

The Production of Refractory Crystals by Vapour Transport Reactions

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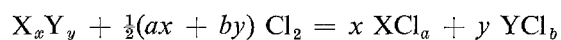
A thermodynamic analysis is made of the conditions under which compounds of high melting point can be efficiently transported in the gas phase by means of volatile compounds of limited stability. The possibilities of transporting silicon carbide, tantalum silicides, and uranium borides by this means are discussed to illustrate the method of calculation. A simple graphical method of constructing simultaneous tangents to three matched integral free energy diagrams is illustrated.

1. Introduction

In a previous communication [1] the authors described how Ellingham diagrams, in which the standard free energy of formation of gaseous compounds suitable for vapour transport reactions are plotted as a function of temperature, could be used to determine the optimum thermodynamic conditions for the transport of elements.

Similar considerations can be applied to the vapour transport of compounds, and we consider below the transport of high-melting refractory compounds which are difficult to produce in a specific form, e.g. single crystals, by other means.

Considering the general transport equation



in which the compound to be produced, X_xY_y , is transported by means of two volatile chlorides XCl_a and YCl_b , the three fundamental conditions for efficient transport of the elements previously defined [1] must be obeyed. (i) The chlorides must be volatile. (ii) The chlorides must have adequately large heats of formation. (iii) The chlorides must have entropies of formation which counter-balance the heats of formation so that their free energies of formation have suitable values at a convenient temperature and pressure. In addition, because a compound is now being considered, two new conditions must be obeyed. (iv) The partial pressures of XCl_a and YCl_b must be approxi-

mately in the stoichiometric ratio of the compound, and (v) the chemical potentials of X and Y in the gaseous phase at the points where a compound is to be vaporised and deposited must have values in the ranges over which the compound exists. If the first of these new conditions is not obeyed, the process will be inefficient because the bulk of one of the volatile chlorides will be recycled (in a closed apparatus) or will pass through the apparatus unchanged (in a flow-through apparatus). If the second of the new conditions is not observed, it is probable that the wrong compound will be deposited, or one of the elements, or possibly no product at all.

The inter-relationship of the partial pressure of a transporting gaseous species, e.g. XCl_a , the chemical potentials of its components, and its free energy of formation, can be derived from the integral free energy diagram of the X/Cl_2 system. Some of the properties of these diagrams are described in the next section.

2. Integral Free Energy Diagrams

Fig. 1 represents the integral free energies of formation per gram atom of the elements of a system in which X is a solid and Y a gas under all the temperatures considered. Two stable, stoichiometric compounds X_2Y and XY_2 are produced, and at 25° C these are crystalline solids which form no solid solutions. At 1000° C the compounds are liquids which are miscible in all proportions, but dissolve neither X nor Y. At 2000° C the compounds are gaseous.

Considering the system at 25° C it is clear that the compound X₂Y can exist in equilibrium with X at values of ΔḠ_X from 0 (a_X = 1) to -25000 cal (a_X = 4.5 × 10⁻¹⁹) and with Y at values of ΔḠ_Y ranging from -90000 cal (a_Y = 10⁻⁶⁶) to -35000 cal (a_Y = 2 × 10⁻²⁶). It is important to note, however, that it does not specify the conditions for stability of a compound merely to state the ranges of activities of the elements in equilibrium with a compound, because for a given value of a_X there is one corresponding value of a_Y only which is in equilibrium with X₂Y at unit activity.

The activities of X and Y which are in equilibrium with X₂Y at an activity less than unity can be calculated from the integral free energy curves. For instance, the line AB on fig. 1, which represents systems having chemical

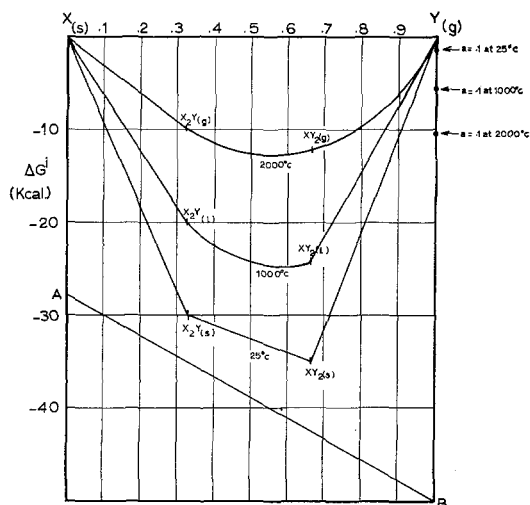


Figure 1 Integral free energy diagram (hypothetical). The values of ΔḠ_Y, corresponding to a_Y = 0.1 at 25, 1000, and 2000° C, are shown on the right hand side.

potentials μ_X = -28000 and μ_Y = -40000 cal, passes 5000 cal below the composition X₂Y at 25° C and this indicates that for the reactions

$$\frac{2}{3}X(s) + \frac{1}{3}Y(s) = \frac{1}{3}X_2Y(s)$$

$$\Delta G^1 = -\frac{1}{3} RT \ln a_{X_2Y} + \frac{2}{3} RT \ln a_X + \frac{1}{3} RT \ln a_Y$$

so that

$$\frac{1}{3} RT \ln a_{X_2Y} = -5000$$

and

$$a_{X_2Y} = 10^{-11}$$

At the higher temperatures, the formation of liquid and gaseous mixtures results in curved

sections of the integral free energy lines, but the line tangent to the diagram at any composition is still related to the partial molar free energies of the components as before. In the integral free energy diagrams following, these curved sections have been omitted because the magnitude of the change in ΔG¹ caused by mixing is small compared with the values under consideration.

Fig. 2 illustrates another feature of integral free energy diagrams. It represents the system

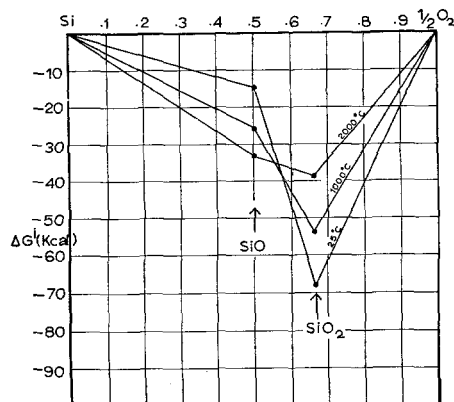
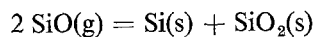


Figure 2 Integral free energy diagram for Si/½O₂ system.

Si/½O₂ and it may be seen that at 25° C ΔG¹ for SiO gas is less negative than that of a mixture of Si and SiO₂ by 39000 cal. This indicates that SiO is not stable with respect to Si and SiO₂ at this temperature and that the disproportionation reaction



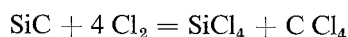
will take place to the point where the partial pressure of SiO will be only 6 × 10⁻⁵⁸ atm so that it is virtually complete. At 1000° C a similar situation exists, but at 2000° C gaseous SiO can exist at 1 atm pressure in equilibrium with liquid Si and SiO₂. The stability of SiO at high temperatures provides a route for the transport of SiO₂ by means of a reducing gas, such as hydrogen, and this reaction will be considered further below.

3. Matched Integral Free Energy Diagrams

When the transport of the compound X_xY_y by means of volatile chlorides is considered, it is necessary to know the three binary integral free energy diagrams for the systems X/Y, X/½Cl₂ and Y/½Cl₂. If a ternary system containing all

three elements is in equilibrium it is clearly necessary that the values of ΔG_X should be the same on the X ends of the X/Y, and the $X/\frac{1}{2}Cl_2$ diagrams. It is similarly necessary for the values of ΔG_Y and $\Delta G_{\frac{1}{2}Cl_2}$ to be the same in the pairs of diagrams in which they appear.

Fig. 3 represents the systems concerned in the transport of silicon carbide by means of chlorine according to the reaction



This system is interesting because it involves the transport of a relatively simple refractory compound and involves only one compound in each of the binary diagrams. By drawing them so that the $\frac{1}{2}Cl_2/Si$ and Si/C systems are adjacent the condition that ΔG_{Si} is the same for both compounds can be readily visualised. Similarly the Si/C and $C/\frac{1}{2}Cl_2$ diagrams are presented on a common ordinate so that the values of ΔG^i can be compared also.

It may be seen that ΔG^i_{SiC} is rather small, and that it is relatively unaffected by temperature (because the entropy of formation of SiC from its solid or liquid elements is small). $SiCl_4$ is much more stable than CCl_4 , indeed at $2000^\circ C$ the CCl_4 pressure in equilibrium with one atmosphere of chlorine and with carbon is considerably less than 1 atm.

From the symmetry of the SiC diagram, it may be seen that the values of $\Delta \bar{G}_{Si}$ and $\Delta \bar{G}_C$ in equilibrium with pure SiC at $1000^\circ C$ have the same ranges and lie between 0 and -12000 cal. If these extreme values of $\Delta \bar{G}_{Si}$ and $\Delta \bar{G}_C$ are extended into the $Si/\frac{1}{2}Cl_2$ diagrams through the values of ΔG^i for $SiCl_4$ and CCl_4 , the corresponding values of $\Delta G_{\frac{1}{2}Cl_2}$ in equilibrium with SiC and these silicon and carbon potentials

are obtained. It is clear that these values on the $Si/\frac{1}{2}Cl_2$ and $C/\frac{1}{2}Cl_2$ diagrams, cannot be made equal. As a result, very small pressures of CCl_4 will be encountered in equilibrium with SiC under any circumstances, so that the chemical transport of SiC by chlorine will always be a highly inefficient process. It may be noted that SiC is a good material to use in contact with chlorine gas at high temperatures because of this poor transport.

4. Selection of Efficient Transport Processes

From the considerations outlined above, it is clear that the values of the integral free energies of formation for the two gaseous compounds responsible for the transport of the two elements in a binary compound must be matched if the transport process is to be an efficient one. Under these conditions it will be found that approximately equal values exist for the partial free energies of the elements involved in the adjacent integral molar free energy diagrams. In order to select suitable compounds for use as transporting agents for silicides, carbides and borides it is useful to construct Ellingham diagrams for the chemical potentials of those silicon, carbon and boron compounds which are sufficiently volatile to be considered in this connexion. Figs. 4, 5 and 6 represent such diagrams.

For the purposes of illustrating the selection of suitable transport processes for refractory compounds the silicides of tantalum, the borides of uranium and a further consideration of the case of silicon carbide will be used as examples.

Many cases are to be found in the literature of processes for the transport of refractory compounds where the deposition process is

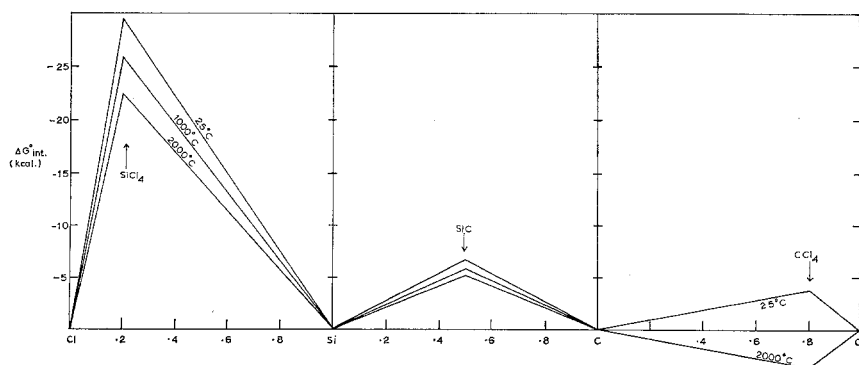


Figure 3 Matched integral free energy diagrams for Si/C/Cl system.

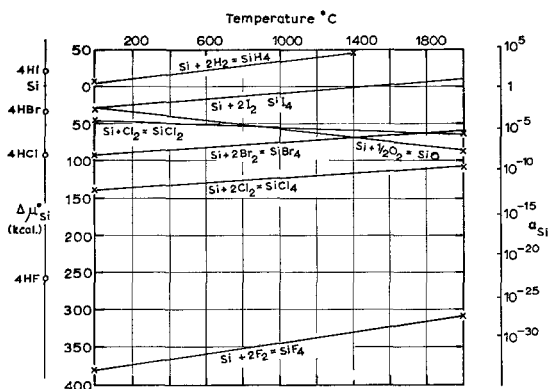


Figure 4 Silicon potentials of gaseous compounds.

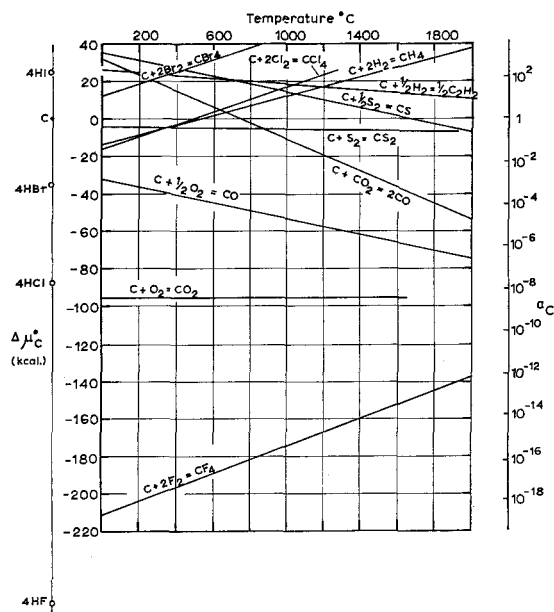


Figure 5 Carbon potentials of gaseous compounds.

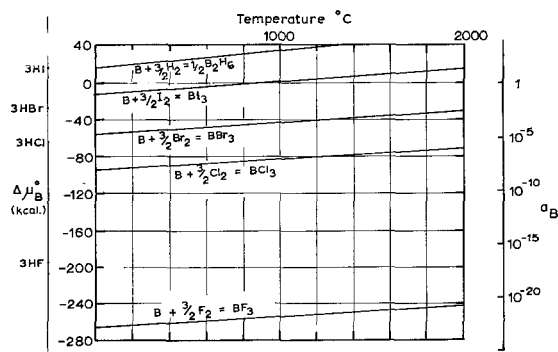


Figure 6 Boron potentials of gaseous compounds.

carried out under conditions far from chemical equilibrium. For example, SiC is produced by the thermal decomposition of methylated silicon hydrides which are exceedingly unstable under the conditions used, the process taking place violently as soon as the temperature is high enough for the potential energy barriers to the reaction to be overcome. The products of such processes are rarely homogeneous and control of the degree of supersaturation of the compound cannot be achieved. For this reason we will consider only those processes which can be carried out under controlled conditions near to the equilibrium point.

5. Transport of Tantalum Silicides

Consideration of the transport of tantalum silicides is complicated by the existence of several compounds in the Ta/Si and Ta/1/2Cl₂ systems. It is a useful example to consider, however, because the thermodynamical quantities for the systems involved are known, and also because tantalum silicides display a resistance to oxidation at high temperatures which makes them useful materials for protective coatings.

From fig. 4 it may be seen that the only suitable transporting gases for silicon are the halides, because the hydride is too unstable and SiO is only produced in appreciable quantities at temperatures in excess of 1900° C. Fig. 7 which is a set of integral free energy diagrams for the system Ta/Si/Cl shows that the stabilities of SiCl₄ and TaCl₄ are approximately equal at 1000° C.

The fact that there are no less than four tantalum silicides introduces further complications into the choice of suitable conditions for the deposition of any one of them singly. From fig. 7 it is clear that if, for instance, equal partial pressures of SiCl₄ and TaCl₄ were present at the point of deposition, the particular tantalum silicide produced would be one of the compounds near to the middle of the Ta/Si diagram, from the general symmetry of the three systems. It is desirable, however, to determine the relative partial pressures of the transporting gases which will be in equilibrium with each of the tantalum silicides at various temperatures.

In general, if the three integral free energy diagrams of such a system are known, it is possible to set up three equations with three unknowns ($\Delta\bar{G}_{Ta}$, $\Delta\bar{G}_{3Cl_2}$, $\Delta\bar{G}_{Si}$) and to determine the potentials of the three elements

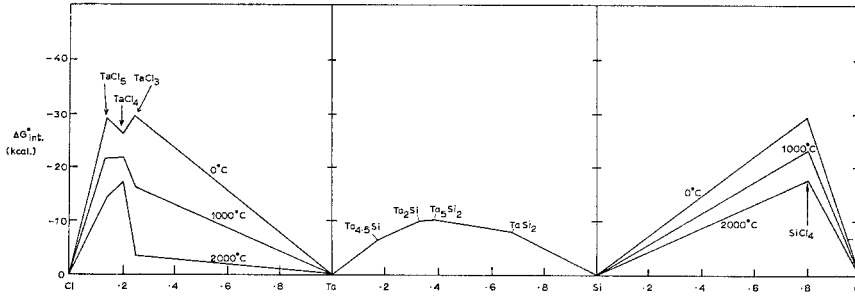


Figure 7 Matched integral free energy diagrams for Ta/Si/Cl system.

corresponding to any compositions in the three diagrams. The solutions are of the form

of the tangent plane from the integral free energy peaks necessary to produce the various

$$\Delta \bar{G}_x = \frac{bc \cdot \Delta G^1_{XY} + (ac - c) \Delta G^1_{YZ} + (ab - a - b + 1) \Delta G^1_{XZ}}{bc + (ac - c) + (ab - a - b + 1)}$$

where ΔG^1_{XY} etc are the integral free energies of formation of the three compounds concerned, a , b , and c are the atom fractions of the elements in the three compounds. It would clearly be a major problem to establish all the stability conditions for a system in which a series of compounds are produced in one or more of the binary integral free energy diagrams, although this could be carried out by means of a computer.

A graphical solution to this problem which will be sufficient in most cases can be devised by so constructing the diagrams in fig. 7 that they can be folded to form a solid triangular figure in which each corner represents one of the elements. It is then easy to find the required tangent plane to the system which delineates simultaneously on all three sides of the figure, the mutually consistent tangents to the integral free energy curves. This solves the equations above graphically, even under more complex conditions than those envisaged in setting up these equations. Fig. 8 is a photograph of such a model based on fig. 7.

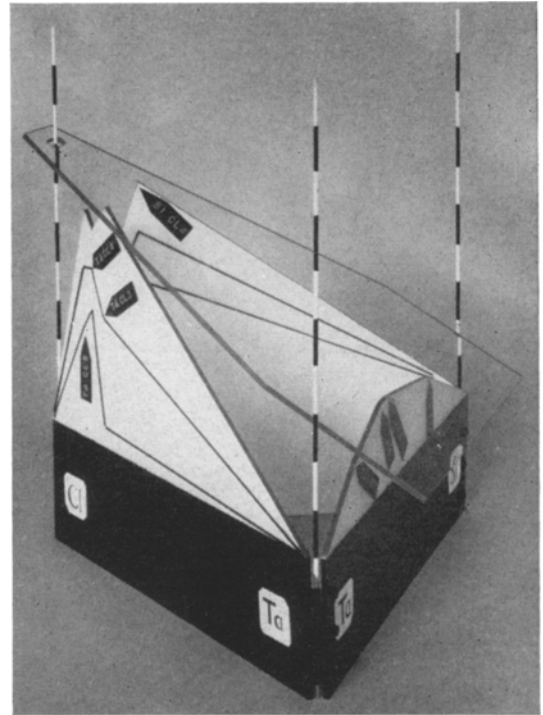


Figure 8 Three-dimensional model of Ta/Si/Cl system showing construction of tangent planes.

If the Ta/Si/Cl system is examined in this way, it is found that at 1000° C when the partial pressures of TaCl₄ and SiCl₄ are equal, the tantalum silicide phase produced will be Ta₂Si. Since the vapour species of TaCl₄ and SiCl₄ contain the same number of atoms Ta₂Si will be the solid phase in equilibrium with the gas containing equal partial pressures of the two gaseous halides irrespective of the total pressures of the system [1]. The relative partial pressures of TaCl₄ and SiCl₄ in equilibrium with all the Ta/Si compounds can be determined

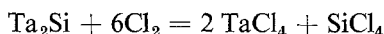
from the solid model by measuring the distances compounds, from which their activities and hence their partial pressures can be calculated. The ranges of relative pressures corresponding to the four compounds are given in table I.

It is clear, as mentioned above, that the chlorides of Ta and Si are too stable to provide

TABLE I Ratios of TaCl₄ to SiCl₄ partial pressures in equilibrium with various Ta/Si compounds.

Compound	$p_{\text{TaCl}_4}/p_{\text{SiCl}_4}$ ratio
Ta ₉ Si ₂	10 ⁴ - 10 ⁸
Ta ₂ Si	10 ⁸ - 0.9
Ta ₅ Si ₃	0.9 - 10 ⁻²
TaSi ₂	10 ⁻² - 5 × 10 ⁻⁵

an efficient means of transporting the tantalum silicides at easily achievable temperatures, and that it would be more convenient to use halides which are less stable. Efficient transport can be achieved when the value of the equilibrium constant K for example for the reaction



is close to unity. For this condition

$$\Delta G^\circ_{\text{Ta}_2\text{Si}} = 2 \Delta G^\circ_{\text{TaCl}_4} + \Delta G^\circ_{\text{SiCl}_4}$$

or, in terms of integral free energies

$$3 \Delta G^i_{\text{Ta}_2\text{Si}} = 10 \Delta G^i_{\text{TaCl}_4} + 5 \Delta G^i_{\text{SiCl}_4}$$

and in the case of chlorides this will be achieved only at very high temperatures. At 1000° C the chlorides are more stable than Ta₂Si by about 300 Kcal.

In order to establish that a given transport process will be efficient, however, it is necessary for the transporting compound to be decomposable at a convenient temperature, and the chlorides are evidently too stable for this reason. It would be possible to lower the chlorine potential of the system by introducing hydrogen, which would have the effect of lowering the temperature at which the gaseous chlorides decomposed. In this system, however, there would be a serious danger of contaminating the product with hydrogen if this procedure were resorted to.

It is a consequence of the bond energy model for heats of formation of gaseous halides discussed by the authors [1] that the difference between the free energies of formation of silicon and tantalum halides will be approximately the same irrespective of the choice of halogen; it is thus probable that the other halides will also provide approximately matched pairs of transporting compounds, but with different stabilities; the fluorides will be more stable and the bromides and iodides less stable.

Fig. 7 was constructed from the following data: Ta/Si system, Myers and Searcy [2]; Ta/Cl system, Schäfer and Kahlenberg [3]; Si/Cl

system, Kubaschewski, Evans and Alcock [4]. It will be noted that only one line is drawn for the Ta/Si system, and this is because the entropies of formation of the tantalum silicides are so small that their free energies of formation do not vary appreciably with temperature. Silicon forms only one gaseous chloride, but tantalum forms three such compounds, TaCl₅ (boiling point 242° C), TaCl₄ (sublimes at 433° C) and TaCl₃ which has a high sublimation point. TaCl₅ or TaCl₄ are thus suitable transporting species, and since TaCl₃ disproportionates into Ta and TaCl₄ at temperatures above 500° C, the process should be carried out at temperatures higher than this to obtain appreciable partial pressures of tantalum halides in the gas phase.

The gaseous bromides and iodides will be less stable than the chlorides by about 23 and 54 Kcal per mole of Br₂ and I₂ gas respectively. Since the reaction under consideration involves six moles of halogen gas, the free energy of the reaction in terms of bromides and iodides will be less negative by 138 and 324 Kcal respectively, from which it appears that the iodides are the most interesting transporting compounds.

Fig. 9 is an Ellingham diagram for the transport of all the Ta/Si compounds by iodine at a total pressure of 1 atm. It may be noted that they may all be so transported at moderate temperatures, and that the most efficient process

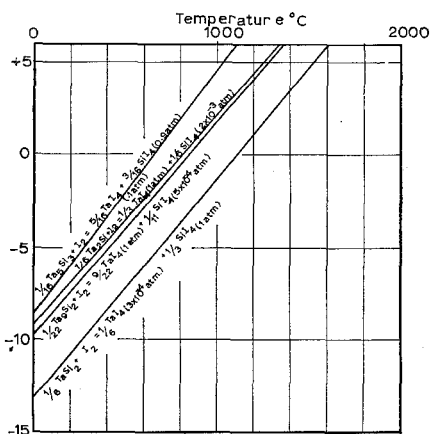


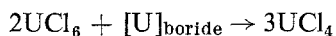
Figure 9 Ellingham diagram for transport of various Ta/Si compounds.

will be for the transport of the two silicides in the centre of the composition range because the partial pressures of the iodides will be closer to their required stoichiometric ratios.

6. Transport of Uranium Borides

The uranium borides provide another series of compounds for which adequate integral free energy data exist for the assessment of the transport of refractory compounds of potential interest. Fig. 10 was constructed using the following data: U/Cl and U/B systems, Rand and Kubaschewski [5]; B/Cl system, Kubaschewski, Evans and Alcock [4]. It is clear that in this system, the great difference between the integral free energies of formation of uranium chlorides and of boron chloride will be a serious obstacle in devising an efficient transporting process for the uranium borides. Consideration of a three-dimensional model of the system similar to that shown in fig. 8 shows that when the partial pressures of BCl_3 and UCl_4 are equal, UB_{12} will be the equilibrium phase at all temperatures, and UB_4 and UB_2 will be reproduced only under conditions when the pressures of BCl_3 and UCl_4 are so different that efficient transport cannot be achieved.

If an attempt were made to transport UB_{12} starting from the compound and chlorine gas, then according to the principle of local equilibrium there is a considerable risk of the formation of solid uranium trichloride on the surface of the boride. This solid layer could prevent the transporting reaction from taking place, even at high temperatures. In order to avoid the formation of the trichloride it is better to use uranium hexachloride preferably admixed with tetrachloride as the starting gaseous system. In this case the partial pressures of UCl_6 and UCl_4 may be adjusted so as to avoid the formation of solid UCl_3 when held in contact with a fixed uranium activity of the uranium boride. The transporting reactions will now be



and

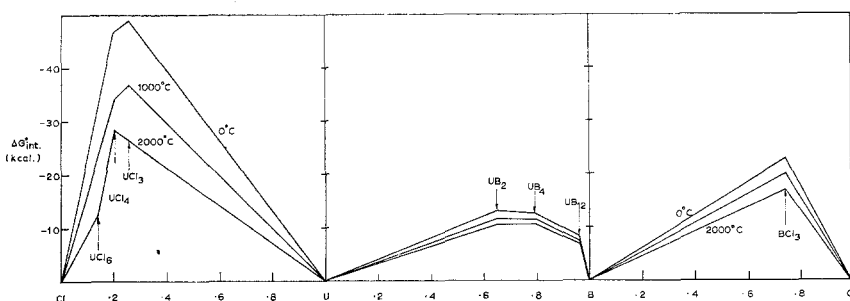
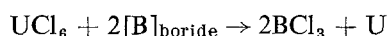


Figure 10 Matched integral free energy diagrams for U/B/Cl system.

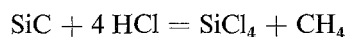
7. Transport of SiC by HCl gas

As was seen above, the transport of SiC by chlorine gas must always be a highly inefficient process because of the large difference in the free energies of formation of SiCl_4 and CCl_4 gases. It is possible to ameliorate this situation by the introduction of a fourth element into the system which will lower the chlorine potential and at the same time provide an alternative means for the transport of the carbon.

From figs. 4 and 5 it may be seen that hydrogen can be considered as a possible fourth element, because its presence will lower the chlorine potential of the system and because methane is of approximately the same stability as carbon tetrachloride gas. The interactions of the four elements taken pairwise are quantitatively:

Si — Cl	very strong
H — Cl	strong
Si — C	fairly strong
C — Cl	weak
C — H	weak
Si — H	very weak

It is thus probable that as SiC is reacted with HCl gas, the process taking place may be represented by the equation



a reaction of 4/2 multiplicity (2/1 for half quantities). Figs. 11 and 12 represent the partial molar free energies of formation of the binary compounds in the system Si/C/Cl/H, and an Ellingham diagram showing the transport process and the binary reactions from which it is made up. From the latter, it may be seen that the above transport process should take place at temperatures centred about 740° C. The transport process should take place at a useful efficiency between 550 and 950° C.

From fig. 4 it may be seen that there is a limitation on the range of operating temperatures which may be chosen because of the instability

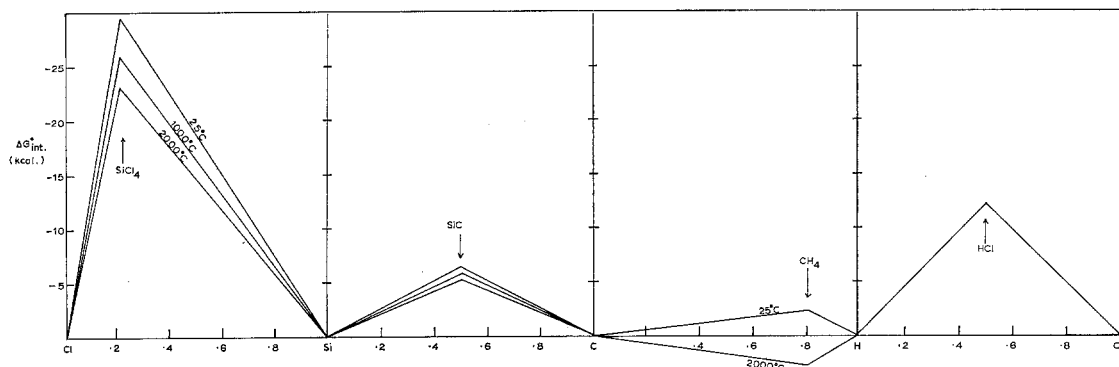


Figure 11 Matched integral free energy diagrams for Si/C/H/Cl system.

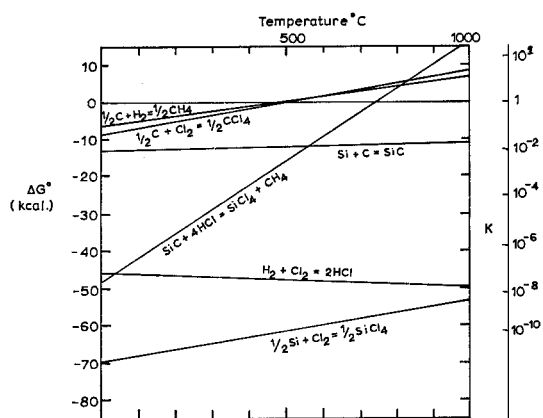


Figure 12 Ellingham diagram for transport of SiC by HCl.

of CH_4 with respect to carbon and hydrogen at unit activity at temperatures above 500°C . The CH_4/H_2 ratios in equilibrium with carbon at 500 and 950°C are 1.0 and 0.03 respectively. Optimum transport of SiC by HCl will thus occur in the presence of a considerable excess of hydrogen gas.

It should be noted that in this instance the introduction of hydrogen into the system is useful because CH_4 is about as stable as CCl_4 . It would not be a useful way of overcoming the problem of transport in the U/B/Cl system because the boron hydrides are too unstable to provide a transport mechanism for boron. This mis-match is due to the large difference in the integral free energies of formation of uranium halides and boron halides which is not affected by the introduction of hydrogen into the system.

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