

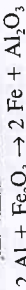
which has the solution $T = 859$ K, which is less than the melting temperature of Mg. Thus in order to produce liquid U and liquid MgF_2 at 1773 K, the stoichiometric reactants must be preheated to 859 K. The enthalpy-temperature diagram for the process is shown in Fig. 6.16. Taking the relative zero of enthalpy to be $H_{UF_4,298} + H_{Mg,298}$, the line ab represents the influence of the supply of 101,291 joules of heat to 1 mole of UF_4 and 2 moles of Mg, which is to increase the temperature of the system from 298 to 859 K. At the point b the reactants are placed in an adiabatic container and are allowed to react completely, which causes the change in enthalpy

$$\begin{aligned} \Delta H_{859} &= \Delta H_{298} + \int_{298}^{859} (c_{p,U} + 2c_{p,MgF_2} - c_{p,UF_4} + 2c_{p,Mg})dT \\ &= -32,880 + [29.55(859 - 298)] - \left[\frac{42.97 \times 10^{-3}}{2} (859^2 - 298^2) \right] \\ &\quad + 29.93 \times 10^5 \left(\frac{1}{859} - \frac{1}{298} \right) + \left[\frac{23.68 \times 10^{-6}}{3} (859^3 - 298^3) \right] \\ &= -226,642 \text{ J} \end{aligned}$$

The reaction causes the enthalpy to decrease from b to c and the sensible heat produced increases the temperature of the products along cd . The line contains four jogs; ed at 941K (for the heat of transformation of α -U to β -U), fg at 1049K (the heat of transformation of β -U to γ -U), hi at 1409K (the heat of melting of U) and kj at 1536 K which represents the heat of melting of 2 moles of MgF_2 . As the reaction has been conducted adiabatically, $H_i = H_f$. In practice the system does not follow the line $b \rightarrow c \rightarrow d$, which would require that all of the heat of the reaction be released isothermally before being made available to increase the temperature of the products. In practice the temperature of the system begins to increase as soon as the reaction begins, but, as enthalpy is a state function, the difference between its value in state 1 and its value in state 2 is independent of the process path taken by the system between the states.

Example 2

A mixture of Fe_2O_3 and Al, present in the molar ratio 1:2, is placed in an adiabatic container at 298 K, and the Thermit reaction



is allowed to proceed to completion. Calculate the state and the temperature of the reaction products.

From the thermochemical data

$$H_{Al_2O_3,298} = -1,675,700 \text{ J/mole}$$

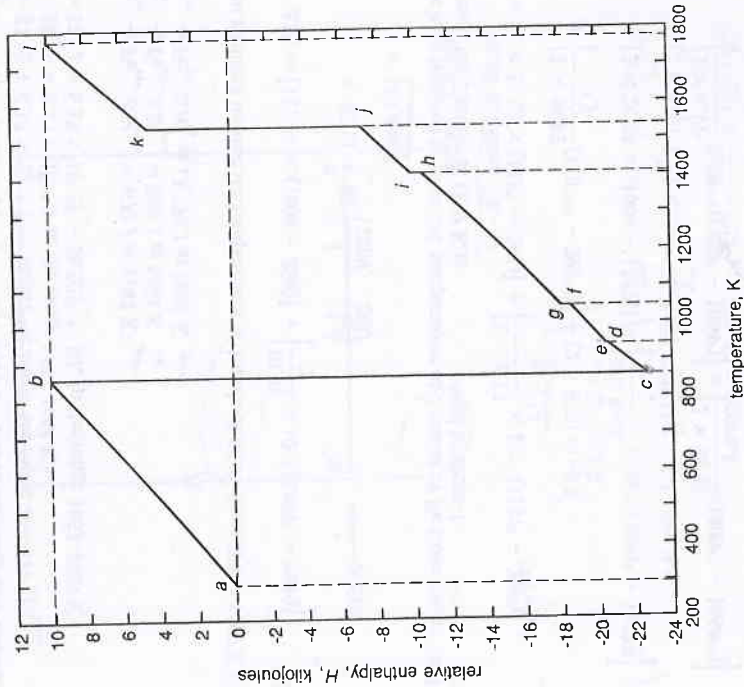


Figure 6.16

and

$$H_{Fe_2O_3,298} = -823,400 \text{ J/mole}$$

the heat released by the Thermit reaction at 298 K is calculated as

$$\Delta H_{298} = -1,675,700 + 823,400 = -852,300 \text{ J}$$

and this heat raises the temperature of the reaction products. Assume, first, that the sensible heat raises the temperature of the products to the melting temperature of Fe, 1809 K, in which state the reactants occur as 2 moles of liquid Fe and 1 mole of solid Al_2O_3 . The molar heat capacities and molar heats of transformation are

Handwritten note: ΔH_{298} is negative!