

Use of parameter perturbation for free energy minimization: the effect of stoichiometry on zirconium yield during zirconium halide reduction by hydrogen

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Abstract

A parameter perturbation technique has been devised to solve the simultaneous equations that arise during the formulation of the free energy minimization problem. The technique has been used to calculate the equilibrium concentrations of the species that form during the reduction of zirconium tetrahalides with hydrogen as a function of temperature and hydrogen to zirconium halide ratio. It was found that appreciable amounts of condensed phase elemental zirconium can form at temperatures in the range 3000–4000 K and at hydrogen to halide ratios greater than 32 if halides other than the fluoride are reduced.

INTRODUCTION

In complex reacting chemical systems, it is often of importance to calculate the effects of reagent stoichiometry, pressure and temperature on the equilibrium concentrations of the reaction products. Free energy minimization [1–3] is a powerful technique for attaining this end. To solve the simultaneous non-linear equations that arise during the formulation of the free energy minimization problem, it is necessary to use iterative methods that do not require initial estimates sufficiently accurate to ensure convergence, as such estimates cannot be easily made for the equations being discussed. Methods that can be considered are the downhill simplex method of Nelder and Mead [4], conjugate gradient methods [5] and parameter perturbation [6]. In the present study a parameter perturbation technique was devised that solved the equations in a satisfactory manner. The technique was used to study the effect of stoichiometry on the thermodynamic equilibria that exist during the high temperature reduction

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of zirconium tetrahalides to elemental zirconium by hydrogen in plasmas. The optimum temperature and hydrogen to zirconium halide ratio that are necessary to obtain a high yield of condensed phase zirconium were established by means of the technique.

PARAMETER PERTURBATION PROCEDURE

For a maximum of n species, each of which can be present as one or more of p possible phases, in the system at equilibrium, q simultaneous non-linear equations can be written for the ideal state

$$RT \ln y_i^u + \sum_k a_{ik} \lambda_k + \mu_i^u = 0 \quad (i = 1, \dots, n; \quad u = 1, \dots, p)$$

where y_i^u = mole fraction of species i as phase u in the equilibrium mixture, a_{ik} = the number of atoms of the k th element present in each molecule of species i , λ_k = Lagrange undetermined multiplier for element k , $\mu_i^u = \Delta G_i^u(P, T)$ = Gibbs free energy of formation of species i , phase u , as a function of pressure P and temperature T , and R = gas constant.

For the m elements present in the system, a further m material balance equations must be written

$$\sum_i a_{ik} y_i^u - A_k / \sum_i n_i^u = 0 \quad (k = 1, \dots, m; \quad u = 1, \dots, p)$$

where A_k = total number of atomic weights of the k th element present in the system, and n_i^u = number of moles of species i , phase u , in the system at equilibrium.

In addition it is required that

$$\sum_i y_i^u - 1 = 0$$

Using matrix notation, the above set of $q + m + 1$ equations can be written as the set of equations

$$f_j(\mathbf{x}) = 0 \quad (j = 1, \dots, q + m + 1)$$

where \mathbf{x} is the vector $[y_1, y_2, \dots, y_n, \lambda_1/RT, \lambda_2/RT, \dots, \lambda_m/RT, \sum_i n_i^u]$ having dimension $q + m + 1$. The values of the elements in \mathbf{x} are unknown and must be found. We define a further set of equations

$$g_j(\mathbf{x}) = 0 \quad (j = 1, \dots, q + m + 1)$$

for which the solution \mathbf{x} is known. The set $g_j(\mathbf{x}) = 0$ may be “deformed” into the set $f_j(\mathbf{x}) = 0$ by means of a finite number N of increments

$$g_j^h(\mathbf{x}) = g_j^{h-1}(\mathbf{x}) + \frac{h}{N} [f_j(\mathbf{x}) - g_j^{h-1}(\mathbf{x})] \quad (h = 1, \dots, N)$$

The known solution \mathbf{x}^0 , of the initial set of equations $g_j^0(\mathbf{x})$ is used as an estimate for the iterative solution of $g_j^1(\mathbf{x})$ to give \mathbf{x}^1 . Because \mathbf{x}^1 will differ only slightly from \mathbf{x}^0 the attainment of convergence is likely when a Newton or quasi-Newton [7, 8] method is used to solve for \mathbf{x}^1 . The procedure progresses by incrementing h ; when $h = N$, $g_j^h(\mathbf{x}) = f_j(\mathbf{x})$ and \mathbf{x}^h is the required solution [6].

It is unnecessary to increment the value of h in equal steps $\Delta h = 1$, or to assign a fixed value to N . The value of the coefficient h/N can be substituted by a perturbation coefficient κ that is independent of h and N to give the modified equation

$$g_j^h(\mathbf{x}) = g_j^{h-1}(\mathbf{x}) + \kappa [f_j(\mathbf{x}) - g_j^{h-1}(\mathbf{x})] \quad (h = 1, \dots, N)$$

It is important to choose the value of κ so that convergence to the solution of $g_j^h(\mathbf{x})$ is ensured. In the present study, a procedure was devised for doing this that resulted in an adequately accurate solution in the minimum of time. In this method the absolute value of the largest element χ in the vector $\mathbf{x}^h - \mathbf{x}^{h-1}$ was calculated after each perturbation, and was used to establish a new value of κ according to Table 1. The perturbation was repeated until χ was less than 10^{-5} . Newton's method was used to obtain the solution of $g_j^h(\mathbf{x})$ at each value of h , and was preferred over quasi-Newton methods such as that of Broyden [8], which gave larger round-off errors.

The initial estimate for each mole fraction y_i^u was set at $1/q$ and that of each Lagrange coefficient λ_k , as well as that of the total number of moles $\sum_i n_i^u$, at 1. The set of equations $g_j^0(\mathbf{x}) = 0$ was formed by setting $\mu_i^u = -1(RT \ln y_i^u + \sum_k a_{ik} \lambda_k)$ for the first q equations, $A_k / \sum_i n_i^u = \sum_u \sum_i a_{ik} y_i^u$ for each element and $\sum_i n_i^u = 1$.

In practice it was found that each Newton solution took only two or three iterations to solve to a precision of 10^{-5} . For 30 simultaneous equations, approximately 150 perturbations were required to complete the calculation, and this took about 30 s on a 33 MHz machine fitted with an 80386 processor and an 80387 numeric processor. The computer program was written in c++ language and compiled so as to optimize speed.

TABLE 1

Values of perturbation coefficient κ for various ranges of χ ($s = q + m + 1$)

Range of χ	>20	10–20	1–10	0.1–1	0.01–0.1	< 0.01
κ	$1/640s$	$1/320s$	$1/160s$	$1/80s$	$1/40s$	$1/20s$

EQUILIBRIUM CALCULATIONS

The main purpose of the calculation was to investigate the influence of H_2 to ZrX_4 ratio and temperature on the yield of zirconium during the reduction of ZrX_4 ($X = F, Cl, Br$ or I) with hydrogen in a high temperature plasma. The equilibrium concentration of the species phases $H_2(\text{gas})$, $H(\text{gas})$, $H^+(\text{gas})$, $H^-(\text{gas})$, $Zr(\text{gas})$, $Zr(\text{liquid})$, $Zr(\text{solid})$, $Zr^+(\text{gas})$, $Zr^-(\text{gas})$, $X_2(\text{gas})$, $X(\text{gas})$, $X^+(\text{gas})$, $X^-(\text{gas})$, $ZrX(\text{gas})$, $ZrX_2(\text{gas})$, $ZrX_2(\text{liquid})$, $ZrX_2(\text{solid})$, $ZrX_3(\text{gas})$, $ZrX_3(\text{solid})$, $ZrX_4(\text{gas})$, $ZrX_4(\text{solid})$ and $HX(\text{gas})$ were calculated at a pressure of 0.1 MPa and at a number of temperatures between 1000 and 6000 K and with H_2 to ZrX_4 ratios in the range 0.5–128. Values for the required Gibbs free energies were taken from the JANAF tables [9].

RESULTS AND DISCUSSION

Figure 1 shows plots of the logarithm of the mole fraction of each species present in the system at equilibrium versus the temperature for the reaction $ZrF_4(\text{gas}) + 2H_2(\text{gas})$. Only species with mole fractions higher than 10^{-6} are shown. It is evident from the plots that all three phases of

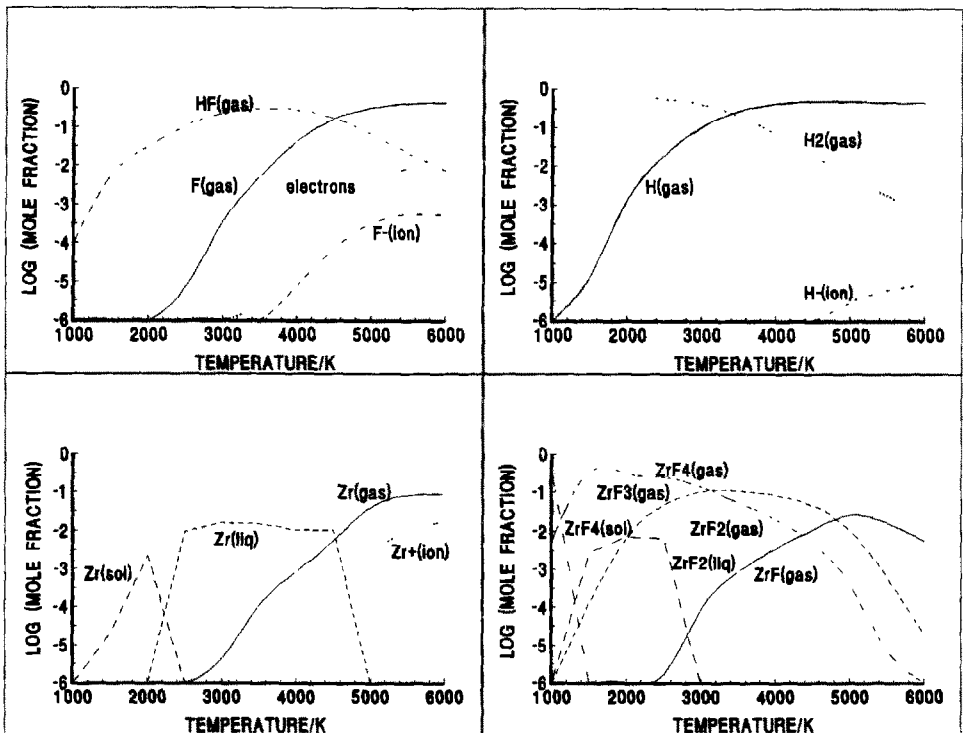


Fig. 1. Equilibrium concentrations of species formed during the reaction $ZrF_4 + 2H_2$ as a function of temperature.

elemental zirconium can form at temperatures above about 3000 K, although only small amounts of the solid phase exist below the melting point (2125 K for β -Zr). Appreciable amounts of the gaseous phase are present above about 5000 K but, as a result of the relatively low ionization energy of zirconium ($\Delta U_0 = 660 \text{ kJ mol}^{-1} = 6.84 \text{ eV}$), ionization of the gas to Zr^+ ions starts at 3000 K. Also formed in appreciable quantities are the highly stable lower halides ZrF_3 , ZrF_2 and ZrF . ZrF , present as a free radical, is very stable and is not easily reduced to zirconium by hydrogen. For the reduction of the other zirconium tetrahalides, using the same hydrogen to halide molar ratio, similar results for the equilibrium concentrations of the equivalent species were obtained. However, in these cases it was found that the lower halides were less stable and were reduced to elemental zirconium at lower temperatures than in the case of zirconium tetrafluoride.

Figures 2 and 3 are three-dimensional plots showing the yield of zirconium as a function of temperature and hydrogen to halide ratio for the reactions

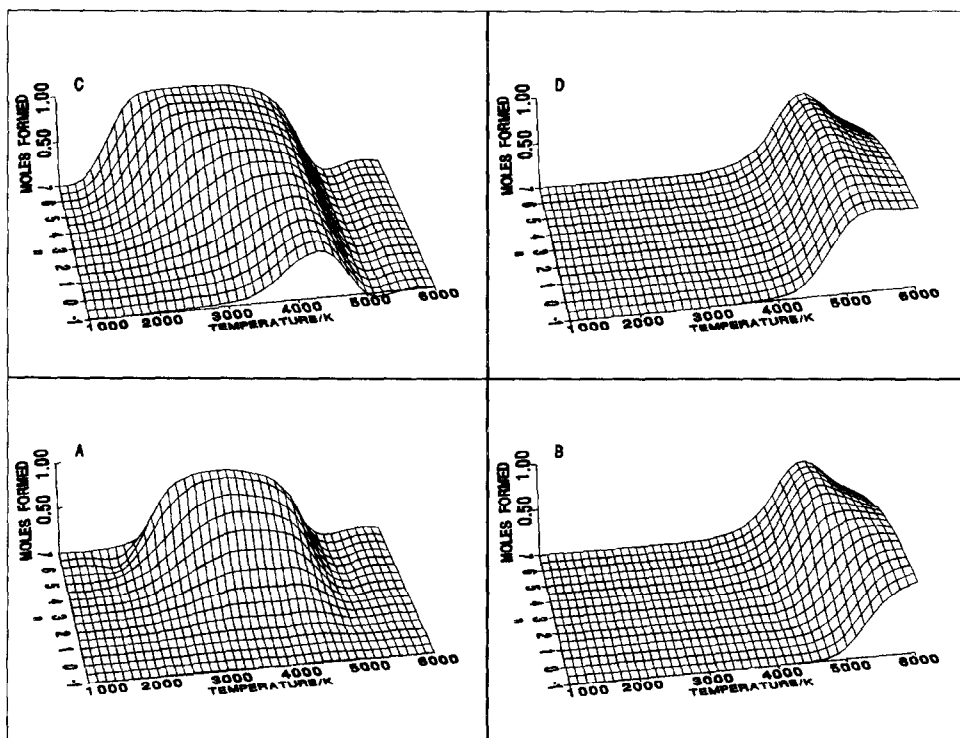


Fig. 2. Moles of elemental zirconium formed as a function of temperature and the parameter n . (A) Condensed phase and (B) gaseous phase Zr formed from ZrF_4 ; (C) condensed phase and (D) gaseous phase Zr formed from ZrCl_4 .

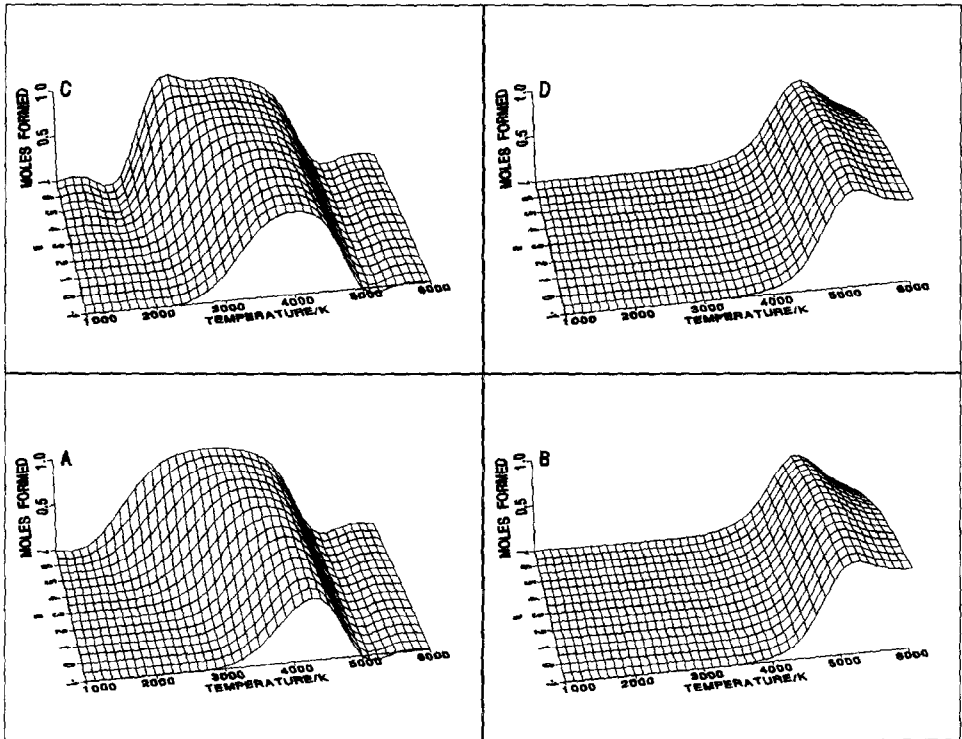


Fig. 3. Moles of elemental zirconium formed as a function of temperature and the parameter n . (A) Condensed phase and (B) gaseous phase Zr formed from ZrBr_4 ; (C) condensed phase and (D) gaseous phase Zr formed from ZrI_4 .

In these plots the independent variables are the temperature and n , the latter as defined in the above equation. The yield is shown as the dependent variable and is equal to the number of zirconium formed from one mole of halide. Comparison of Fig. 2A and Fig. 2C shows that the yield of total condensed phase zirconium is much higher for the reduction of ZrCl_4 than for the reduction of ZrF_4 at equivalent temperatures and stoichiometries. Figures 3A and 3C show that both ZrB_4 and ZrI_4 give higher yields of condensed phase zirconium than either ZrF_4 or ZrCl_3 , ZrI_4 giving the highest yield over the widest ranges of temperature and hydrogen to halide ratio. For gaseous zirconium (Figs. 2B, 2D, 3B and 3D) the yields for the reduction of ZrCl_4 , ZrBr_4 and ZrI_4 are similar and are higher than those for the reduction of ZrF_4 . The effect of ionization of the gaseous zirconium can be seen in Figs 3B and 3D, the plane having a negative slope above about 5000 K.

Although Figs. 2 and 3 show the general shapes of the yield surfaces it is difficult to read values from them. In high temperature plasmas the gaseous zirconium rapidly recombines with fluorine species in a homogeneous reaction. In the case of condensed phase zirconium, the heteroge-

neous recombination reaction is slower and removal of these phases from the reaction zone can be achieved. The yield of condensed phase zirconium is thus of primary interest and the contour plots of Fig. 4 give a better indication of the effects of temperature and stoichiometry on these yields. In these plots the axes again represent the temperature and the parameter n , and the contour lines show the yields of condensed phase (solid + liquid) zirconium. The solid contour lines in Fig. 4 represent a yield of 0.9 mole per mole of halide, and it is evident that this is obtained at temperatures from just above 1500 K up to the boiling point of zirconium (3900 K). For ZrCl_4 (Fig. 4B) and ZrBr_4 (Fig. 4C) the condensed phases exist at values of n above about 4, whereas in the case of ZrI_4 the liquid phase is already formed at values of n above about 2. For values of n larger than 6 ($\text{Hr}/\text{ZrX}_4 = 64$), good yields of condensed phase zirconium can be obtained at temperatures between 2500 and 3900 K if ZrCl_4 , ZrBr_4 or ZrI_4 is reduced. For ZrF_4 (Fig. 4A) it is evident that only relatively low yields are obtained in the range of temperatures and hydrogen to halide ratios used.

Although high yields of condensed phase zirconium can be obtained according to the calculations, the effects of nucleation and growth of nuclei have not been considered. The critical supersaturation ratio

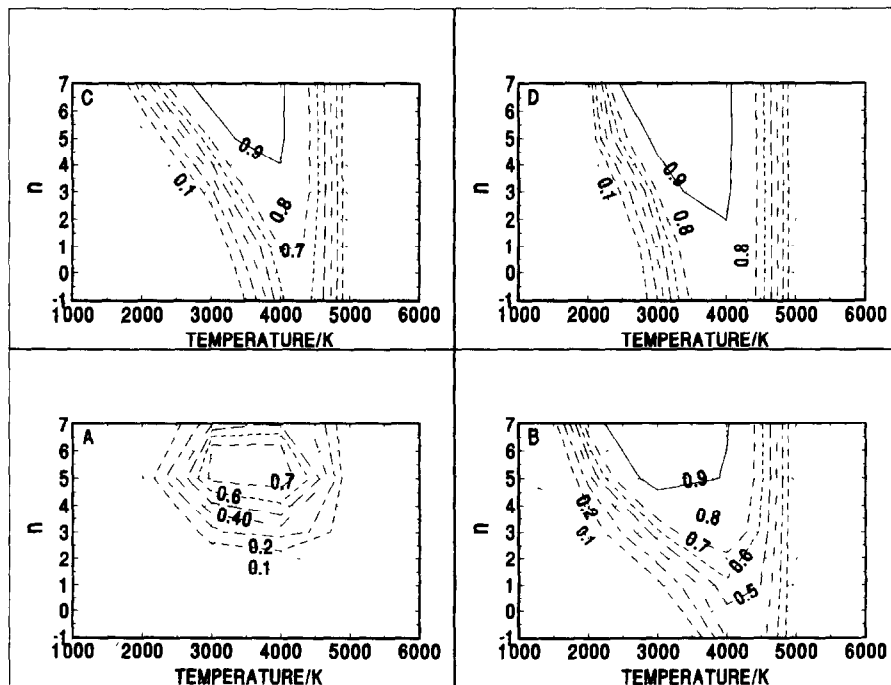


Fig. 4. Yield of condensed phase zirconium from the reduction of (A) ZrF_4 , (B) ZrCl_4 , (C) ZrBr_4 , and (D) ZrI_4 .

required to obtain condensed phase zirconium also needs to be investigated.

CONCLUSIONS

The parameter perturbation procedure is suitable for solving up to about 30 simultaneous equations that arise during free energy minimization in a reasonable time on a personal computer.

According to the calculations, zirconium tetrahalides, with the exception of zirconium tetrafluoride, can be reduced at temperatures in the range 3000–4000 K and H_2/ZrX_4 molar ratios higher than 32 to give yields of condensed phase zirconium in excess of 90%.

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