AP Chemistry Unit 9 Easier Practice Set

Applications of Thermodynamics

Building Confidence with Entropy, Gibbs Free Energy, and Spontaneity

APChemistryRescue.com

📋 Practice Set Information

- **Total Points:** 75 points
- **Suggested Time:** 70–100 minutes
- **Questions:** 10 (scaffolded from entropy predictions → ΔG calculations → spontaneity → ΔG-K relationship)
- **Topics:** Entropy (ΔS), Gibbs free energy (ΔG), spontaneity, temperature dependence, $\Delta G° = -RT \ln K$
- **Skills:** Entropy predictions, ΔS° calculations, $\Delta G = \Delta H - T\Delta S$, spontaneity analysis, crossover temperature, equilibrium connections

🔬 ESSENTIAL THERMODYNAMICS FORMULAS & CONSTANTS

GIBBS FREE ENERGY:

$\Delta G = \Delta H - T\Delta S$ (at any temperature)

$\Delta G° = \Delta H° - T\Delta S°$ (standard conditions: 25°C = 298 K)

$\Delta G° = \Sigma\Delta G°_f(\text{products}) - \Sigma\Delta G°_f(\text{reactants})$

SPONTANEITY CRITERIA:

$\Delta G < 0$ → Spontaneous (thermodynamically favorable)

$\Delta G = 0$ → At equilibrium (no net change)

$\Delta G > 0$ → Non-spontaneous (reverse is spontaneous)

ENTROPY CALCULATIONS:

$$\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})$$

NOTE: S° for elements is NOT zero! (unlike ΔH°_f)

GIBBS FREE ENERGY AND EQUILIBRIUM:

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$R = 8.314\ \text{J/(mol·K)} = 0.008314\ \text{kJ/(mol·K)}$$

⚡ Critical Sign Conventions:

- **$\Delta S > 0$:**

  Entropy increases (more disorder/freedom)
- **$\Delta S < 0$:**

  Entropy decreases (less disorder/more order)
- **$\Delta H < 0$:**

  Exothermic (releases heat)
- **$\Delta H > 0$:**

  Endothermic (absorbs heat)
- **$\Delta G < 0$:**

  Spontaneous at given T
- **$\Delta G > 0$:**

  Non-spontaneous at given T

🔥 Unit Conversion (CRITICAL!):

ΔH is typically in

kJ/mol

ΔS is typically in

J/(mol·K)

Must convert:

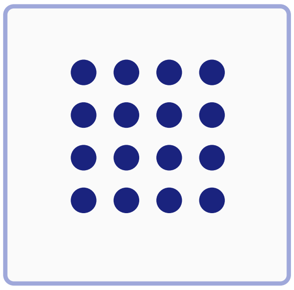
1 kJ = 1000 J

For $\Delta G = \Delta H - T\Delta S$, convert ΔS to kJ/(mol·K) by dividing by 1000, OR convert ΔH to J/mol by multiplying by 1000

Question 1: Predicting Entropy Changes (Qualitative) (8 points)

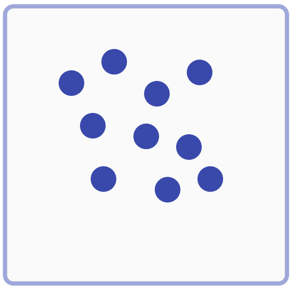
Entropy (S) is a measure of disorder or molecular freedom. Higher entropy = more disorder.

SOLID



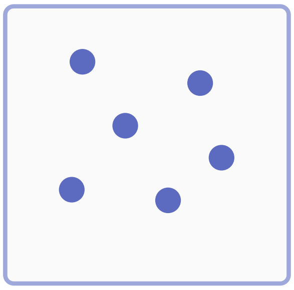
LOW Entropy
Ordered, fixed positions

LIQUID



MODERATE Entropy
Random, mobile

GAS



HIGH Entropy
Widely dispersed, free

(a) Predict whether ΔS is **positive or negative** for each process:

(i) $H_2O(s) \rightarrow H_2O(l)$ (ice melting)

(ii) $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ (3 moles gas → 2 moles gas)

(iii) $NH_3(g) \rightarrow NH_3(aq)$ (dissolving ammonia)

Work Space:

(b) Which substance has higher entropy at 25°C: **$CH_4(g)$ or**

$C_{10}H_{22}$(l) (decane, a liquid hydrocarbon)? Explain using molecular complexity and state.

Work Space:

(c) Explain why entropy generally **increases** when:

- Temperature increases
- Pressure decreases (for gases)
- A solid dissolves in water

Work Space:

Question 2: Calculating ΔS° (Quantitative) (8 points)

Calculate ΔS° for the combustion of methane:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Standard Molar Entropies (S°) at 25°C:

Substance	S° (J/(mol·K))
CH_4(g)	186

$O_2(g)$	205
$CO_2(g)$	214
$H_2O(g)$	189

Formula:

$\Delta S° = \Sigma S°(\text{products}) - \Sigma S°(\text{reactants})$

Remember:

Multiply each S° by its stoichiometric coefficient!

(a) Calculate **ΣS°(products)**. Show your work.

Work Space:

(b) Calculate **ΣS°(reactants)**. Show your work.

Work Space:

(c) Calculate **ΔS°**. Include units. Is ΔS° positive or negative? Does this make sense for this reaction?

Work Space:

Question 3: ΔG Sign Analysis (Four Quadrants) (9 points)

The spontaneity of a reaction depends on both ΔH and ΔS through the equation **$\Delta G = \Delta H - T\Delta S$**. The four possible combinations are shown below:

$\Delta H < 0$ (exothermic)
$\Delta S > 0$ (entropy increases)

$\Delta G = (-) - T(+) = (-)$ at ALL temperatures

ALWAYS SPONTANEOUS

$\Delta H > 0$ (endothermic)
$\Delta S < 0$ (entropy decreases)

$\Delta G = (+) - T(-) = (+)$ at ALL temperatures

NEVER SPONTANEOUS

$\Delta H < 0$ (exothermic)
$\Delta S < 0$ (entropy decreases)

$\Delta G = (-) - T(-) = ?$

Spontaneous at LOW T
(ΔH term dominates)

$\Delta H > 0$ (endothermic)
$\Delta S > 0$ (entropy increases)

$\Delta G = (+) - T(+) = ?$

Spontaneous at HIGH T
(TΔS term dominates)

(a) For a reaction with $\Delta H^\circ = -150$ kJ/mol and $\Delta S^\circ = +200$ J/(mol·K), predict whether ΔG° is positive or negative at 298 K. Calculate ΔG° to verify.

Unit conversion:

$\Delta S^\circ = +200 \text{ J/(mol·K)} = +0.200 \text{ kJ/(mol·K)}$

Work Space:

(b) For a reaction with ΔH° = +50 kJ/mol and ΔS° = −100 J/(mol·K), is this reaction spontaneous at 298 K? Will it ever be spontaneous at any temperature?

Work Space:

(c) For a reaction with ΔH° = +30 kJ/mol and ΔS° = +150 J/(mol·K), which term (ΔH or TΔS) dominates at low temperature? At high temperature? At what type of temperature will this reaction become spontaneous?

Work Space:

Question 4: Temperature Dependence and Crossover Temperature (10 points)

The decomposition of calcium carbonate is:

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

ΔH° = +178 kJ/mol ΔS° = +161 J/(mol·K)

(a) Based on the signs of ΔH° and ΔS°, at what type of temperature (high or low) will this reaction be spontaneous?

Work Space:

(b) Calculate ΔG° at **298 K**. Is the reaction spontaneous at room temperature?

Work Space:

(c) Calculate the **crossover temperature** (T at which ΔG° = 0) using T = ΔH°/ΔS°. Above this temperature, the reaction is spontaneous.

At equilibrium:

$\Delta G° = 0$

$0 = \Delta H° - T\Delta S°$

$T = \Delta H°/\Delta S°$

Convert units:

ΔS° = 161 J/(mol·K) = 0.161 kJ/(mol·K)

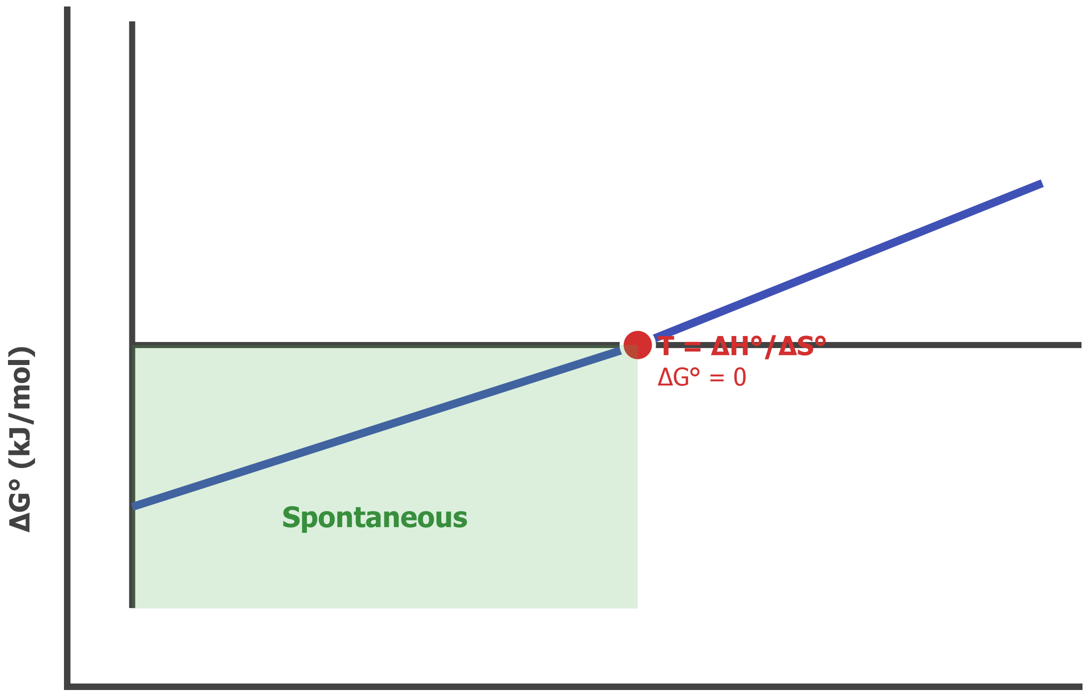
Work Space:

(d) Calculate ΔG° at **1200 K**. Is the reaction spontaneous at this temperature?

Work Space:

Question 5: ΔG vs. Temperature Graph (8 points)

For a reaction with ΔH° = −50 kJ/mol and ΔS° = −100 J/(mol·K) = −0.100 kJ/(mol·K), the graph of ΔG° vs. T is shown below:



(ΔG° < 0) Non-spontaneous

(ΔG° > 0) +50 0 −50 0 500 1000 Slope = −ΔS° (positive slope because ΔS° < 0) y-intercept = ΔH°

(a) Explain why the slope of the line is **positive** (ΔG increases with T) for this reaction.

Work Space:

(b) What is the physical meaning of the **y-intercept** (where the line crosses the y-axis at T = 0)?

Work Space:

(c) At what temperature is ΔG° = 0? Below this temperature, is the reaction spontaneous or non-spontaneous?

Work Space:

Question 6: Gibbs Free Energy of Formation (7 points)

Calculate ΔG° for the reaction using standard free energies of formation:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Substance	ΔG°_f (kJ/mol)
$NO(g)$	+87
$O_2(g)$	0
$NO_2(g)$	+51

$$\Delta G^\circ\_rxn = \Sigma\Delta G^\circ\_f(products) - \Sigma\Delta G^\circ\_f(reactants)$$

(a) Calculate ΔG°_rxn. Show all work with stoichiometric coefficients.

Work Space:

(b) Is this reaction spontaneous at 25°C under standard conditions?

Work Space:

Question 7: ΔG° and Equilibrium Constant (10 points)

The relationship between Gibbs free energy and the equilibrium constant is:

$$\Delta G^\circ = -RT \ln K$$

R = 8.314 J/(mol·K) | T in Kelvin | Use natural log (ln), NOT $\log_{10}$

(a) For a reaction with $K = 1.0 \times 10^5$ at 298 K, calculate ΔG°. Is the reaction product-favored or reactant-favored?

Steps:

1. $\Delta G^\circ = -RT \ln K$
2. $R = 8.314$ J/(mol·K), $T = 298$ K
3. $\ln(1.0 \times 10^5) = \ln(100{,}000) \approx 11.51$
4. Convert J to kJ (÷1000)

Work Space:

(b) For a reaction with $\Delta G° = +20$ kJ/mol at 298 K, calculate K.

Rearrange:

$\ln K = -\Delta G°/(RT)$

$K = e^{[-\Delta G°/(RT)]}$

Work Space:

(c) Complete the table showing the relationship between ΔG°, K, and spontaneity:

ΔG°	K value	Spontaneity
$\Delta G° < 0$		
$\Delta G° = 0$		
$\Delta G° > 0$		

Work Space:

Question 8: Phase Transitions and Entropy (6 points)

For the melting of ice at 0°C (273 K):

$H_2O(s) \rightarrow H_2O(l)$ ΔH°_fus = +6.01 kJ/mol

(a) Calculate ΔS°_fus for this phase transition. Use ΔG = 0 at equilibrium (melting point).

At melting point:

ΔG = 0 (solid and liquid coexist)

$0 = \Delta H - T\Delta S$

$\Delta S = \Delta H/T$

Work Space:

(b) Is ΔS positive or negative for melting? Explain why this makes sense.

Work Space:

Question 9: ΔG and Non-Standard Conditions (7 points)

Under non-standard conditions, use:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Q = reaction quotient (like K, but with non-equilibrium concentrations)

For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta G^\circ = -33$ kJ/mol at 298 K.

A reaction mixture contains: $[N_2] = 1.0$ M, $[H_2] = 1.0$ M, $[NH_3] = 0.10$ M.

(a) Calculate **Q** for this mixture.

Work Space:

(b) Calculate **ΔG** under these conditions. Is the reaction spontaneous in the forward direction?

Work Space:

Question 10: Conceptual Synthesis (4 points)

(a) A student claims: "If ΔG is negative, the reaction will occur quickly." Is this correct? Explain the difference between **thermodynamics** (ΔG) and **kinetics** (rate).

Work Space:

(b) Explain why ΔG = 0 at equilibrium, even though the forward and reverse reactions are still occurring.

Work Space:

END OF PRACTICE SET

Total: 75 points | Answer key begins on next page

📘 COMPLETE ANSWER KEY & SCORING GUIDE

Question 1: Predicting Entropy Changes (8 points)

(a) Predict ΔS sign (3 points, 1 pt each):

(i) $H_2O(s) \rightarrow H_2O(l)$: $\Delta S > 0$ (positive). Ice melting increases disorder as molecules go from fixed lattice positions to mobile liquid state.

(ii) $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$: $\Delta S < 0$ (negative). 3 moles of gas → 2 moles of gas; fewer gas molecules means less disorder.

(iii) $NH_3(g) \rightarrow NH_3(aq)$: $\Delta S < 0$ (negative). Free gas molecules → dissolved molecules with restricted motion in solution.

(b) Higher entropy: CH_4 or $C_{10}H_{22}$? (2 points):

$CH_4(g)$ has higher entropy at 25°C. (1 pt) Even though $C_{10}H_{22}$ is more complex (higher molecular complexity usually → higher S), CH_4 is a GAS while $C_{10}H_{22}$ is a LIQUID. The effect of physical state (gas > liquid >> solid) dominates over molecular complexity. Gases have much higher entropy due to freedom of motion. (1 pt)

(c) Why entropy increases (3 points, 1 pt per explanation):

- **Temperature increases:** Higher T → more kinetic energy → more possible molecular motions/arrangements → higher entropy.
- **Pressure decreases (gases):** Lower P → larger volume → gas molecules more spread out → more positional disorder → higher entropy.
- **Solid dissolves:** Ordered crystal lattice → dispersed ions/molecules in solution → increased disorder → higher entropy.

Scoring: (a) 3 pts; (b) 2 pts; (c) 3 pts

Question 3: ΔG Sign Analysis (9 points)

(a) ΔH° = −150 kJ/mol, ΔS° = +200 J/(mol·K) (3 points):

This is ΔH < 0, ΔS > 0 → always spontaneous (favorable quadrant). (0.5 pt)

$$\Delta G° = \Delta H° - T\Delta S° = -150 \text{ kJ/mol} - (298 \text{ K})(0.200 \text{ kJ/(mol·K)})$$

$$= -150 - 59.6 = -210 \text{ kJ/mol}$$

ΔG° < 0 (negative), so **spontaneous** at 298 K. (1.5 pts for calculation; 1 pt for conclusion)

(b) ΔH° = +50 kJ/mol, ΔS° = −100 J/(mol·K) (3 points):

$$\Delta G° = +50 - (298)(−0.100) = +50 + 29.8 = +79.8 \text{ kJ/mol}$$

Not spontaneous at 298 K (ΔG° > 0). (1 pt)

This is ΔH > 0, ΔS < 0 → **never spontaneous** at any temperature. Both terms make ΔG positive: (+) − T(−) = (+) + (+) = always (+). (2 pts for explanation)

(c) ΔH° = +30 kJ/mol, ΔS° = +150 J/(mol·K) (3 points):

Low T: ΔH term dominates (TΔS small), so ΔG ≈ ΔH > 0 (non-spontaneous). (1 pt)

High T: TΔS term dominates, so ΔG = (+) − large (+) = (−) (spontaneous). (1 pt)

This reaction becomes spontaneous at **high temperature**. (1 pt)

Scoring: (a) 3 pts; (b) 3 pts; (c) 3 pts

Question 7: ΔG° and Equilibrium Constant (10 points)

(a) Calculate ΔG° from K = 1.0 × 10⁵ (4 points):

$$\Delta G° = -RT \ln K = -(8.314 \text{ J/(mol·K)})(298 \text{ K}) \ln(1.0 \times 10^5)$$

$$\ln(10^5) = 11.51$$

$$\Delta G° = -(8.314)(298)(11.51) = -28,520 \text{ J/mol} = -28.5 \text{ kJ/mol}$$

(2 pts for calculation; 1 pt for unit conversion)

Product-favored (K >> 1 and ΔG° < 0 both indicate products predominate at equilibrium). (1 pt)

(b) Calculate K from ΔG° = +20 kJ/mol (3 points):

$$\ln K = -\frac{\Delta G°}{RT} = -\frac{20,000 \text{ J/mol}}{(8.314)(298)} = -\frac{20,000}{2478} = -8.07$$

$$K = e^{-8.07} = 3.1 \times 10^{-4}$$

(2 pts for calculation; 1 pt for answer)

(c) Complete table (3 points, 1 pt per row):

ΔG°	K value	Spontaneity
ΔG° < 0	K > 1	Product-favored (spontaneous forward)
ΔG° = 0	K = 1	At equilibrium (equal amounts)
ΔG° > 0	K < 1	Reactant-favored (non-spontaneous forward)

Scoring: (a) 4 pts; (b) 3 pts; (c) 3 pts

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