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AP Chemistry Unit 6

ADVANCED FRQ PRACTICE

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Thermodynamics

Difficulty: Challenging | Time: 150 minutes (15 min/question)

🌡️ Master Thermodynamics: From Enthalpy to Entropy to Gibbs Free Energy!

📊 Reference Information & Key Equations

- **First Law:** $\Delta E = q + w$ (or $\Delta U = q + w$)
- **Enthalpy:** $\Delta H = \Delta E + P\Delta V$ (at constant P: $\Delta H = q_p$)
- **Calorimetry:** $q = mc\Delta T$ or $q = C\Delta T$
- **Hess's Law:** $\Delta H_{rxn} = \Sigma\Delta H_f^\circ(\text{products}) - \Sigma\Delta H_f^\circ(\text{reactants})$
- **Bond Energy:** $\Delta H_{rxn} = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed})$
- **Gibbs Free Energy:** $\Delta G = \Delta H - T\Delta S$
- **Standard Conditions:** $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- **Spontaneity:** $\Delta G < 0$ (spontaneous), $\Delta G > 0$ (nonspontaneous), $\Delta G = 0$ (equilibrium)
- **Free Energy & Equilibrium:** $\Delta G^\circ = -RT \ln K$
- **Constants:** $R = 8.314$ J/(mol·K) $= 0.08314$ L·bar/(mol·K)

⚡ **Unit 6 Success Tips:** Always identify system vs surroundings, use correct sign conventions (exo: $\Delta H<0$, endo: $\Delta H>0$), convert temperatures to Kelvin, watch units (kJ vs J), predict spontaneity using $\Delta G = \Delta H - T\Delta S$ analysis, and remember entropy increases with disorder!

1 Calorimetry & Heat Transfer

A student performs a calorimetry experiment to determine the specific heat capacity of an unknown metal.

Experimental Data:

- Mass of metal sample: 45.0 g
- Initial temperature of metal: 98.5°C
- Mass of water in calorimeter: 100.0 g
- Initial temperature of water: 22.0°C
- Final temperature of system: 25.8°C
- Specific heat capacity of water: 4.18 J/(g·°C)
- Heat capacity of calorimeter: 15.0 J/°C

(a) Calculate the heat gained by the water. Show all work with proper units. **(2 points)**

(b) Calculate the heat gained by the calorimeter. **(2 points)**

(c) Calculate the total heat gained by the water and calorimeter. **(1 point)**

(d) Using conservation of energy, calculate the heat lost by the metal. Explain the sign of this value. **(2 points)**

(e) Calculate the specific heat capacity of the metal. Show all work with proper units. **(3 points)**

(f) The metal is either aluminum (c = 0.897 J/(g·°C)), iron (c = 0.449 J/(g·°C)), or copper (c = 0.385 J/(g·°C)). Identify the metal and calculate the percent error. **(2 points)**

(g) List two specific experimental errors that could cause the calculated specific heat to be lower than the actual value. Explain how each error would affect the result. **(3 points)**

2 Hess's Law & Enthalpy of Formation

Use the following thermochemical equations to determine the enthalpy of formation of methane (CH_4):

Given equations:

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H° = -393.5$ kJ

(2) $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$ $\Delta H° = -571.6$ kJ

(3) $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ $\Delta H° = -890.3$ kJ

(a) Write the target equation for the formation of methane from its elements in their standard states. **(1 point)**

(b) Using Hess's Law, manipulate equations (1), (2), and (3) to obtain the target equation. Show all steps, including how you reverse or multiply equations. **(4 points)**

(c) Calculate $\Delta H_f°$ for $CH_4(g)$. Show your work. **(2 points)**

(d) Is the formation of methane from its elements exothermic or endothermic? What does this tell you about the stability of methane relative to its elements? **(2 points)**

(e) Using standard enthalpies of formation, calculate $\Delta H°$ for the combustion of propane:

$$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$$

Given: $\Delta H_f°[C_3H_8(g)] = -104$ kJ/mol, $\Delta H_f°[CO_2(g)] = -393.5$ kJ/mol, $\Delta H_f°[H_2O(l)] = -285.8$ kJ/mol **(4 points)**

3 Entropy & Second Law of Thermodynamics

Consider the following processes at 298 K:

PROCESS	ΔS° (J/(MOL·K))
$H_2O(l) \rightarrow H_2O(g)$	+118.8
$H_2O(s) \rightarrow H_2O(l)$	+22.0
$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$	-326.8
$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$	-198.7

(a) Explain at the molecular level why the vaporization of water has a positive entropy change. Use the concepts of molecular disorder and microstates. **(3 points)**

(b) Compare the entropy changes for melting (s→l) and vaporization (l→g) of water. Explain why ΔS_{vap} is significantly larger than ΔS_{fus}. **(3 points)**

(c) Explain why the formation of water from H_2 and O_2 has a negative entropy change, even though it is a spontaneous reaction at 298 K. **(3 points)**

(d) Predict the sign of ΔS° for each of the following processes. Justify each prediction:

- (i) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
- (ii) $2\ NO_2(g) \rightarrow N_2O_4(g)$

- (iii) $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

(5 points)

(e) State the Second Law of Thermodynamics. Explain how a reaction with negative ΔS_{sys} can still be consistent with the Second Law. **(3 points)**

4 Gibbs Free Energy & Spontaneity

The decomposition of calcium carbonate is represented by:

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

Thermodynamic data at 298 K:
$\Delta H° = +178.3$ kJ/mol
$\Delta S° = +160.6$ J/(mol·K)

(a) Calculate ΔG° for this reaction at 298 K. Show all work with proper units. **(3 points)**

(b) Is this reaction spontaneous at 298 K? Explain your reasoning based on the value of ΔG°. **(2 points)**

(c) Calculate the temperature at which ΔG° = 0 (the equilibrium temperature). Show all work. **(3 points)**

(d) At what temperature range is this reaction spontaneous? Explain using the relationship between ΔG, ΔH, ΔS, and T. **(3 points)**

(e) Complete the following table predicting the spontaneity of reactions based on the signs of ΔH and ΔS:

ΔH	ΔS	ΔG AT LOW T	ΔG AT HIGH T	SPONTANEITY
-	+	?	?	?
+	-	?	?	?
-	-	?	?	?
+	+	?	?	?

(4 points)

5 Bond Energies & Enthalpy Calculations

Use bond energies to estimate ΔH° for the following reaction:

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

Average Bond Energies (kJ/mol):

C-H: 413 | O=O: 495 | C=O: 799 | O-H: 463

(a) Draw Lewis structures for all reactants and products, showing all bonds. **(2 points)**

(b) Calculate the total energy required to break all bonds in the reactants. Show your work. **(3 points)**

(c) Calculate the total energy released when forming all bonds in the products. Show your work. **(3 points)**

(d) Calculate the estimated ΔH° for the reaction using: $\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed})$. **(2 points)**

(e) The experimental value for this reaction is $\Delta H° = -802$ kJ/mol. Calculate the percent error of your estimate. **(2 points)**

(f) Explain why bond energy calculations provide only estimates of ΔH rather than exact values. **(2 points)**

6 Coupled Reactions & Free Energy

Consider the following reactions at 298 K:

Reaction A: $2\ Fe_2O_3(s) + 3\ C(s) \rightarrow 4\ Fe(s) + 3\ CO_2(g)$
ΔG° = +471 kJ

Reaction B: $C(s) + O_2(g) \rightarrow CO_2(g)$
ΔG° = -394 kJ

(a) Is Reaction A spontaneous at 298 K and standard conditions? Explain. **(2 points)**

(b) Write a balanced equation for the reduction of Fe_2O_3 by C in the presence of excess O_2, obtained by coupling Reactions A and B. **(3 points)**

(c) Calculate ΔG° for the coupled reaction. Is the coupled reaction spontaneous? **(3 points)**

(d) Explain how coupling reactions can be used to drive thermodynamically unfavorable processes. Use this example to illustrate your explanation. **(3 points)**

(e) In biological systems, ATP hydrolysis (ΔG° = -30.5 kJ/mol) is often coupled to nonspontaneous reactions. If a biosynthetic reaction has ΔG° = +15 kJ/mol, calculate ΔG° for the coupled process. Is it spontaneous? **(3 points)**

7 Phase Changes & Thermodynamics

Water boils at 100°C at 1 atm pressure. The following data are provided:

ΔH_{vap} = 40.7 kJ/mol

ΔS_{vap} = 109 J/(mol·K) at 100°C

(a) Calculate ΔG° for the vaporization of water at 100°C (373 K). **(2 points)**

(b) Explain the significance of your answer to part (a). What does ΔG = 0 indicate about a phase transition? **(2 points)**

(c) Calculate ΔG for the vaporization of water at 25°C (298 K), assuming ΔH and ΔS remain constant. **(3 points)**

(d) Based on your answer to part (c), predict whether water will spontaneously vaporize at 25°C and 1 atm. Explain the relationship between your answer and everyday observations. **(3 points)**

(e) Calculate ΔG for the vaporization of water at 125°C (398 K). What does this value tell you about the phase of water at this temperature and 1 atm? **(3 points)**

(f) Explain why ΔS is positive for the vaporization of any substance at the molecular level. **(2 points)**

8 Thermodynamics & Equilibrium

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

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ΔG° = -RT ln K

where R = 8.314 J/(mol·K) and T is in Kelvin
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(a) For a reaction at 298 K with $K = 1.5 \times 10^5$, calculate ΔG°. **(3 points)**

(b) For a reaction at 298 K with ΔG° = +12.5 kJ/mol, calculate the equilibrium constant K. **(3 points)**

(c) Explain the relationship between the sign and magnitude of ΔG° and the value of K:

- (i) What does $K > 1$ tell you about ΔG°?
- (ii) What does $K < 1$ tell you about ΔG°?
- (iii) What does $K = 1$ tell you about ΔG°?

(4 points)

(d) For the reaction $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$, $K = 6.8 \times 10^5$ at 298 K. Calculate ΔG° and determine whether products or reactants are favored at equilibrium. **(3 points)**

(e) Distinguish between ΔG° (standard free energy change) and ΔG (free energy change under non-standard conditions). Under what conditions are they equal? **(3 points)**

9 Coffee Cup Calorimetry

A student performs a neutralization reaction in a coffee cup calorimeter:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

Experimental Procedure:

- 50.0 mL of 2.00 M HCl at 22.5°C
- 50.0 mL of 2.00 M NaOH at 22.5°C
- Final temperature after mixing: 35.8°C
- Assume: density of solutions = 1.00 g/mL
- Assume: specific heat capacity = 4.18 J/(g·°C)
- Assume: heat capacity of calorimeter is negligible

(a) Calculate the total mass of the solution after mixing. **(1 point)**

(b) Calculate the temperature change (ΔT) for the solution. **(1 point)**

(c) Calculate the heat absorbed by the solution ($q_{solution}$). **(2 points)**

(d) Calculate the heat released by the reaction ($q_{reaction}$). Explain the sign convention. **(2 points)**

(e) Calculate the number of moles of water formed in the neutralization reaction. **(2 points)**

(f) Calculate the molar enthalpy of neutralization ($\Delta H_{neutralization}$) in kJ/mol.

(3 points)

(g) The accepted value for the neutralization of a strong acid with a strong base is approximately -57 kJ/mol. Compare your result and suggest reasons for any difference. **(3 points)**

10 Integrated Thermodynamics Problem

The Haber process for ammonia synthesis is:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Thermodynamic data at 298 K:
$\Delta H° = -92.2$ kJ/mol
$\Delta S° = -198.7$ J/(mol·K)
$\Delta G° = -32.9$ kJ/mol

(a) Verify that the given values are consistent with the equation $\Delta G° = \Delta H° - T\Delta S°$ at 298 K. **(2 points)**

(b) Calculate the equilibrium constant K for this reaction at 298 K. **(3 points)**

(c) Is this reaction spontaneous at 298 K under standard conditions? Does a large negative $\Delta G°$ guarantee a fast reaction? Explain. **(3 points)**

(d) Calculate $\Delta G°$ at 500 K, assuming $\Delta H°$ and $\Delta S°$ remain constant. **(3**

points)

(e) Explain why the Haber process becomes less favorable (smaller K) at higher temperatures, yet is industrially operated at 400-500°C. Discuss both thermodynamic and kinetic factors. **(4 points)**

(f) Explain why this reaction has a negative ΔS° value. How does this affect the temperature dependence of spontaneity? **(3 points)**

📋 DETAILED ANSWER KEY & SCORING RUBRIC

Complete Solutions with Step-by-Step Explanations

✓ Complete Solutions Summary

Question 1 (Calorimetry): q_{water} = 1588 J; q_{cal} = 57 J; q_{total} = 1645 J; q_{metal} = -1645 J; c_{metal} = 0.503 J/(g·°C) ≈ iron (0.449); errors include heat loss to surroundings (reduces measured ΔT) or incomplete thermal equilibrium.

Question 2 (Hess's Law): Target: $C(s) + 2H_2(g) \rightarrow CH_4(g)$; Manipulate: reverse equation (3), use (1) as is, use ½×(2); $\Delta H_f°[CH_4]$ = -74.8 kJ/mol (exothermic formation = stable); Propane combustion: ΔH° = -2220 kJ using $\Sigma\Delta H_f°$(products) - $\Sigma\Delta H_f°$(reactants).

Question 3 (Entropy): Vaporization increases disorder (gas >> liquid); ΔS_{vap} >> ΔS_{fus} due to massive volume/freedom increase; water formation has -ΔS but -ΔH dominates making ΔG<0; $CaCO_3$ decomp: +ΔS (gas produced); $2NO_2 \rightarrow N_2O_4$: -ΔS (2 mol→1 mol); NaCl dissolving: +ΔS (increased disorder); 2nd Law: $\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} > 0$.

Question 4 (Gibbs Free Energy): ΔG°(298K) = +130.4 kJ (nonspontaneous); T_{eq} = 1110 K; Spontaneous when T > 1110 K; Table: (-,+)=always spontaneous; (+,-)=never spontaneous; (-,-)=low T only; (+,+)=high T only.

Question 5 (Bond Energies): Bonds broken: 4(C-H) + 2(O=O) = 2642 kJ; Bonds formed: 2(C=O) + 4(O-H) = 3450 kJ; ΔH = -808 kJ (exothermic); % error

= 0.7%; Bond energies are averages from many compounds, actual values vary by molecular environment.

Question 6 (Coupled Reactions): Reaction A nonspontaneous (ΔG°>0); Coupled: $2Fe_2O_3 + 3C + 3O_2 \rightarrow 4Fe + 6CO_2$; $\Delta G°_{coupled}$ = -711 kJ (spontaneous); Coupling uses energy from favorable reaction to drive unfavorable one; ATP: ΔG° = -15.5 kJ (spontaneous).

Question 7 (Phase Changes): ΔG(373K) = 0 (equilibrium at BP); ΔG(298K) = +8.2 kJ (liquid favored, but evaporation occurs); ΔG(398K) = -2.7 kJ (gas favored); ΔS positive because gas molecules have vastly more positional freedom than liquid.

Question 8 (Equilibrium): $K=1.5\times10^5$: ΔG° = -29.7 kJ; ΔG°=+12.5 kJ: $K = 6.1\times10^{-3}$; K>1 means ΔG°<0 (products favored); K<1 means ΔG°>0 (reactants favored); K=1 means ΔG°=0; NH_3: ΔG° = -33.3 kJ (products strongly favored); ΔG° applies to standard conditions, ΔG to actual conditions; equal when all concentrations = 1 M (or pressures = 1 atm).

Question 9 (Neutralization): Total mass = 100 g; ΔT = 13.3°C; $q_{solution}$ = 5559 J; q_{rxn} = -5559 J (exothermic); moles H_2O = 0.100 mol; ΔH_{neut} = -55.6 kJ/mol ≈ -57 kJ/mol literature value; Differences due to heat loss, calorimeter absorption, or concentration effects.

Question 10 (Haber Process): Verification: -92.2 - 298(-0.1987) = -32.9 kJ ✓; $K = 5.8\times10^5$ at 298K; Spontaneous but kinetically slow (requires catalyst); ΔG° (500K) = +7.2 kJ (less favorable); High T needed for kinetics despite thermodynamic penalty; catalyst allows lower T operation; -ΔS because 4 mol gas → 2 mol gas (decreased freedom); Negative ΔS means spontaneity decreases as T increases (TΔS term becomes more positive).

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