

Entropy, Gibbs energy and spontaneity

AP Chemistry · Worksheet answers

Each answer shows the formula, the substitution and the result with its unit, final values in bold. Pay special attention to unit conversions between J and kJ and to the sign of each quantity, as these cost the most marks.

Level: AP Chemistry · **Curriculum:** AP Chem Unit 9

Problem 1 Predict the sign of ΔS

(a) **positive**: ions in solution are more dispersed. (b) **negative**: two gas molecules become one. (c) **positive**: a gas is produced. (d) **negative**: condensation.

Problem 2 Rank by entropy

A solid has the least freedom, a liquid more, and a gas the most. **Fe(s), then H₂O(l), then He(g)**, with S° of 27.3, 69.9 and 126.2 J/(mol·K).

Problem 3 Entropy of water formation

$\Delta S^\circ = 2(69.9) - [2(130.7) + 205.1] = 139.8 - 466.5 = -\mathbf{326.7 \text{ J/(mol}\cdot\text{K)}}$. Three gas molecules become a liquid, so entropy falls.

Problem 4 A simple ΔG calculation

$\Delta S = -0.100 \text{ kJ/K}$. $\Delta G = -40.0 - (298)(-0.100) = -40.0 + 29.8 = -\mathbf{10.2 \text{ kJ}}$. ΔG is negative, so it is spontaneous.

Problem 5 Endothermic but spontaneous

$\Delta G = 50.0 - (400)(0.150) = 50.0 - 60.0 = -\mathbf{10.0 \text{ kJ}}$. It is spontaneous because the entropy term outweighs the positive ΔH .

Problem 6 Four cases

1. **D** (ΔH negative, ΔS positive): both terms favour a negative ΔG .
2. **B** (both positive): $-\Delta S$ outweighs ΔH only when T is large.
3. **C** (both negative): ΔH outweighs $-\Delta S$ only when T is small.

Problem 7 Entropy of methane combustion

1. $\Delta S^\circ = [213.8 + 2(188.8)] - [186.3 + 2(205.1)] = 591.4 - 596.5 = -\mathbf{5.1 \text{ J/(mol}\cdot\text{K)}}$.

2. Three gas molecules of reactants give three gas molecules of products, so the number of gas particles hardly changes and ΔS° is close to zero.

Problem 8 Decomposition of limestone

1. $\Delta S^\circ = 39.8 + 213.8 - 92.9 = \mathbf{160.7 \text{ J/(mol}\cdot\text{K)}}$.
2. $\Delta G^\circ = 178.3 - (298)(0.1607) = \mathbf{130.4 \text{ kJ}}$, non-spontaneous.
3. $T = \Delta H^\circ / \Delta S^\circ = 178\,300 / 160.7 = \mathbf{1110 \text{ K}}$.

Problem 9 Free energy of formation

$\Delta G^\circ = \Sigma \Delta G^\circ_f(\text{products}) - \Sigma \Delta G^\circ_f(\text{reactants}) = (-603.3 - 394.4) - (-1128.8) = \mathbf{+131.1 \text{ kJ}}$.
This agrees with +130.4 kJ from $\Delta H^\circ - T\Delta S^\circ$, within rounding, and the positive value shows decomposition is not spontaneous at 298 K.

Problem 10 Melting of ice

1. $T = 6010 / 22.0 = \mathbf{273 \text{ K}}$.
2. At 263 K: $\Delta G = 6010 - (263)(22.0) = \mathbf{+224 \text{ J/mol}}$. At 283 K: $\Delta G = 6010 - (283)(22.0) = \mathbf{-216 \text{ J/mol}}$.
3. Melting is spontaneous at 283 K, where ΔG is negative.

Problem 11 Boiling of ethanol

1. At equilibrium $\Delta S = \Delta H / T = 38\,600 / 351 = \mathbf{110 \text{ J/(mol}\cdot\text{K)}}$.
2. The liquid becomes a gas, with far greater freedom of motion.

Problem 12 K from ΔG°

$\ln K = -\Delta G^\circ / RT = 20\,000 / (8.314 \times 298) = 8.072$. $K = e^{8.072} = \mathbf{3.2 \times 10^3}$.

Problem 13 ΔG° from K

$\Delta G^\circ = -RT \ln K = -(8.314)(298)(\ln 1.0 \times 10^{-5}) = -2477.6 \times (-11.513) = +28\,524 \text{ J} = \mathbf{+28.5 \text{ kJ}}$. A K below 1 gives a positive ΔG° : reactants are favoured.

Problem 14 Free energy away from standard state

1. $\Delta G = \Delta G^\circ + RT \ln Q = 10\,000 + (8.314)(298)(\ln 1.0 \times 10^{-3}) = 10\,000 - 17\,115 = \mathbf{-7.1 \text{ kJ}}$.
2. ΔG is negative, so the **forward reaction proceeds**. Q is below K, so the system shifts to the right.

Problem 15 Reading a ΔG against T line

1. Slope = $[20 - (-20)] / (500 - 300) = +0.20 \text{ kJ/K}$. Since slope = $-\Delta S$, **$\Delta S = -0.20 \text{ kJ/(mol}\cdot\text{K)} = -200 \text{ J/(mol}\cdot\text{K)}$** .
2. $-20 = \Delta H - (300)(-0.20) = \Delta H + 60$, so **$\Delta H = -80 \text{ kJ}$** .
3. $T = \Delta H/\Delta S = -80 / -0.20 = \textbf{400 K}$.

Problem 16 Making sulfur trioxide

1. $\Delta H^\circ = 2(-395.7) - 2(-296.8) = \textbf{-197.8 kJ}$; $\Delta S^\circ = 2(256.8) - [2(248.2) + 205.1] = \textbf{-187.9 J/(mol}\cdot\text{K)}$.
2. $\Delta G^\circ = -197.8 - (298)(-0.1879) = \textbf{-141.8 kJ}$.
3. $T = -197.8 / -0.1879 = \textbf{1053 K}$.

Problem 17 Temperature and the equilibrium constant

1. $\Delta G^\circ = -197.8 - (800)(-0.1879) = \textbf{-47.5 kJ}$.
2. $\ln K = 47\,500 / (8.314 \times 800) = 7.14$, so $K = \textbf{1.3} \times 10^3$.
3. K is smaller at high T, but the rate is far greater. A catalyst and a moderate temperature compromise between yield and speed.

Problem 18 Coupled reactions

1. $\Delta G^\circ(\text{total}) = 13.8 + (-30.5) = \textbf{-16.7 kJ}$.
2. $\ln K = 16\,700 / (8.314 \times 298) = 6.74$; $K = \textbf{8.5} \times 10^2$.
3. The sum of the free energy changes is negative, so the combined process is spontaneous even though the first step alone is not.

Problem 19 Instant cold pack

1. $\Delta G = 25.7 - (298)(0.1087) = 25.7 - 32.4 = \textbf{-6.7 kJ/mol}$.
2. The increase in entropy as ions disperse in water outweighs the energy absorbed ($-\Delta S$ is more negative than ΔH is positive).
3. $T = 25\,700 / 108.7 = \textbf{236 K}$, far below the freezing point of water, so dissolving is spontaneous at every temperature at which the solution exists.

Problem 20 Entropy of the universe

1. $\Delta S(\text{surr}) = +92\,200 / 298 = \textbf{309.4 J/(mol}\cdot\text{K)}$.
2. $\Delta S(\text{univ}) = 309.4 + (-198.7) = \textbf{110.7 J/(mol}\cdot\text{K)}$.
3. $-\Delta G/T = -(-33\,000)/298 = 110.7 \text{ J/(mol}\cdot\text{K)}$, which matches within rounding, because $\Delta S(\text{univ}) = \Delta S - \Delta H/T = -\Delta G/T$. It is positive, so the reaction is spontaneous.