

6.9 NUMERICAL EXAMPLES

Example 1

A mixture of Fe₂O₃ and Al, present in the molar ratio 1:2, is adiabatically contained along with some Fe at 25°C. If the Thermit reaction (Fe₂O₃ + 2Al = Al₂O₃ + 2Fe) is allowed to proceed to completion, calculate the molar ratio of Fe to Fe₂O₃ in the initial mixture which, on completion of the reaction, will give liquid Fe and solid Al₂O₃ at 1600°C. Given:

- $H_{298}(\text{Fe}_2\text{O}_3) = -196,300$ calories/mole
- $H_{298}(\text{Al}_2\text{O}_3) = -400,000$ calories/mole
- $c_p(\text{Al}_2\text{O}_3) = 25.48 + 4.25 \times 10^{-3} T - 6.82 \times 10^5 T^{-2}$ calories/mole-degree in the temperature range 298 – 1873°K
- $c_p(\text{Fe}\alpha) = 4.18 + 5.92 \times 10^{-3} T$ calories/degree-mole from 273 to 1033°K
- $c_p(\text{Fe}\beta) = 9.0$ calories/degree-mole from 1033 to 1181°K
- $c_p(\text{Fe}\gamma) = 1.84 + 4.66 \times 10^{-3} T$ calories/degree-mole from 1181 to 1674°K
- $c_p(\text{Fe}\delta) = 10.5$ calories/degree-mole from 1674 to 1808°K
- $c_p(\text{Fe}l) = 10.0$ calories/degree-mole from 1808 to 1873°K

- For Fe α \rightarrow Fe β $\Delta H_{\text{trans}} = 1200$ calories/mole at $T_{\text{trans}} = 1033^\circ\text{K}$
- For Fe β \rightarrow Fe γ $\Delta H_{\text{trans}} = 220$ calories/mole at $T_{\text{trans}} = 1181^\circ\text{K}$
- For Fe γ \rightarrow Fe δ $\Delta H_{\text{trans}} = 210$ calories/mole at $T_{\text{trans}} = 1674^\circ\text{K}$
- For Fe δ \rightarrow Fe l $\Delta H_m = 3300$ calories/mole at $T_m = 1808^\circ\text{K}$

Consider the system per mole of Fe₂O₃ and consider the process path,

- I. Fe₂O₃ + 2Al \Rightarrow 2Fe + Al₂O₃ at 298°K, followed by
- II. (2 + n)Fe + Al₂O₃ at 298°K \Rightarrow (2 + n)Fe + Al₂O₃ at 1873°K

where n is the number of moles of Fe present in the initial mixture per mole of Fe₂O₃. As the system is adiabatically contained, $\Delta H_I + \Delta H_{II} = 0$. For the Thermit reaction at 298°K



and combination of Eqs. (6.12) and (6.15) gives

$$\Delta S = S(P_2, T_2) - S(P_1, T_1) = \int_{T_1}^{T_2} c_p d \ln T - \int_{P_1}^{P_2} \alpha V dP \quad (6.17)$$

Just as it was required that the temperature dependence of c_p be known for integration of Eqs. (6.1) and (6.13), strictly, it is required that the pressure dependence of V and α be known for integration of Eqs. (6.14) and (6.15). However, for condensed phases being considered over small ranges of pressure, both of these pressure dependencies can usually be ignored.

6.8 SUMMARY

In this chapter it has been seen that knowledge of the heat capacities of substances and the heats of formation of compounds allows enthalpy and entropy changes to be evaluated for any process, i.e., for phase changes and chemical reactions. In practice the heat-capacity and heat-of-formation data used in such calculations are experimentally determined by calorimetric methods. In dealing with enthalpy it is conventional to assign the value of zero to the enthalpy of elements in their stable state of existence at 298°K; but as the entropy of all substances (which are in complete internal equilibrium) at 0°K is zero, then any substance in any thermodynamic state has a calculable absolute entropy.

Although both enthalpy and entropy are dependent on pressure and temperature, the pressure dependency of H and S of substances occurring in condensed phases is normally small enough to be neglected in most applications (which involve pressure variation in the range of 0 to 1 atmosphere).

The determination of ΔH_T and ΔS_T for any reaction at any temperature (and pressure) allows the all-important Gibbs free energy change for the reaction to be calculated as

$$\Delta G_T = \Delta H_T - T\Delta S_T$$

As consideration of the Gibbs free energy in any isothermal, isobaric process provides the criterion of reaction equilibrium; it is seen that the equilibrium state of a reaction system can be determined from a knowledge of the thermochemical properties of the components of the system. An examination of this is started in Chap. 7.