Introduction to thermodynamics Part 3: Answers

1. To start, look at each process and decide whether there is greater disorder in the system after the change than before.
If more disordered, entropy increases and ΔS is positive
If less disorded, entropy decreases and ΔS is negative.

a) Perfume molecules spread through the room: There is an increase in disorder compared to the perfume molecules in the bottle. ΔS = positive

b) $CO_2(s) \longrightarrow CO_2(g)$. A gas is more disordered than a solid because the molecules move around much more than in a solid. ΔS = positive.

c) $N_2O_4(g) \longrightarrow 2NO_2(g)$. There are more molecules after the change and more ways to arrange these additional molecules. ΔS = positive.

d) $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$: Two types of ions in solution combine to form one compound. The ions are free to move in solution but become more bound to other ions in the solid. There is an increase in order. ΔS is negative.

2. Convert temperature to Kelvin: $100^oC \longrightarrow 373K$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} = \frac{+40\,700\ J\,mol^{-1}}{373} = 109\ JK^{-1}mol^{-1}$$

3. To calculate: $\Delta S_r = \Delta S(\text{Products}) - \Delta S(\text{reactants})$

a) $\Delta S = S(CO_2(g)) - [S(C(\text{graphite})) + S(O_2(g))]$
$= (213.7) - (5.7 + 205.1) = +2.9\ JK^{-1}mol^{-1}$

b) $\Delta S = [2 \times S(NH_3(g))] - [S\,N_2(g) + 3 \times (S(H_2(g))]$
$= (2 \times 192.5) - (191.6 + (3 \times 130.7))$
$= -198.7\ JK^{-1}mol^{-1}$

4c) $\Delta C_p = C_p(\text{products}) - C_p\ \text{reactants}$

$= C_p(CO_2) - (C_p(\text{graphite}) + C_p(O_2))$

$= 37.1 - (8.5 + 29.4) = -0.8\ JK^{-1}mol^{-1}$

$\Delta S_T = \Delta S_{298} + \Delta C_p \ln T/298K$

$= +2.96 + [-0.8 \times \ln(1023/298)]$

$= -1.9\ JK^{-1}mol^{-1}$

Use the same reasoning for b).

b) $\Delta S_{298} = -198.7\ JK^{-1}mol^{-1}$

$\Delta C_p = [2 \times C_p(NH_3)] - [C_p(N_2) + 3 \times C_p(H_2)]$

$= -45.3\ JK^{-1}mol^{-1}$

$\Delta S_{1023} = -198.7 + \left[-45.3 \times \ln\left(\frac{1023}{298}\right)\right]$

$= -246\ JK^{-1}mol^{-1}$

5. a) $0^\circ C \rightarrow 273K$

$\Delta G_{Fus} = \Delta H_{Fus} - T\Delta S_{Fus}$

$= +6.01 - [273 \times (+22 \times 10^{-3})] = 0\ kJmol^{-1}$

b) At $10^\circ C$ (283K)

$\Delta G_{Fus} = \Delta H_{Fus} - T\Delta S_{Fus}$

$= 6.01 - [283 \times (+22 \times 10^{-3})] = -0.22\ kJmol^{-1}$

c) At $-10^\circ C$ (263K)

$\Delta G_{Fus} = \Delta H_{Fus} - T\Delta S_{Fus}$

$= 6.01 - [263 \times (+22 \times 10^{-3})] = +0.22\ kJmol^{-1}$

At T_m, $\Delta G = 0$

Above T_m, ΔG = negative = Spontaneous

Below T_m, ΔG = Positive = Not Spontaneous.

6 The reaction is spontaneous on heating. The data tells you that the reaction is endothermic with a positive ΔS.

a) First, use ΔH and S values to calculate ΔS_{298} and ΔH_{298} using

$$\Delta G_f = \Delta H_r - T\Delta S_r$$

b) As temperature increases, $-T\Delta S_r$ becomes more important. The reaction is endothermic, so has a positive ΔH_r. It becomes spontaneous at temperatures above that at which $\Delta G_r = 0$.

a) $\Delta H_{298} = \Delta H$ (products) $- \Delta H$ (reactants)

$= [0 + (3 \times -393.5)] - [2 \times (-824.2) + 0] = +467.9\ kJmol^{-1}$

$\Delta S_{298} = \Delta S$ (products) $- \Delta S$ (reactants)

$= [4 \times (27.3) + 3 \times (213.7)] = +558.4\ JK^{-1}mol^{-1}$

$\Delta G = \Delta H - T\Delta S$

$= +467.9 - 298 \times 558.4 \times 10^{-3} = +302\ kJmol^{-1}$

b) ΔG is positive so reaction is non spontaneous at 298K. It becomes spontaneous at temperatures at which: $\Delta G = \Delta H - T\Delta S = 0$

When $\Delta G = 0$, $T\Delta S = \Delta H$

$$T = \frac{\Delta H}{\Delta S} = \frac{467.9}{558 \times 10^{-3}} = 838K$$

=) ΔH_r = ΔH (Products) − ΔH (Reactants)

$= [(0 + -393.5)] - [(-601.7) + (-110.5)]$

$= +318.7\ kJmol^{-1}$

ΔS_r = S (products) − S (reactants)

$= (32.7 + 213.7) - (26.9 + 197.7)$

$= +21.8\ JK^{-1}mol^{-1}$

$\Delta G = \Delta H_r - T\Delta H_r$

$= 318.7 - [298 \times (21.8 \times 10^{-3})] = +312.2\ kJmol^{-1}$

ΔCp = Cp (products) − Cp (reactants)

$= (24.9\ JK^{-1}mol^{-1} + 37.1\ JK^{-1}mol^{-1}) - (37.1 + 29.1)$

$= -4.2\ JK^{-1}mol^{-1}$

$\Delta H_{T_2} = \Delta H_{T_1} + \Delta Cp\,\Delta T$

$\Delta H_{1298} = \Delta H_{298} + \Delta Cp\,(1298 - 298)$

$= 318 + [(-4.2 \times 10^{-3}) \times 1000] = +314.5\ kJmol^{-1}$

$\Delta S_T = \Delta S_{298} + \Delta Cp\ \ln\left(\frac{T}{298}\right)$

$\Delta S_{1298} = \Delta S_{298} + \Delta Cp\ \ln(1298/298)$

$= +21.8 + (-4.2 \times 1.471) = +15.62\ JK^{-1}mol^{-1}$

$\Delta G_{1298} = \Delta H_{1298} - T\Delta S_{1298}$

$= 314.5 - [1298 \times 15.62 \times 10^{-3}] = +294\ kJmol^{-1}$