Answers to Self-Check Questions

1. $\Delta S^{\ominus} = -284.6 \text{ J mol}^{-1} \text{ K}^{-1}$
$\Delta H_r^{\ominus} = (-314.4) - [(-46.2) + (-92.3)] = -175.9 \text{ kJ mol}^{-1}$
$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} = (-175.9) - 298\ (-284.6/1000) = -91.1 \text{ kJ mol}^{-1}$
Since $\Delta G^{\ominus} < 0$, the reaction is spontaneous.

[Note: The reaction is spontaneous despite the decrease in entropy because it is enthalpy–driven as strong ionic bonds are formed.]

2. $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

(a) $X(s) \longrightarrow Y(s) + Z(g)$ $\quad \Delta H^{\ominus} = +250 \text{ kJ mol}^{-1}$
$\Delta S^{\ominus} > 0 \Rightarrow -T\Delta S^{\ominus} < 0$

In this case, $\Delta G^{\ominus} < 0$ when the negative $-T\Delta S^{\ominus}$ outweighs the positive $\Delta H^{\ominus}$ at high temperatures. Hence the reaction is thermodynamically feasible at high T where $T > \frac{\Delta H^{\ominus}}{\Delta S^{\ominus}}$ such that $\Delta G^{\ominus} < 0$.

(b) $2X(g) + Y(g) \longrightarrow 2Z(g)$ $\quad \Delta H^{\ominus} = -100 \text{ kJ mol}^{-1}$
$\Delta S^{\ominus} < 0 \Rightarrow -T\Delta S^{\ominus} > 0$

In this case, $\Delta G^{\ominus} < 0$ when the negative $\Delta H^{\ominus}$ outweighs the positive $-T\Delta S^{\ominus}$ at low temperatures. Hence the reaction is thermodynamically feasible at low T where $T < \frac{\Delta H^{\ominus}}{\Delta S^{\ominus}}$ such that $\Delta G^{\ominus} < 0$.

(c) $X(l) \longrightarrow Y(l) + Z(g)$ $\quad \Delta H^{\ominus} = -200 \text{ kJ mol}^{-1}$
$\Delta S^{\ominus} > 0 \Rightarrow -T\Delta S^{\ominus} < 0$

In this case, $\Delta G^{\ominus} < 0$ at all temperatures because both $\Delta H^{\ominus}$ and $-T\Delta S^{\ominus}$ are negative. The reaction is thermodynamically feasible at all T.

(d) $2X(s) + 2Y(g) \longrightarrow Z(g)$ $\quad \Delta H^{\ominus} = +50 \text{ kJ mol}^{-1}$
$\Delta S^{\ominus} < 0 \Rightarrow -T\Delta S^{\ominus} > 0$

In this case, $\Delta G^{\ominus} > 0$ at all temperatures because both $\Delta H^{\ominus}$ and $-T\Delta S^{\ominus}$ are positive. The reaction is <u>not</u> thermodynamically feasible at all T.

3. Ans: **A**
According to the equation, there is <u>decrease</u> in number of moles of gas in the forward reaction, thus $\Delta S < 0$. Since H-bonds are formed between CO_2 and H_2O, $\Delta H < 0$.

4. Ans: **B**
$SOCl_2 + Ba(OH)_2 \rightarrow BaSO_4 + 2HCl$
Since a reaction occurs vigorously, $\Delta G < 0$
Since temperature decreases, the reaction is endothermic $\Rightarrow \Delta H > 0$
$\Delta G = \Delta H - T\Delta S$
Since $\Delta G < 0$ and $\Delta H > 0$, $-T\Delta S$ is negative. Thus, ΔS is positive.

5. Ans: **D**
White tin $\rightarrow$ Grey tin
$\Delta H_f^{\ominus} = -2.09 - 0 = -2.09 \text{ kJ mol}^{-1} = -2090 \text{ J mol}^{-1}$
$\Delta S_f^{\ominus} = S^{\ominus}(\text{products}) - S^{\ominus}(\text{reactants}) = 44.1 - 51.4 = -7.3 \text{ J K}^{-1} \text{ mol}^{-1}$ ←

$\Delta G^{\ominus} = -2090 - (273+12)(-7.3) = -2090 - 285(-7.3)$

Note:
It is stated in learning outcome (d) that the calculation of $\Delta S^{\ominus}$ using $S^{\ominus}$, is **not** required but it is needed here.