Unit 4 · Chemical Thermodynamics

ANSWER KEY · FOR TEACHERS

Full marks 33

Give the marks for the points in the marking scheme; an answer in other words that says the same is right.

1 Key words

K · 4

1. isolated
2. intensive
3. state function
4. enthalpy
5. endothermic
6. entropy
7. spontaneous
8. Gibbs free energy

Each carries 0.5 mark.

2 Label the diagram

U · 2

1. $CO_2(g) + 2H_2O(g)$
2. $CO_2(g) + 2H_2O(l)$
3. -88 kJ
4. -890 kJ

Each carries 0.5 mark.

3 Multiple choice

i. **c.** enthalpy — K · 1

Enthalpy depends only on the state of the system. Heat and work are path functions: how much of each is exchanged depends on how the change is made.

ii. **c.** +650 J — A · 1

$\Delta E = q + w$. Heat absorbed and work done on the system are both positive: $\Delta E = +250 + 400 =$ **+650 J**.

iii. **b.** $C(s) + O_2(g) \rightarrow CO_2(g)$ — U · 1

$\Delta H = \Delta E + \Delta n_g RT$. Only for $C + O_2 \rightarrow CO_2$ is there one mole of gas on each side (the carbon is solid), so $\Delta n_g = 0$ and $\Delta H = \Delta E$.

iv. **c.** ice melting — U · 1

Melting turns an ordered crystal into a liquid whose molecules move about: more disorder. Freezing and condensing do the opposite, and the ammonia reaction turns 4 mol of gas into 2.

v. **a.** spontaneous at every temperature — U · 1

$\Delta G = \Delta H - T\Delta S$: with ΔH negative and $-T\Delta S$ negative too, ΔG is negative at every temperature.

4 Short answers

a. MARKING SCHEME — U · 2

- ✓ ΔH is the same by any route, in one step or several.
- ✓ One use: finding an enthalpy change that can't be measured directly.

b. MARKING SCHEME — U · 2

- ✓ Spontaneous: goes on by itself (an example).
- ✓ Non-spontaneous: needs energy from outside all the time (an example).

c. MARKING SCHEME — A · 3

- ✓ Bonds broken 851 kJ.
- ✓ Bonds formed 1025 kJ.
- ✓ $\Delta H = -174$ kJ/mol, exothermic.

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5 Long answer

ANSWER U · 4

Gibbs free energy, G = H − TS, is a state function whose decrease at constant temperature and pressure is the most useful work a process can do; its sign tells whether a process is spontaneous. $\Delta G = \Delta H - T\Delta S$. $\Delta G < 0$: spontaneous; $\Delta G > 0$: non-spontaneous.
With ΔH and ΔS both positive, at low temperatures ΔH outweighs $T\Delta S$, so ΔG is positive and the reaction does not go; at high temperatures $T\Delta S$ outweighs ΔH, ΔG becomes negative and it goes (as limestone decomposes only when strongly heated). It changes over at $T = \Delta H/\Delta S$.
$\Delta G = 0$ means the system is at **equilibrium**: neither direction is favored.

MARKING SCHEME

- ✓ G = H − TS, the energy available for useful work; its sign decides spontaneity.
- ✓ $\Delta G = \Delta H - T\Delta S$, with $\Delta G < 0$ spontaneous.
- ✓ Both positive: non-spontaneous at low T, spontaneous at high T (above $\Delta H/\Delta S$).
- ✓ $\Delta G = 0$: equilibrium.

6 Numerical problems

a. **ANSWER** A · 4

i. $\Delta H^\circ = [2(-393.5) + 2(-285.8)] - [52.4 + 3(0)] = -787.0 - 571.6 - 52.4 =$ **−1411.0 kJ/mol**.
ii. $\Delta n_g = 2 - (1 + 3) = -2$ (water is liquid). $\Delta E = \Delta H - \Delta n_g RT = -1411.0 - (-2)(8.314 \times 10^{-3})(298) = -1411.0 + 4.96 =$ **−1406.0 kJ/mol**.
iii. Molar mass of C_2H_4 = 28 g/mol: 1411.0/28 = **50.4 kJ/g**.
iv. 1000/50.4 = **19.8 g**.

MARKING SCHEME

- ✓ $\Delta H^\circ c = -1411.0$ kJ/mol.
- ✓ $\Delta E = -1406.0$ kJ/mol, with $\Delta n_g = -2$.
- ✓ 50.4 kJ/g.
- ✓ 19.8 g.

b. **ANSWER** A · 4

i. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 57{,}200 - 298 \times 175.8 = 57{,}200 - 52{,}388 =$ **+4,812 J/mol (+4.8 kJ/mol)**: positive, so not spontaneous under standard conditions.
ii. $T = \Delta H^\circ/\Delta S^\circ = 57{,}200/175.8 =$ **325 K** (52 °C).
iii. $\Delta G^\circ = -2.303RT \log K$: $\log K = -4812/(2.303 \times 8.314 \times 298) = -0.843$, so **K = 0.14**.
iv. $\Delta G^\circ = 57{,}200 - 400 \times 175.8 =$ **−13,120 J/mol (−13.1 kJ/mol)**: spontaneous.

MARKING SCHEME

- ✓ $\Delta G^\circ = +4.8$ kJ/mol at 298 K, not spontaneous.
- ✓ Spontaneous above 325 K.
- ✓ K = 0.14.
- ✓ $\Delta G^\circ = -13.1$ kJ/mol at 400 K.

7 Think

ANSWER HA · 3

Spontaneity is decided by $\Delta G = \Delta H - T\Delta S$, not by ΔH alone. Dissolving is endothermic ($\Delta H > 0$), but the ordered crystal breaks up into ions spread through the water, a large increase in disorder ($\Delta S > 0$). At room temperature $T\Delta S$ is larger than ΔH, so ΔG is negative and the salt dissolves by itself.

MARKING SCHEME

- ✓ Spontaneity depends on $\Delta G = \Delta H - T\Delta S$, not on ΔH alone.
- ✓ Dissolving increases entropy greatly (ordered crystal → ions spread through water).
- ✓ $T\Delta S > \Delta H$, so $\Delta G < 0$.

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8 Activity: Warm or cold when it dissolves?

(not marked)

WHAT STUDENTS SHOULD FIND

Ammonium chloride ($\Delta H°_{sol}$ +14.8 kJ/mol) and urea (+15.4 kJ/mol) make the water colder: endothermic, fit for a cold pack. Anhydrous calcium chloride (−82.8 kJ/mol) and sodium hydroxide (−44.5 kJ/mol) make it warmer: exothermic, fit for a self-heating pack. Whatever dissolves by itself has a negative ΔG; for the endothermic ones the entropy must have increased enough that $T\Delta S$ outweighs ΔH.

Marks by level	Knowledge	Understanding	Application	Higher ability	Total
Marks	5	13	12	3	**33**

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