Example 2.D

The phase transformation in pure iron may be represented as follows:

$$\langle\alpha\text{-Fe}\rangle \xrightarrow{1033K} \langle\beta\text{-Fe}\rangle \xrightarrow{1183K} \langle\gamma\text{-Fe}\rangle \xrightarrow{1673K} \langle\delta\text{-Fe}\rangle \xrightarrow{1812K} \{Fe\}.$$

Calculate the standard entropy of pure iron at 1627°C (*1900 K*) if its standard entropy at 25°C (*298 K*) is 6.50 cal/deg/mole (*27.20 J/K/mol*).

Given:

$$C_{P,\langle\alpha\text{-Fe}\rangle} = 4.18 + 5.92 \times 10^{-3}\, T \text{ cal/deg/mole}$$
$$(17.49 + 24.77 \times 10^{-3}\, T \text{ J/K/mol}).$$

$$C_{P,\langle\beta\text{-Fe}\rangle} = 9.0 \text{ cal/deg/mole}$$
$$(37.66 \text{ J/K/mol}).$$

$$C_{P,\langle\gamma\text{-Fe}\rangle} = 1.84 + 4.66 \times 10^{-3}\, T \text{ cal/deg/mole}$$
$$(7.70 + 19.50 \times 10^{-3}\, T \text{ J/K/mol}).$$

$$C_{P,\langle\delta\text{-Fe}\rangle} = 10.50 \text{ cal/deg/mole } (43.93 \text{ J/K/mol}).$$

$$C_{P,\{Fe\}} = 10.0 \text{ cal/deg/mole } (41.84 \text{ J/K/mol}).$$

$$\langle\alpha\text{-Fe}\rangle \longrightarrow \langle\beta\text{-Fe}\rangle \quad ; \Delta H^o_{1033} = 660 \text{ cal/mole } (2761.4 \text{ J/mol}).$$

$$\langle\beta\text{-Fe}\rangle \longrightarrow \langle\gamma\text{-Fe}\rangle \quad ; \Delta H^o_{1183} = 215 \text{ cal/mole } (899.6 \text{ J/mol}).$$

$$\langle\gamma\text{-Fe}\rangle \longrightarrow \langle\delta\text{-Fe}\rangle ; \Delta H^o_{1673} = 165 \text{ cal/mole } (690.4 \text{ J/mol}).$$

$$\langle\delta\text{-Fe}\rangle \longrightarrow \{Fe\} \quad ; \Delta H^o_{1812} = 3670 \text{ cal/mole } (15{,}355 \text{ J/mol}).$$

Solution: In the present example, several phase transformations are taking place in iron between 25°C and 1627°C, and therefore the entropy change of these must be considered in order to calculate the standard entropy of iron at 1627°C. Thus,

$$S^o_{1900,\{Fe\}} = S^o_{298,\langle\alpha\text{-Fe}\rangle} + \int_{298}^{1033} \frac{C_{P,\langle\alpha\text{-Fe}\rangle}}{T}\, dT + \frac{\Delta H^o_{1033,(\alpha\to\beta)}}{1033}$$

$$+ \int_{1033}^{1183} \frac{C_{P,<\beta\text{-Fe}>}}{T} dT + \frac{\Delta H^o_{1183,(\beta\rightarrow\gamma)}}{1183}$$

$$+ \int_{1183}^{1673} \frac{C_{P,<\gamma\text{-Fe}>}}{T} dT + \frac{\Delta H^o_{1673,(\gamma\rightarrow\delta)}}{1673}$$

$$+ \int_{1673}^{1812} \frac{C_{P,<\delta\text{-Fe}>}}{T} dT + \frac{\Delta H^o_{1812,(\delta\rightarrow\text{liquid})}}{1812}$$

$$+ \int_{1812}^{1900} \frac{C_{P,\{Fe\}}}{T} dT .$$

Putting the appropriate values in the above,

$$S^o_{1900,\{Fe\}} = 6.5 + \int_{298}^{1033} \left(\frac{4.18}{T} + 5.92 \times 10^{-3} \right) dT + \frac{660}{1,033}$$

$$+ \int_{1033}^{1183} \frac{9.0}{T} dT + \frac{215}{1,183} + \int_{1183}^{1673} \left(\frac{1.84}{T} + 4.66 \times 10^{-3} \right) dT$$

$$+ \frac{165}{1,673} + \int_{1673}^{1812} \frac{10.5}{T} dT + \frac{3,670}{1,812}$$

$$+ \int_{1812}^{1900} \frac{10.0}{T} dT$$

$$= 6.5 + 4.18 (\ln 1033 - \ln 298) + 5.92 \times 10^{-3} (1033 - 298)$$
$$+ 0.63 + 9 (\ln 1183 - \ln 1033) + 0.18 + 1.84$$
$$(\ln 1673 - \ln 1183) + 4.66 \times 10^{-3} (1673 - 1183) + 0.10$$
$$+ 10.5 (\ln 1812 - \ln 1673) + 2.02 + 10.0$$
$$(\ln 1900 - \ln 1812)$$
$$= \underline{24.41 \text{ cal/deg/mole}}.$$

Example 2.E

Small droplets of gold have been observed to supercool by a maximum amount of approximately 230°C. What is the entropy change associated with the isothermal solidification of 1 g-atom of such supercooled gold? What is the entropy change of the surroundings if they are assumed to remain at the same temperature as the supercooled gold? Also, calculate the total entropy change.

Given: $C_{P,\langle Au\rangle,}$ = 5.0 cal/deg/mole *(20.92 J/K/mol)*.

$C_{P,\{Au\}}$ = 7.0 cal/deg/mole *(29.29 J/K/mol)*.

Melting point of gold = 1063°C *(1336 K)*.

Heat of fusion of gold, ΔH_f = 3,050 cal/mole *(12,761 J/mol)*.

Solution: This is an example of irreversible process. The entropy change of the system can be calculated by considering a series of reversible steps leading from a supercooled gold at 1063 - 230 = 833°C. One such series might be as follows:

(1) Supercooled liquid gold is transformed reversibly from 833° to 1063°C (melting point of gold).
{Au} at 833°C → {Au} at 1063°C; ΔS_1.

(2) At 1063°C, liquid gold is transformed reversibly to solid gold.
{Au} at 1063°C → <Au> at 1063°C; ΔS_2.

(3) The solid gold is brought from 1063°C to 833°C.
<Au> at 1063°C → <Au> at 833°C; ΔS_3.

On adding (1), (2) and (3), we get the required reaction, i.e.

{Au} at 833°C → <Au> at 833°C; (2.E.1)

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3.$$

$$\Delta S_1 = \int_{1106}^{1336} \frac{C_{P,\{Au\}}}{T} \, dT$$

$$= \int_{1106}^{1336} \frac{7.0}{T} \, dT$$

$$= 1.32 \text{ cal/deg.}$$

$$\Delta S_2 = \frac{\text{Enthalpy change of the reaction (2)}}{(1{,}063 + 273)}$$

$$= \frac{-(\text{Heat of fusion of gold})}{1{,}336}$$

$$= \frac{-3{,}050}{1{,}336}$$

$$= -2.28 \text{ cal/deg.}$$

$$\Delta S_3 = \int_{1336}^{1106} \frac{C_{P,<Au>}}{T} \, dT$$

$$= \int_{1336}^{1106} \frac{5.0}{T} \, dT$$

$$= -0.94 \text{ cal/deg.}$$

$$\therefore \quad \Delta S_1 + \Delta S_2 + \Delta S_3 = 1.32 - 2.28 - 0.94$$

$$= \underline{-1.90 \text{ cal/deg.}}$$

Now consider the surroundings. The irreversible process is able to transfer heat reversibly to the isothermal reservoir. The temperature of the surroundings is the same as that of the supercooled gold i.e. 833^oC.

$$\Delta S_{surroundings} = \frac{\text{Heat absorbed by the surroundings}}{\text{Temperature of the surroundings}} .$$

Now, total heat evolved from the system = $\Delta H_1 + \Delta H_2 + \Delta H_3$, where ΔH_1, ΔH_2 and ΔH_3 are the heats of reaction of (1), (2) and (3), and can be calculated as follows:

$$\Delta H_1 = \int_{1106}^{1336} C_{P,\{Au\}}\, dT$$

$$= \int_{1106}^{1336} 7.0\, dT$$

$$= 1{,}610 \text{ cal.}$$

$$\Delta H_2 = -3{,}050 \text{ cal.}$$

$$\Delta H_3 = \int_{1336}^{1106} C_{P,\langle Au\rangle}\, dT$$

$$= \int_{1336}^{1106} 5.0\, dT$$

$$= -1{,}150 \text{ cal.}$$

∴ Total heat evolved from the system = 1,610 - 3,050 - 1,150

= -2,590 cal.

Hence, the heat absorbed by the surroundings is equal to 2,590 cal.

$$\therefore \quad \Delta S_{surroundings} = \frac{2{,}590}{1{,}106}$$

$$= \underline{2.34 \text{ cal/deg.}}$$

Total entropy change of the reaction (2.E.1)

$$= \Delta S_{system} + \Delta S_{surroundings}$$

$$= -1.90 + 2.34$$

$$= \underline{0.44 \text{ cal/deg.}}$$