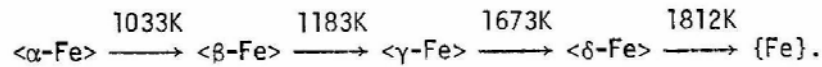


Example 2.D

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



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

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

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

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

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

$$\langle \alpha\text{-Fe} \rangle \longrightarrow \langle \beta\text{-Fe} \rangle ; \Delta H_{1033}^0 = 660 \text{ cal/mole} (2761.4 \text{ J/mol}).$$

$$\langle \beta\text{-Fe} \rangle \longrightarrow \langle \gamma\text{-Fe} \rangle ; \Delta H_{1183}^0 = 215 \text{ cal/mole} (899.6 \text{ J/mol}).$$

$$\langle \gamma\text{-Fe} \rangle \longrightarrow \langle \delta\text{-Fe} \rangle ; \Delta H_{1673}^0 = 165 \text{ cal/mole} (690.4 \text{ J/mol}).$$

$$\langle \delta\text{-Fe} \rangle \longrightarrow \{\text{Fe}\} ; \Delta H_{1812}^0 = 3670 \text{ cal/mole} (15,355 \text{ J/mol}).$$

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,

$$S_{1900,\{\text{Fe}\}}^0 = S_{298,\langle \alpha\text{-Fe} \rangle}^0 + \int_{298}^{1033} \frac{C_{P,\langle \alpha\text{-Fe} \rangle}}{T} dT + \frac{\Delta H_{1033,\langle \alpha \rightarrow \beta \rangle}^0}{1033}$$

$$\begin{aligned}
& + \int_{1033}^{1183} \frac{C_{P, <\beta\text{-Fe}>}}{T} dT + \frac{\Delta H_{1183, (\beta \rightarrow \gamma)}^0}{1183} \\
& + \int_{1183}^{1673} \frac{C_{P, <\gamma\text{-Fe}>}}{T} dT + \frac{\Delta H_{1673, (\gamma \rightarrow \delta)}^0}{1673} \\
& + \int_{1673}^{1812} \frac{C_{P, <\delta\text{-Fe}>}}{T} dT + \frac{\Delta H_{1812, (\delta \rightarrow \text{liquid})}^0}{1812} \\
& + \int_{1812}^{1900} \frac{C_{P, \{\text{Fe}\}}}{T} dT .
\end{aligned}$$

Putting the appropriate values in the above,

$$\begin{aligned}
S_{1900, \{\text{Fe}\}}^0 &= 6.5 + \int_{298}^{1033} \left[ \frac{4.18}{T} + 5.92 \times 10^{-3} \right] dT + \frac{660}{1,033} \\
& + \int_{1033}^{1183} \frac{9.0}{T} dT + \frac{215}{1,183} + \int_{1183}^{1673} \left[ \frac{1.84}{T} + 4.66 \times 10^{-3} \right] dT \\
& + \frac{165}{1,673} + \int_{1673}^{1812} \frac{10.5}{T} dT + \frac{3,670}{1,812} \\
& + \int_{1812}^{1900} \frac{10.0}{T} dT \\
& = 6.5 + 4.18 ( \ln 1033 - \ln 298 ) + 5.92 \times 10^{-3} (1033 - 298) \\
& + 0.63 + 9 ( \ln 1183 - \ln 1033 ) + 0.18 + 1.84 \\
& + ( \ln 1673 - \ln 1183 ) + 4.66 \times 10^{-3} (1673 - 1183) + 0.10 \\
& + 10.5 ( \ln 1812 - \ln 1673 ) + 2.02 + 10.0 \\
& + ( \ln 1900 - \ln 1812 ) \\
& = \underline{24.41 \text{ cal/deg/mole.}}
\end{aligned}$$

Example 2.E

Small droplets of gold have been observed to supercool by a maximum amount of approximately  $230^{\circ}\text{C}$ . 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:  $C_{p, \langle \text{Au} \rangle} = 5.0 \text{ cal/deg/mole } (20.92 \text{ J/K/mol})$ .

$$C_{p, \{ \text{Au} \}} = 7.0 \text{ cal/deg/mole } (29.29 \text{ J/K/mol})$$

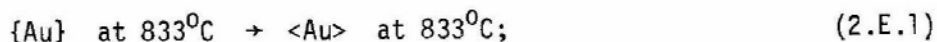
$$\text{Melting point of gold} = 1063^{\circ}\text{C} (1336 \text{ K})$$

$$\text{Heat of fusion of gold, } \Delta H_f = 3,050 \text{ cal/mole } (12,761 \text{ J/mol})$$

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  $1063 - 230 = 833^{\circ}\text{C}$ . One such series might be as follows:

- (1) Supercooled liquid gold is transformed reversibly from  $833^{\circ}$  to  $1063^{\circ}\text{C}$  (melting point of gold).  
 $\{ \text{Au} \}$  at  $833^{\circ}\text{C} \rightarrow \{ \text{Au} \}$  at  $1063^{\circ}\text{C}$ ;  $\Delta S_1$ .
- (2) At  $1063^{\circ}\text{C}$ , liquid gold is transformed reversibly to solid gold.  
 $\{ \text{Au} \}$  at  $1063^{\circ}\text{C} \rightarrow \langle \text{Au} \rangle$  at  $1063^{\circ}\text{C}$ ;  $\Delta S_2$ .
- (3) The solid gold is brought from  $1063^{\circ}\text{C}$  to  $833^{\circ}\text{C}$ .  
 $\langle \text{Au} \rangle$  at  $1063^{\circ}\text{C} \rightarrow \langle \text{Au} \rangle$  at  $833^{\circ}\text{C}$ ;  $\Delta S_3$ .

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



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

$$\begin{aligned}\Delta S_1 &= \int_{1106}^{1336} \frac{C_{P, \{Au\}}}{T} dT \\ &= \int_{1106}^{1336} \frac{7.0}{T} dT \\ &= 1.32 \text{ cal/deg.}\end{aligned}$$

$$\begin{aligned}\Delta S_2 &= \frac{\text{Enthalpy change of the reaction (2)}}{(1,063 + 273)} \\ &= \frac{-(\text{Heat of fusion of gold})}{1,336} \\ &= \frac{-3,050}{1,336} \\ &= -2.28 \text{ cal/deg.}\end{aligned}$$

$$\begin{aligned}\Delta S_3 &= \int_{1336}^{1106} \frac{C_{P, \langle Au \rangle}}{T} dT \\ &= \int_{1336}^{1106} \frac{5.0}{T} dT \\ &= -0.94 \text{ cal/deg.}\end{aligned}$$

$$\begin{aligned}\therefore \Delta S_1 + \Delta S_2 + \Delta S_3 &= 1.32 - 2.28 - 0.94 \\ &= \underline{-1.90 \text{ cal/deg.}}\end{aligned}$$

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°C.

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

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

$$\begin{aligned}\Delta H_1 &= \int_{1106}^{1336} C_{p,\{Au\}} dT \\ &= \int_{1106}^{1336} 7.0 dT \\ &= 1,610 \text{ cal.}\end{aligned}$$

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

$$\begin{aligned}\Delta H_3 &= \int_{1336}^{1106} C_{p,\langle Au \rangle} dT \\ &= \int_{1336}^{1106} 5.0 dT \\ &= -1,150 \text{ cal.}\end{aligned}$$

$$\begin{aligned}\therefore \text{Total heat evolved from the system} &= 1,610 - 3,050 - 1,150 \\ &= -2,590 \text{ cal.}\end{aligned}$$

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

$$\begin{aligned}\therefore \Delta S_{\text{surroundings}} &= \frac{2,590}{1,106} \\ &= \underline{2.34 \text{ cal/deg.}}\end{aligned}$$

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

$$\begin{aligned}&= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= -1.90 + 2.34 \\ &= \underline{0.44 \text{ cal/deg.}}\end{aligned}$$