

Entropy and Gibbs Free Energy

Answer key with worked solutions

A. Understanding

1. Concepts.

(a) A measure of how **spread out** energy and matter are (the number of ways particles and energy can be arranged). (b) In a spontaneous process, the **total entropy of the universe increases**. (c) $\Delta G = \Delta H - T\Delta S$: melting has a positive ΔS , and at 25 °C the **$T\Delta S$ term is larger than ΔH** , so ΔG is negative even though ΔH is positive.

2. Signs of ΔS .

(a) + (liquid $\rightarrow$ gas) (b) - (3 mol gas $\rightarrow$ 2 mol) (c) + (ordered solid $\rightarrow$ mobile ions) (d) + (a gas is formed) (e) **close to zero** (2 mol gas on each side)

3. Four cases.

(a) **All temperatures** (ΔH -, ΔS +) (b) **Never** (ΔH +, ΔS -) (c) **Only at low T**, below $T = \frac{60 \text{ kJ}}{0.150 \text{ kJ/K}} = 400 \text{ K}$ (d) **Only at high T**, above $T = \frac{90 \text{ kJ}}{0.200 \text{ kJ/K}} = 450 \text{ K}$

B. Calculations

4. ΔS° of methane combustion.

$$\Delta S^\circ = [213.8 + 2(70.0)] - [186.3 + 2(205.2)] = 353.8 - 596.7 = -242.9 \text{ J/K}$$

Negative because **3 mol of gas** become **1 mol of gas** (the water is liquid).

5. ΔH° and ΔG° .

$$\Delta H^\circ = [-393.5 + 2(-285.8)] - [-74.6 + 2(0)] = -890.5 \text{ kJ}$$

$$\Delta G^\circ = -890.5 \text{ kJ} - (298.15 \text{ K})(-0.2429 \text{ kJ/K}) = -890.5 \text{ kJ} + 72.42 \text{ kJ} = -818.1 \text{ kJ}$$

(spontaneous)

6. Melting ice.

$$(a) T = \frac{6.01 \text{ kJ/mol}}{0.0220 \text{ kJ mol}^{-1} \text{ K}^{-1}} = \mathbf{273 \text{ K}} \text{ (0 } ^\circ\text{C, the melting point)}$$

(b) At 263.15 K: $\Delta G = 6.01 \text{ kJ/mol} - (263.15 \text{ K})(0.0220 \text{ kJ mol}^{-1} \text{ K}^{-1}) = \mathbf{+0.221 \text{ kJ/mol}}$: ice does **not** melt.

At 283.15 K: $\Delta G = 6.01 \text{ kJ/mol} - (283.15 \text{ K})(0.0220 \text{ kJ mol}^{-1} \text{ K}^{-1}) = \mathbf{-0.219 \text{ kJ/mol}}$: ice **melts** spontaneously.

7. Limestone at 1200 K.

$\Delta G^\circ = 179.2 \text{ kJ} - (1200 \text{ K})(0.1602 \text{ kJ/K}) = 179.2 \text{ kJ} - 192.2 \text{ kJ} = \mathbf{-13.0 \text{ kJ}}$: spontaneous (1200 K is above the switching temperature, 1119 K).

8. K from ΔG° .

$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{1.00 \times 10^4 \text{ J/mol}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} = -4.034$$

$K = e^{-4.034} = \mathbf{0.0177}$: K is less than 1, so **reactants** are favoured.

C. Challenge

9. Daniell cell.

(a) $\Delta G^\circ = -nFE^\circ = -(2 \text{ mol})(96485 \text{ C/mol})(1.10 \text{ V}) = -2.123 \times 10^5 \text{ J} = \mathbf{-212 \text{ kJ}}$ ($\text{C} \times \text{V} = \text{J}$)

(b) $\ln K = -\frac{\Delta G^\circ}{RT} = \frac{2.123 \times 10^5 \text{ J/mol}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} = 85.63$, so $K = e^{85.63} \approx \mathbf{1.5 \times 10^{37}}$

The reaction goes essentially **to completion**: at equilibrium almost no Cu^{2+} would remain.