 K.

Fig. 4 demonstrates the pressure dependence of the total number of moles. This dependence is strongest about 3000 and about 6000 K, where the dissociation processes occur. At 2000 K there is hardly any pressure dependence as all uranium- and carbon fluorides are still stable. Above 8000 K the dependence is also small because most binary molecules have dissociated.

We have noticed during our calculations that the concentration of dimers like C_2F_2 , U_2F_{10} and also of the group C_3 , C_4 , C_5 etc. increases if pressures increase. But their mole fractions stay below 0.001, for temperatures between 2000 and 6000 K.

Our gaseous system is very complicated. Dissociation processes of various components depend each in their own way on temperature and pressure. Therefore a “normal” equation of state like the ideal gas law cannot be applied without taking into account the influences of chemical processes.

3. A numerical equation of state

The total number of moles in table 3 reflects the degree of dissociation and ionization at various temperatures and pressures. This total number of moles $n(P, T)$ implies a volume V , to be calculated by

$$PV = n(P, T)RT. \quad (1)$$

In fig. 5 we present the pressure P as a function of the volume V , with the temperature T as a parameter.

Per definition the compressibility factor for a real gas is given by

$$C(=Pv)/(RT), \quad (2)$$

where v is the molar volume of the gas at the temperature T (see Smith [12]). In a gas mixture we have $V = v \sum n_i$. An increase in temperature, at constant pressure, results in extra dissociation. This effect causes a larger volume than expected from the ideal gas law. One can normalize the factor C , relative to an ideal gas, by

$$C_{\text{norm}} = n(P, T)/n(P_i, T_i), \quad (3)$$

where $n(P_i, T_i)$ are the total number of moles at the initial conditions of pressure and temperature (2.5 MPa; 2000 K). In fig. 3 the total number of moles n has been plotted as a function of T with P as parameter. With the values of n taken from this figure one can demonstrate that C_{norm} varies between 1 and 6.

In case of compression of our gas mixture from a large volume V_2 to a smaller volume V_1 , keeping the temperature T constant, we will observe an increase in

Fig. 5. A (P, V) diagram for the gaseous system U-C-F-e-ions for a given quantity of material and taking into account dissociation and ionization.

Fig. 6. Log P as a function of log V ; P = pressure in MPa; V = volume in m^3 . Parameter: temperature in K. System: U:C:F:e:ions. Number of moles available: F:U:C = 4.00:0.70:0.18.

pressure which is less than for an ideal gas. Then we say that the gas is more compressible than an ideal gas.

$$(P_1/P_2)_{\text{mixture}} = \frac{n_1(P_1, T)}{n_2(P_2, T)} \left(\frac{V_2}{V_1} \right), \quad (4)$$

where $(n_1/n_2) < 1$ due to recombination. In order to get a mathematical expression for the equation of state we try

$$^{10}\log P = a \ ^{10}\log V + b, \quad (5)$$

or

$$PV^{-a(T)} = 10^{b(T)} \quad (6)$$

The values for P and V from fig. 5 have been plotted in fig. 6, according to eq. (5). We see for every temperature a straight line. The coefficients " a " and " b " are temperature dependent. In order to find the numerical values of these coefficients for every temperature we have introduced values of P and V as obtained from SOLGASMIX into a "least square fit" computer program [13]. This program could finally reproduce the input data from fig. 5 within 7%. The highest deviations are where dissociation processes are most active.

We calculated a and b in the temperature range of 2000 to 10000 K, applying small temperature intervals of 200 K. Some selected values are given in table 5. We notice that $|a| < 1$ because of molecular recombination processes. For an ideal gas $|a| = 1$. In fig. 7a we see the values of " a " as a function of temperature. In fig. 7b

Fig. 7. (a) The coefficient " a " of eq. (5) as a function of temperature. (x) calculated points; (—) interpolated line (eqs. (7a) and (8a)). (b) The coefficient " b " of eq. (5) as a function of temperature. (x) = calculated points; (—) = interpolated line (eqs. (7b) and (8b)).

Table 5

The coefficients "a" and "b" of the equation " $\log P = a \log V + b$ " as a function of temperature, adjusted to the pressure range of 1 to 100 bar and for a ratio F:U:C = 4.00:0.70:0.18. V is in liters

Temperature (K)	a	b
2000	-0.998	2.16
3000	-0.899	2.31
4000	-0.941	2.67
5000	-0.880	2.76
6000	-0.859	2.93
7000	-0.904	3.18
8000	-0.959	3.42
9000	-0.969	3.51
10000	-0.976	3.58

the same for "b". These values have been curve-fitted by the computer program "Cricket graph" [14]. The resulting equations are:

For the temperature range: 2000 K $\leq T < 4200$ K (with $T = 10^3 T'$)

$$a(T) = -3.3576 + 6.69339 T' - 6.452637(T')^2 + 2.801388(T')^3 - 0.5611048(T')^4 + 0.042220499(T')^5, \quad (7a)$$

$$b(T) = 0.0287 + 0.4469T' + 1.925646(T')^2 - 1.3965195(T')^3 + 0.35629045(T')^4 - 0.03104086(T')^5. \quad (7b)$$

For the temperature range 4200 K $\leq T \leq 10000$ K (with $T = 10^3 T'$)

$$a(T) = 2.1393 - 3.19189T' + 1.169843(T')^2 - 0.19514(T')^3 + 0.0151843(T')^4 - 4.48793 \times 10^{-4}(T')^5, \quad (8a)$$

$$b(T) = -3.17545 + 5.66073T' - 2.067737(T')^2 + 0.3552273(T')^3 - 0.02841493(T')^4 + 8.58538 \times 10^{-4}(T')^5. \quad (8b)$$

The values of a and b given in table 5 and the set of eqs. (7a)–(8b) can be used to calculate the (P, V) diagram of a cyclic process in the pressure range of 1 to 100 bars, for temperatures between 2000 and 10000 K (accuracy within 7%).

3.1. Normalization procedure

The coefficients a and b of eq. (6) have been calculated for a total quantity of 0.876 moles of gas, for a fixed ratio F:U:C = 4.00:0.70:0.18, corresponding with chemical equilibrium in a U-C-F gas mixture in contact with a graphite wall (2000 K, 2.5 MPa). These conditions were chosen for historical reasons and are not relevant to the equation of state. Of course one can also multiply this quantity 0.876 with a factor m , to get any other quantity of gas, keeping the ratio F:U:C the same. But then we should keep in mind that:

- the coefficient a depends only on the chemical composition of the gaseous mixture, and is independent of m ;
- the coefficient b has to be replaced by $b' = b - a \log m$ which follows directly from $V' = mV$ and $P(V'/m)^{-a} = 10^b$.

The equation of state of the new system, with (0.876 m) moles, is then given by $P(V')^{-a} = 10^{b'}$.

4. Specific heats of the (U-C-F-e) gas mixture

The procedure applied before the ratio c_p/c_v can be calculated, consists of two steps:

- (1) calculation of the mean values of c_p for the gaseous mixtures, corresponding with the various equilibrium compositions;
- (2) calculation of the difference $c_p - c_v$.

Values of c_p/c_v have to be calculated in the temperature range of 2000 K to 10000 K for pressures of 0.1, 2.5 and 10 MPa.

4.1. Some theoretical considerations

The difference between the heat capacities at constant pressure and at constant volume for any real system is given by

$$C_p - C_v = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P, \quad (9)$$

where V = the volume of the system at temperature T and pressure P , C_p = the heat capacity of the system at constant pressure P , C_v = the heat capacity of the system at constant volume V . See K. Denbigh [17]

Eq. (9) can be written in the form

$$C_p - C_v = TV\alpha^2/\beta, \quad (10)$$

where the *expansion coefficient* α is defined by

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P. \quad (11)$$

For an ideal gas system $\alpha = 1/T$. The isothermal compressibility factor β is defined by

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T. \quad (12)$$

For an ideal gas $\beta = -1/P$. This factor indicates the fractional change of volume with pressure at a constant temperature.

Combining eqs. (10), (11) and (12) one obtains

$$C_p - C_v = \frac{T \left(\frac{\partial V}{\partial T} \right)_P^2}{-\left(\frac{\partial V}{\partial P} \right)_T}. \quad (13)$$

This relation gives the exact thermodynamic difference between the heat capacities at constant pressure and at constant volume for any real system.

Considering eq. (1) for our gaseous mixture (U-C-F-e-ions), values of $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$ can be obtained in terms of the number of moles $n(P, T)$ as follows

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P} \left[n(P, T) + T \left(\frac{\partial n}{\partial T} \right)_P \right], \quad (14)$$

$$\left(\frac{\partial V}{\partial P} \right)_T = \frac{RT}{P} \left[-\frac{n(P, T)}{P} + \left(\frac{\partial n}{\partial P} \right)_T \right]. \quad (15)$$

Considering eqs. (1) and (13) it can be shown that the difference in the molar specific heats, i.e. $c_p - c_v$, can be calculated by dividing eq. (13) by $n(P, T)$, i.e.

$$c_p - c_v = -\frac{T \left(\frac{\partial V}{\partial T} \right)_P^2}{n(P, T) \left(\frac{\partial V}{\partial P} \right)_T}. \quad (16)$$

4.2. Calculation of c_p

Because of the dissociation processes involved, values of c_p have to be calculated according to the relation

$$c_p(P, T) = \sum_{i=1}^N f_i(P, T) c_{p,i}(T) + c_{p,\text{diss}}(P, T), \quad (17)$$

where

- f_i = the equilibrium mole fraction of species i (see figs 1 and 2),
- $c_{p,i}(T)$ = the specific heat of species i at a temperature T ,
- $c_{p,\text{diss}}(P, T)$ = the extra energy needed for dissociation and for an increase in temperature with one degree Kelvin.

This specific heat for our gas mixture can be calculated from the equilibrium compositions and the individual molar enthalpies of each species i , according to the relation

$$c_p(P, T) = \frac{\sum_{i=1}^N n_i(P, T_2) H_i(T_2) - \sum_{i=1}^N n_i(P, T_1) H_i(T_1)}{[\bar{n}_{\text{tot}}(P)](T_2 - T_1)}, \quad (18)$$

Fig. 8. Total specific heat c_p and molar specific heat $\bar{c}_p$ of the gaseous system U-C-F-e-ions as a function of temperature. The difference between both curves, for each temperature, is called the "residual" or "excess" contribution.

Fig. 9. (a) The individual specific heats of the main higher valent fluorides as a function of temperature [7]. (b) The individual specific heats of uranium, fluorine and the main lower valent fluorides as a function of temperature [7].

where

n_i = number of moles of species i ,

H_i = molar enthalpy of species i ,

$$\bar{n}_{\text{tot}}(P) = \frac{n_{\text{tot}}(P, T_2) + n_{\text{tot}}(P, T_1)}{2}.$$

The molar enthalpy of each species has been calculated by SOLGASMIX according to the general relation

$$H_i(T) = \int_{298}^T c_{p,i}(T) dT + \Delta H_{f,i,298.15}^{\circ} \quad (19)$$

ΔH_f is the heat of formation.

By considering the different equilibrium compositions and the corresponding enthalpies at the temperatures T_2 and T_1 , we took the extra energy needed for dissociation into account. In fig. 8 we give values of c_p as a function of temperature for pressures of 1, 25 and 100 bar. In order to demonstrate the influence of dissociation on the specific heat values we have presented in these figures also a curve representing the molar mean specific heat $\bar{c}_p(T)$, which is given by the first term of eq. (17).

The specific heats of the main dissociating species, inclusive the specific heats of fluorine and uranium monatomic gas are given in figs 9a and 9b.

4.3. Calculation of $c_p - c_v$ and c_p/c_v

Values of $c_p - c_v$ were calculated from eqs. (13) to (16). In order to find reliable values of $(\partial n/\partial T)_P$, equilibrium compositions were calculated in the temperature range of 2000 to 10000 K at intervals of 200 K, for constant pressures of 1, 25 and 100 bar. In order to obtain values of $(\partial n/\partial P)_T$ a bandwidth of 10% of the corresponding pressure was considered. This means that for every temperature we calculated equilibrium compositions at the pressures: 0.9, 1.0 and 1.1 bar; 22.5,

25.0 and 27.5 bar; 90, 100 and 110 bar. Values of $c_p - c_v$ in units of R are given in fig. 10.

From the results of the eqs. (16) and (17) values of c_p/c_v can be calculated. They are also given in fig. 10.

5. Expansivity and compressibility of our mixture

In tables 6 and 7 we give some values of the expansion coefficient α and the compressibility factor β as calculated for our gaseous mixture, according to eqs. (11) and (12). Values of $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$ were computed for the temperature and pressure intervals given above. We see that the influence of the temperature on the expansion coefficient α is much bigger than on the compressibility factor β , which is in agreement with figs. 3 and 4.

6. Dissociation energies

The dissociation energies of the uranium and carbon fluorines can be calculated from the enthalpies of the corresponding species according to the relationship

$$D_{\text{XF}_n}(T) = H_{\text{XF}_{n-1}}(T) + H_{\text{F}}(T) - H_{\text{XF}_n}(T),$$

for $X = \text{U}$, $n = 1, \dots, 6$ or $X = \text{C}$, $n = 1, \dots, 4$.

Some values have been given in table 8, and are compared with experimental data given in the literature, for 298.15 K.

7. Discussion

7.1. Accuracy of the thermodynamic data

The fundamental thermodynamic data used by us were recently assessed by the National Data Bank in

Fig. 10. Values of $c_p - c_v$ and c_p/c_v (system U-C-F-e-ions) as a function of temperature, for the pressures of 1, 25 and 100 bar.

Table 6
The expansion coefficient α (in 10^3 K^{-1}) of our gas mixture for various temperatures and pressures

Pressure (bar)	Temperature (K)			
	3000	5000	7000	9000
1	0.98	0.63	0.19	0.13
25	0.84	0.49	0.37	0.15
100	0.56	0.36	0.43	0.18
α ideal gas	0.33	0.20	0.14	0.11

Table 7

The compressibility factor β (in bar^{-1}) of our gas mixture for various temperatures and pressure

Pressure (bar)	β ideal gas	Temperature (K)			
		3000	5000	7000	9000
1	1	1.11	1.15	1.03	1.01
25	0.04	0.043	0.044	0.046	0.041
100	0.01	0.0104	0.0106	0.0119	0.0107

Harwell [7]. They differed slightly from the data used by us in previous papers [5]. The influence on the chemical composition of our gas mixture in free contact with the graphite wall was impressive however. We therefore did a thorough analysis about the influence of the officially indicated uncertainties in the newest British data on the calculated abundance of the main components in the boundary gas layer. The results are in table 9. A list of basic data plus their official uncertainties, for the 50 components in our gaseous system can be obtained from the authors or from the Data Bank in Harwell [7].

7.2. High pressure regime

At a pressure of 100 bar and a wall temperature of 2000 K changes in the composition as indicated in table 9 might have remarkable consequences.

- Condensation

The partial pressure of UF_4 will be between 13 and 27 bar, according to table 9. But at about 20 bar UF_4 starts to condense on the wall. This means that the

Table 8

Dissociation energies in eV per molecule^a of uranium and carbon fluorides at various temperatures

Species	Experimental values at 298 K	Temperature (K)			
		2000	4000	6000	8000
$\text{UF}_6 \rightarrow \text{UF}_5 + \text{F}$	2.85 [15]	3.21	3.26	—	—
$\text{UF}_5 \rightarrow \text{UF}_4 + \text{F}$	4.47 [15]	4.15	4.15	4.14	4.11
$\text{UF}_4 \rightarrow \text{UF}_3 + \text{F}$	6.48 [15]	6.38	6.32	6.27	6.22
$\text{UF}_3 \rightarrow \text{UF}_2 + \text{F}$	6.53 [15]	6.27	6.10	5.91	5.77
$\text{UF}_2 \rightarrow \text{UF} + \text{F}$	5.96 [15]	5.96	6.14	6.39	6.64
$\text{UF} \rightarrow \text{U} + \text{F}$	6.88 [15]	6.82	7.14	7.54	7.74
$\text{CF}_4 \rightarrow \text{CF}_3 + \text{F}$	5.65 [16]	5.60	5.53	5.44	5.37
$\text{CF}_3 \rightarrow \text{CF}_2 + \text{F}$	3.82 [16]	3.85	3.80	3.84	3.90
$\text{CF}_2 \rightarrow \text{CF} + \text{F}$	5.22 [16]	5.29	5.29	5.23	5.01
$\text{CF} \rightarrow \text{C} + \text{F}$	5.73 [16]	5.85	5.94	6.02	6.10

^a 1 eV per molecule corresponds to 9.64×10^4 joules per mole.

Table 9

Estimated uncertainties in the composition as a result of officially indicated uncertainties in the basic thermodynamic data [7]

Species	Heat of formation $\Delta H_{f,298.15}^\circ$ (kJ mol ⁻¹)	Gibbs free energy $\left(\frac{G - H_{298}}{T}\right)_{5000\text{ K}}$ (J mol ⁻¹ K ⁻¹)	Pressure 100 bar			
			Temperature 2000 K		Temperature 4000 K	
			Mole ^{a)} fraction	Mole fraction ^{b)} range	Mole ^{a)} fraction	Mole fraction ^{b)} range
UF ₅	-1920 ± 30	-631 ± 25	~ 0.60	0.50–0.70	0.12	0.06–0.24
UF ₄	-1600 ± 20	-571 ± 15	~ 0.20	0.27–0.13	0.34	0.38–0.28
CF ₄	-933 ± 1	-433 ± 7	0.18	0.21–0.16	0.02	0.02–0.01
F	-79 ± 1.5	-199 ± 0.02	0.01	0.01–0.01	0.42	0.44–0.37
Other fractions			0.01	0.01–0.01	0.10	0.10–0.10
Total number of moles			0.88	0.89–0.87	1.49	1.60–1.38

Species	Heat of formation $\Delta H_{f,298.15}^\circ$ (kJ mol ⁻¹)	Gibbs free energy $\left(\frac{G - H_{298}}{T}\right)_{5000\text{ K}}$ (J mol ⁻¹ K ⁻¹)	Pressure 1 bar			
			Temperature 2000 K		Temperature 4000 K	
			Mole ^{a)} fraction	Mole fraction ^{b)} range	Mole ^{a)} fraction	Mole fraction ^{b)} range
UF ₅	-1920 ± 30	-631 ± 25	~ 0.56	0.54–0.66	0.00	
UF ₄	-1600 ± 20	-571 ± 15	~ 0.24	0.25–0.15	0.30	0.35–0.25
CF ₄	-933 ± 1	-433 ± 7	0.18	0.20–0.17	0.00	
F	-79 ± 1.5	-199 ± 0.02	0.01	0.01–0.01	0.57	
Other fractions			0.01	0.00–0.01	0.13	
Total number of moles			0.88	0.89–0.87	2.01	2.16–1.85

^{a)} Calculated for the heat of formations given in the second column for a U-C-F gas mixture in chemical equilibrium with a graphite wall at 2000 K.

^{b)} Assessed on the basis of several calculations considering the official uncertainties in ΔH and $(G - H)/T$ for the main components.

partial pressure of UF₄ never can rise above the vapour pressure at 2000 K. Depending on the basic data about UF₄ and UF₅ the max. total pressure will adjust to this limitation. If a higher total pressure is required one has to raise the wall temperature.

– Wall corrosion

If the UF₅ content decreases according to table 9, this will automatically increase the content of UF₄ and CF₄. The extra carbon is taken from the wall. See our recent publication on corrosion [10].

– Total number of moles

In the boundary wall-layer the changes in the total number of moles are negligible. But at higher temperature, away from the wall, the polyatomic fluorine compounds will decompose. For carbon-fluorides this happens already between 2500 and 3500 K, and for uranium-fluorides about 6000 K. At 4000 K we estimate an uncertainty in the total number of moles, due to the uncertainties in the basic data, of less than 10%. For any chemical reaction the reaction rate is directly proportional to the concentration of the

components. This law also holds for the production of nuclear energy. This means that there is a present-day uncertainty of 10%, in the required total gas pressure in a Gas Core Fission Reactor, for a set energy production per unit volume.

– Chemical composition

For certain purposes the chemical composition of the boundary gas layer, at a mean temperature of say 3500 K, will be important. This will especially be the case if this gas mixture is used for the creation of an energetically inverted layer for lasing purposes.

The influence of the spread in composition on the specific heat ratio c_p/c_v is of the order of one percent.

7.3. Medium pressure regime; 1 to 25 bar

The second half of table 9 illustrates the influence of the uncertainties in the basic data, in case of a total pressure of 1 bar. We notice the following:

– Variations in *chemical composition* due to uncertain-

ties in the heat of formation of UF_5 or UF_4 resemble very much the 100 bar case.

- The total number of moles at 1 bar, 4000 K is 30% larger than at 100 bar, 4000 K. The uncertainty in this number is about 10%.

Figs. 1, 2a and 2b illustrate the influence of the pressure on the chemical equilibrium. At a level of (4000 K, 1 bar) UF_5 and CF_4 have degraded into lower valid fluorides and the amount of free fluorine increases relative to (4000 K, 100 bar) with a factor two, for a fixed initial number of moles at 2000 K.

7.4. Low pressure regime; 10^{-2} to 10^{-4} bar

During the last 10 years we see a growing interest of rarified gaseous systems in the pressure range of 10^{-4} to 10^{-2} bar, and at temperatures between 600 and 3000 K. This interest originates from the possibility of etching and material deposition in systems which have resemblance with our U–C–F gaseous system. Sometimes U is replaced by W or Mo and C by Si (see Pauleau [18] and Nordine [19]). In that case the applications are in the industry of semiconductors. We did no calculations in this pressure range.

7.5. Classical deviations from the ideal gas law

Non-ideal behaviour of plasmas, from a point of view of quantum statistics, has been discussed by Kraeft et al. [20] and by Ebeling et al. [21]. They work with chemically idealized systems, like hydrogen or only noble gasses, like Schram et al. [22].

Classical deviations from ideality for our system are estimated as follows:

- The fugacity coefficients, based on critical data. The critical temperatures for CF_4 and UF_6 (or UF_5) are about 228 K and 500 K, respectively. The critical pressures are 37 and about 50 bar. At 2000 K, 25 bar the reduced values for temperature and pressure lead to a fugacity coefficient $1.00 < f/p < 1.03$ (See: ref. [11], Chapter VII, Appendix). For temperatures of 4000 K or higher the gas mixture dominated by F-gas behaves like a noble gas. At these temperatures all f/p values are equal to 1.00.
- Deviations due to ionization. Owing to the large content of electro-negative gasses the concentration of free electrons below 6000 K is negligible. But from our calculations we know that this concentration is $1.7 \times 10^{24} \text{ m}^{-3}$ at 10000 K, 25 bar. Then $(n_{\text{gas}} + n_{\text{ions}})/n_{\text{electrons}} = 12$ in the bulk of the hot plasma. Following Debye and Hückels theory [23] for the mean molar activity coefficient γ_e of the electron gas we find

$\gamma_e = 0.75$. The deviation of the Gibbs free energy, due to the presence of charged species, from the overall Gibbs free energy of the gaseous mixture at 10000 K, 25 bar is only 0.3%.

7.6. The specific heats of individual species

In fig. 9 we give the specific heats of the main individual species in our gaseous mixture. A broad peak appears in the specific heat of the monatomic uranium gas, owing to the influence of the higher electronic levels of the uranium atom on the partition function. For a Boltzmann distribution the population of the levels above 620 cm^{-1} increases from 5% to 40% going from 2000 to 3000 K [24]. Above 4000 K the internal energy of the uranium atom hardly increases, resulting in a decrease of the specific heat. The same influence is visible in table 8, where the dissociation energies of UF and UF_2 increase if the temperature rises from 2000 to 8000 K.

7.7. Comparison with argon gas

Recently De Haas and Schram, using Hsu and Pfender's relations, found that the specific heat of monatomic argon gas increases with a factor 50 between 10000 and 15000 K because of the internal energy of the argon atom, finally emerging into ionization [18,25]. The same effect but on a much larger energy scale occurs in our gas mixture for CF_n , resp. UF_m compounds. But instead of ionizing they dissociate.

- In both cases the extra energy needed for the splitting of the compound molecule is manifested by a peak in the specific heat as a function of the temperature (fig. 8).
- This peak becomes lower and broader with increasing pressure.
- At low temperatures in both cases the specific heat of the gas has its ideal-gas value. For monatomic argon gas this is $5/2 R$ below 8000 K. In our work we see for higher pressures (25 to 100 bar) at 2000 K for a mixture of UF_5 , UF_4 and CF_4 a value of $c_p/c_v = 1.1$. This is in good agreement with the statistical relation, for bigger molecules, in an ideal gas

$$c_p/c_v = 1 + 2/f,$$

where f is the number of degrees of freedom ($f = 3n$, where n is the number of atoms in the molecule). Experimental data obtained in shockwave experiments in UF_6 gas show the same c_p/c_v value [26].

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References

- [1] M.J.P.C. Nieskens, H.N. Stein and J. Kistemaker, *Ind. Eng. Chem. Systems* 17 (1978) 256.
- [2] J. Kistemaker and M.J.P.C. Nieskens, *Energy Conversion* 18 (1978) 67.
- [3] J. Kistemaker, *Ned. Tijdschr. Natuurk.* B53 (1987) 12.
- [4] W. Boersma-Klein, F. Kelling, J. Kistemaker and R.J. Heyboer, *High Temp. Sci.* 18 (1984) 131.
- [5] W. Boersma-Klein, F. Kelling, J. Kistemaker and R.J. Heyboer, *J. Nucl. Mater.* 130 (1985) 418.
- [6] G. Eriksson, *Chem. Scripta* 8 (1975) 100.
- [7] M.H. Rand, Data for Species in the C-F-U-electron system, Report of the Material Division, Harwell Laboratory, Didcot.
- [8] T.I. Barry, *Chemical Thermodynamics for Industry* (Blackwell, London, 1985).
- [9] N.J. Diaz, E.T. Dugan and C.C. Oliver, *Atomkernenergie-Kerntechnik* 36 (1980) 191.
- [10] J. Kistemaker and W. Boersma-Klein, *High Temp. Sci.* 24 (1987) 37.
- [11] W. Klein, Ph.D. Thesis, Techn. Univ. Eindhoven, The Netherlands (1987).
- [12] J.M. Smith, *Introduction to Chemical Engineering Thermodynamics* (McGraw-Hill, New York, 1949).
- [13] NAG Fortran Library Manual, Mark 9, Vols. 1 and 2, Numerical Algorithms Group, Oxford (1982).
- [14] Cricket Graph, Presentation Graphic-Science and Business, Cricket Software, Gr. Valley Corp. Cent., Malvern, PA, U.S.A.
- [15] K.H. Lau and D.L. Hildenbrand, *J. Chem. Phys.* 76 (1982) 2646.
- [16] D.R. Stull and H.A. Prophet, *Janaf Thermochem. Tables*, 2nd Ed., NSRDS-NBS 37 (1971).
- [17] K. Denbigh, *Principles Chem. Equil.* (Cambridge University Press, Cambridge 1957).
- [18] Y. Pauleau, *Bull. Soc. Chim. France* 4 (1985) 538.
- [19] J.-O. Carlsson and M.J. Boman, *Vac. Sci. Technol. A* 3 (1985) 2298.
- [20] W.D. Kraeft, D. Kremp and G. Röpke, in: *Proc. Int. Conf. on Phenomena in Ionized Gases (XVI ICPIG)*, Düsseldorf, 1983, p. 24.
- [21] W. Ebeling, W.D. Kraeft and D. Kremp, in: *Proc. Int. Conf. on Phenomena in Ionized Gases (XIII ICPIG)*, Berlin, 1977.
- [22] J.C.M. De Haas, Ph.D. Thesis, Technical University Eindhoven, The Netherlands (1986).
- [23] P. Debye and E. Hückel, *Phys. Zeitschr.* 24 (1923) 185 and 305.
- [24] F. Kelling, FOM Institute Amsterdam, private communication.
- [25] K.C. Hsu and E. Pfender, *Plasma Chem. and Plasma Process.* 4 (1984) 219.
- [26] K.P. Schug and H.G. Wagner, *Zeitschr. f. Phys. Chem. Neue Folge* 108 (1977) 173.