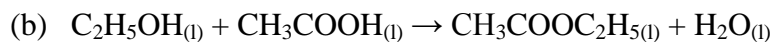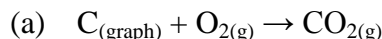Example Web3.1. Using data in Table 3.1 and Appendix 1, calculate the entropy changes at 25 °C and at 750 °C for the following reactions:

(a) $C_{(graph)} + O_{2(g)} \rightarrow CO_{2(g)}$

(b) $C_2H_5OH_{(l)} + CH_3COOH_{(l)} \rightarrow CH_3COOC_2H_{5(l)} + H_2O_{(l)}$

ΔS°_{298} can be calculated using Equation 3.8 and the change on heating to the higher temperature using Equation 3.11. 750 °C = 1023 K.

(a)
$$\Delta_r S^{\circ}_{298} = [S^{\circ}_{298}(CO_2)] - [S^{\circ}_{298}(C) + S^{\circ}_{298}(O_2)]$$

$$= 213.7 \text{ J K}^{-1} \text{ mol}^{-1} - ([5.7 + 205.1) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 2.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta C_p = [C_p(CO_2)] - [C_p(C) + C_p(O_2)]$$

$$= 37.1 \text{ J K}^{-1} \text{ mol}^{-1} - (8.5 + 29.4) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= -0.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r S^{\circ}_{1023} = 2.9 \text{ J K}^{-1} \text{ mol}^{-1} + (-0.8 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{1023}{298}\right)$$

$$= +1.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

(c)
$$\Delta_r S^{\circ}_{298} = [S^{\circ}_{298}(H_2O) + S^{\circ}_{298}(CH_3COOC_2H_5)] - [S^{\circ}_{298}(CH_3COOH) + S^{\circ}_{298}(C_2H_5OH)]$$

$$= [69.9 + 259.4] \text{ J K}^{-1} \text{ mol}^{-1} - [159.8 + 160.7] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 8.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta C_p = (75.3 + 170.1) \text{ J K}^{-1} \text{ mol}^{-1} - (124.3 + 111.5) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 9.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r S^{\circ}_{1023} = 8.8 \text{ J K}^{-1} \text{ mol}^{-1} + 9.6 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln\left(\frac{1023}{298}\right)$$

$$= 20.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

The entropy change in (a) is relatively small since there are the same number of moles of gas in the reactants and the products. In reaction (c), all the components are in the liquid phase so that again the change in entropy is relatively small although it increases at the higher temperature.

Example Web3.2. The standard enthalpy and entropy changes for fusion of water are

$\Delta_{fus}H° = +6.01$ kJ mol^{-1} and $\Delta_{fus}S° = +22.0$ J K^{-1}mol^{-1}. Calculate the change in Gibbs energy when 1.00 mol of ice melts at: (a) 0°C; (b) 10°C; and (c) −10°C.

The Gibbs energy change can be calculated from Equation 3.14, $\Delta G = \Delta H - T\Delta S$

(a) 0 °C = 273 K.

$$\Delta_{fus}G° = \Delta_{fus}H° - T\Delta_{fus}S°$$
$$= +6.01\times10^3 \text{ J mol}^{-1} - [273 \text{ K} \times(+22.0\text{J K}^{-1}\text{mol}^{-1})]$$
$$= 0 \text{ J mol}^{-1}$$

(b) At 10 °C (283 K)

$$\Delta_{fus}G° = \Delta_{fus}H° - T\Delta_{fus}S°$$
$$= +6.01\times10^3 \text{ J mol}^{-1} - [283 \text{ K} \times(+22.0\text{J K}^{-1}\text{mol}^{-1})]$$
$$= - 216 \text{ J mol}^{-1}$$

(c) At −10 °C (263 K)

$$\Delta_{fus}G° = \Delta_{fus}H° - T\Delta_{fus}S°$$
$$= +6.01\times10^3 \text{ J mol}^{-1} - [263 \text{ K} \times(+22.0\text{J K}^{-1}\text{mol}^{-1})]$$
$$= +224 \text{ J mol}^{-1}$$

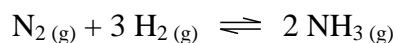At the melting temperature, T_m, the Gibbs energy change is zero. Above T_m melting has a negative

change in Gibbs energy and so is spontaneous; below T_m melting is not spontaneous and has a positive

Gibbs energy change.

Example Web3.3. Find the standard Gibbs energy change at 25 °C and 500 °C for the reaction

involved in the Haber-Bosch process

$$N_{2\,(g)} + 3\,H_{2\,(g)} \rightleftharpoons 2\,NH_{3\,(g)}$$

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From earlier calculations for the equation as written,

$\Delta_r H°_{298} = $ -92.2 kJ mol^{-1} and $\Delta_r H°_{773} = $ - 113.7 kJ mol^{-1}

$\Delta_r S°_{298} = $ - 198.7 J K^{-1} mol^{-1} and $\Delta_r S°_{773} = $ - 241.9 J K^{-1} mol^{-1}.

The Gibbs energy of reaction, $\Delta_r G°$, is calculated from Equation 3.14.

At 298 K

$$\Delta_r G°_{298} = \Delta_r H°_{298} - T\Delta_r S°_{298}$$

$$= \text{-92.2 kJ mol}^{-1} - (298\text{ K})(\text{-198.7}\times10^{-3}\text{ kJ K}^{-1}\text{ mol}^{-1})$$

$$\Delta G°_{298} = \text{-33.0 kJ mol}^{-1}.$$

At 773 K

$$\Delta_r G°_{773} = \Delta_r H°_{773} - T\Delta_r S°_{773}$$

$$= \text{-113.7 kJ mol}^{-1} - (773\text{ K})(\text{-241.9}\times10^{-3}\text{ kJ K}^{-1}\text{ mol}^{-1})$$

$$\Delta_r G°_{773} = \text{+73.3 kJ mol}^{-1}$$

The reaction is spontaneous at 25 °C but becomes non-spontaneous at the higher temperature mainly

due to the unfavourable entropic term becoming dominant.