



# AP Chemistry Unit 6

## ADVANCED FRQ PRACTICE

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Thermodynamics

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

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**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:**  $\Delta H_{rxn} = \sum \Delta H_f^\circ \text{ (products)} - \sum \Delta H_f^\circ \text{ (reactants)}$
- ▶ **Bond Energy:**  $\Delta H_{rxn} = \sum \text{(bonds broken)} - \sum \text{(bonds formed)}$
- ▶ **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:**  $R = 8.314 \text{ J/(mol}\cdot\text{K)} = 0.08314 \text{ L}\cdot\text{bar/(mol}\cdot\text{K)}$

**⚡ 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 ( $c = 0.897 \text{ J}/(\text{g} \cdot \text{°C})$ ), iron ( $c = 0.449 \text{ J}/(\text{g} \cdot \text{°C})$ ), or copper ( $c = 0.385 \text{ J}/(\text{g} \cdot \text{°C})$ ). 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 ( $\text{CH}_4$ ):

**Given equations:**

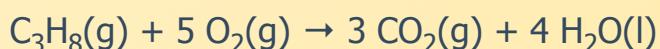
**(a)** Write the target equation for the formation of methane from its elements in their standard states. **(1 point)**

**(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  $\Delta H_f^\circ$  for  $\text{CH}_4(\text{g})$ . 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  $\Delta H^\circ$  for the combustion of propane:



Given:  $\Delta H_f^\circ[\text{C}_3\text{H}_8(\text{g})] = -104 \text{ kJ/mol}$ ,  $\Delta H_f^\circ[\text{CO}_2(\text{g})] = -393.5 \text{ kJ/mol}$ ,  $\Delta H_f^\circ[\text{H}_2\text{O(l)}] = -285.8 \text{ kJ/mol}$  **(4 points)**



## 3

## Entropy & Second Law of Thermodynamics

Consider the following processes at 298 K:

PROCESS	$\Delta S^\circ$ (J/(mol·K))
$\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$	+118.8
$\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)}$	+22.0
$2 \text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{H}_2\text{O(l)}$	-326.8
$\text{N}_2\text{(g)} + 3 \text{H}_2\text{(g)} \rightarrow 2 \text{NH}_3\text{(g)}$	-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  $\Delta S_{\text{vap}}$  is significantly larger than  $\Delta S_{\text{fus}}$ . **(3 points)**

**(c)** Explain why the formation of water from  $\text{H}_2$  and  $\text{O}_2$  has a negative entropy change, even though it is a spontaneous reaction at 298 K. **(3 points)**

**(d)** Predict the sign of  $\Delta S^\circ$  for each of the following processes. Justify each prediction:

- (i)  $\text{CaCO}_3\text{(s)} \rightarrow \text{CaO(s)} + \text{CO}_2\text{(g)}$
- (ii)  $2 \text{NO}_2\text{(g)} \rightarrow \text{N}_2\text{O}_4\text{(g)}$



**(5 points)**

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

**4**

## Gibbs Free Energy & Spontaneity

The decomposition of calcium carbonate is represented by:



**Thermodynamic data at 298 K:**

$$\Delta H^\circ = +178.3 \text{ kJ/mol}$$

$$\Delta S^\circ = +160.6 \text{ J}/(\text{mol}\cdot\text{K})$$

**(a)** Calculate  $\Delta G^\circ$  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  $\Delta G^\circ$ . **(2 points)**

**(c)** Calculate the temperature at which  $\Delta G^\circ = 0$  (the equilibrium temperature). Show all work. **(3 points)**

**(d)** At what temperature range is this reaction spontaneous? Explain using the relationship between  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$ , and  $T$ . **(3 points)**

**(e)** Complete the following table predicting the spontaneity of reactions based on the signs of  $\Delta H$  and  $\Delta S$ :

$\Delta H$	$\Delta S$	$\Delta G$ AT LOW T	$\Delta G$ AT HIGH T	SPONTANEITY
-	+	?	?	?
+	-	?	?	?
-	-	?	?	?
+	+	?	?	?

**(4 points)**

**5**

## Bond Energies & Enthalpy Calculations

Use bond energies to estimate  $\Delta H^\circ$  for the following reaction:



**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  $\Delta H^\circ$  for the reaction using:  $\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed})$ . **(2 points)**

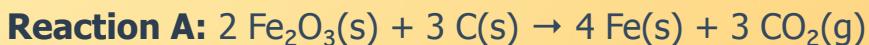
**(e)** The experimental value for this reaction is  $\Delta H^\circ = -802 \text{ kJ/mol}$ . Calculate the percent error of your estimate. **(2 points)**

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

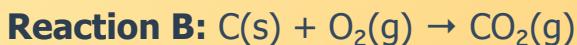
**6**

## Coupled Reactions & Free Energy

Consider the following reactions at 298 K:



$$\Delta G^\circ = +471 \text{ kJ}$$



$$\Delta G^\circ = -394 \text{ kJ}$$

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

**(2 points)**

**(b)** Write a balanced equation for the reduction of  $\text{Fe}_2\text{O}_3$  by C in the presence of excess  $\text{O}_2$ , obtained by coupling Reactions A and B. **(3 points)**

**(c)** Calculate  $\Delta G^\circ$  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 ( $\Delta G^\circ = -30.5 \text{ kJ/mol}$ ) is often coupled to nonspontaneous reactions. If a biosynthetic reaction has  $\Delta G^\circ = +15 \text{ kJ/mol}$ , calculate  $\Delta G^\circ$  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:

$$\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$$

$$\Delta S_{\text{vap}} = 109 \text{ J/(mol}\cdot\text{K}) \text{ at } 100^\circ\text{C}$$

**(a)** Calculate  $\Delta G^\circ$  for the vaporization of water at 100°C (373 K). **(2 points)**

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

**(c)** Calculate  $\Delta G$  for the vaporization of water at 25°C (298 K), assuming  $\Delta H$  and  $\Delta S$  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  $\Delta G$  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  $\Delta S$  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:

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

where  $R = 8.314 \text{ J/(mol}\cdot\text{K)}$  and  $T$  is in Kelvin

**(a)** For a reaction at 298 K with  $K = 1.5 \times 10^5$ , calculate  $\Delta G^\circ$ . **(3 points)**

**(b)** For a reaction at 298 K with  $\Delta G^\circ = +12.5 \text{ kJ/mol}$ , calculate the equilibrium constant  $K$ . **(3 points)**

**(c)** Explain the relationship between the sign and magnitude of  $\Delta G^\circ$  and the value of  $K$ :

- (i) What does  $K > 1$  tell you about  $\Delta G^\circ$ ?
- (ii) What does  $K < 1$  tell you about  $\Delta G^\circ$ ?
- (iii) What does  $K = 1$  tell you about  $\Delta G^\circ$ ?

**(4 points)**

**(d)** For the reaction  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ ,  $K = 6.8 \times 10^5$  at 298 K.

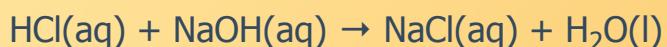
Calculate  $\Delta G^\circ$  and determine whether products or reactants are favored at equilibrium. **(3 points)**

**(e)** Distinguish between  $\Delta G^\circ$  (standard free energy change) and  $\Delta G$  (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:

**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 ( $\Delta T$ ) for the solution. **(1 point)**

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

**(d)** Calculate the heat released by the reaction ( $q_{\text{reaction}}$ ). 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 ( $\Delta H_{\text{neutralization}}$ ) 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:



**Thermodynamic data at 298 K:**

$$\Delta H^\circ = -92.2 \text{ kJ/mol}$$

$$\Delta S^\circ = -198.7 \text{ J/(mol}\cdot\text{K)}$$

$$\Delta G^\circ = -32.9 \text{ kJ/mol}$$

**(a)** Verify that the given values are consistent with the equation  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  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  $\Delta G^\circ$  guarantee a fast reaction? Explain. **(3 points)**

**(d)** Calculate  $\Delta G^\circ$  at 500 K, assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  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  $\Delta S^\circ$  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):**  $q_{\text{water}} = 1588 \text{ J}$ ;  $q_{\text{cal}} = 57 \text{ J}$ ;  $q_{\text{total}} = 1645 \text{ J}$ ;  $q_{\text{metal}} = -1645 \text{ J}$ ;  $c_{\text{metal}} = 0.503 \text{ J}/(\text{g}\cdot^\circ\text{C}) \approx \text{iron (0.449)}$ ; errors include heat loss to surroundings (reduces measured  $\Delta T$ ) or incomplete thermal equilibrium.

**Question 2 (Hess's Law):** Target:  $\text{C(s)} + 2\text{H}_2\text{(g)} \rightarrow \text{CH}_4\text{(g)}$ ; Manipulate: reverse equation (3), use (1) as is, use  $\frac{1}{2}\times(2)$ ;  $\Delta H_f^\circ[\text{CH}_4] = -74.8 \text{ kJ/mol}$  (exothermic formation = stable); Propane combustion:  $\Delta H^\circ = -2220 \text{ kJ}$  using  $\sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$ .

**Question 3 (Entropy):** Vaporization increases disorder (gas  $>>$  liquid);  $\Delta S_{\text{vap}} >> \Delta S_{\text{fus}}$  due to massive volume/freedom increase; water formation has  $-\Delta S$  but  $-\Delta H$  dominates making  $\Delta G < 0$ ;  $\text{CaCO}_3$  decomp:  $+\Delta S$  (gas produced);  $2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4$ :  $-\Delta S$  (2 mol  $\rightarrow$  1 mol);  $\text{NaCl}$  dissolving:  $+\Delta S$  (increased disorder); 2nd Law:  $\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$ .

**Question 4 (Gibbs Free Energy):**  $\Delta G^\circ(298\text{K}) = +130.4 \text{ kJ}$  (nonspontaneous);  $T_{\text{eq}} = 1110 \text{ K}$ ; Spontaneous when  $T > 1110 \text{ K}$ ; Table:  $(-, +)$  = always spontaneous;  $(+, -)$  = never spontaneous;  $(-, -)$  = low T only;  $(+, +)$  = high T only.

**Question 5 (Bond Energies):** Bonds broken:  $4(\text{C-H}) + 2(\text{O=O}) = 2642 \text{ kJ}$ ; Bonds formed:  $2(\text{C=O}) + 4(\text{O-H}) = 3450 \text{ kJ}$ ;  $\Delta H = -808 \text{ kJ}$  (exothermic); % error

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

**Question 6 (Coupled Reactions):** Reaction A nonspontaneous ( $\Delta G^\circ > 0$ );

Coupled:  $2\text{Fe}_2\text{O}_3 + 3\text{C} + 3\text{O}_2 \rightarrow 4\text{Fe} + 6\text{CO}_2$ ;  $\Delta G^\circ_{\text{coupled}} = -711 \text{ kJ}$

(spontaneous); Coupling uses energy from favorable reaction to drive unfavorable one; ATP:  $\Delta G^\circ = -15.5 \text{ kJ}$  (spontaneous).

**Question 7 (Phase Changes):**  $\Delta G(373\text{K}) = 0$  (equilibrium at BP);  $\Delta G(298\text{K}) =$

+8.2 kJ (liquid favored, but evaporation occurs);  $\Delta G(398\text{K}) = -2.7 \text{ kJ}$  (gas favored);  $\Delta S$  positive because gas molecules have vastly more positional freedom than liquid.

**Question 8 (Equilibrium):**  $K = 1.5 \times 10^5$ ;  $\Delta G^\circ = -29.7 \text{ kJ}$ ;  $\Delta G^\circ = +12.5 \text{ kJ}$ ;  $K =$

$6.1 \times 10^{-3}$ ;  $K > 1$  means  $\Delta G^\circ < 0$  (products favored);  $K < 1$  means  $\Delta G^\circ > 0$  (reactants favored);  $K = 1$  means  $\Delta G^\circ = 0$ ;  $\text{NH}_3$ :  $\Delta G^\circ = -33.3 \text{ kJ}$  (products strongly favored);  $\Delta G^\circ$  applies to standard conditions,  $\Delta G$  to actual conditions; equal when all concentrations = 1 M (or pressures = 1 atm).

**Question 9 (Neutralization):** Total mass = 100 g;  $\Delta T = 13.3^\circ\text{C}$ ;  $q_{\text{solution}} =$

5559 J;  $q_{\text{rxn}} = -5559 \text{ J}$  (exothermic); moles  $\text{H}_2\text{O} = 0.100 \text{ mol}$ ;  $\Delta H_{\text{neut}} = -55.6 \text{ kJ/mol} \approx -57 \text{ kJ/mol}$  literature value; Differences due to heat loss, calorimeter absorption, or concentration effects.

**Question 10 (Haber Process):** Verification:  $-92.2 - 298(-0.1987) = -32.9 \text{ kJ} \checkmark$ ;

$K = 5.8 \times 10^5$  at 298K; Spontaneous but kinetically slow (requires catalyst);  $\Delta G^\circ(500\text{K}) = +7.2 \text{ kJ}$  (less favorable); High T needed for kinetics despite thermodynamic penalty; catalyst allows lower T operation;  $-\Delta S$  because 4 mol gas  $\rightarrow$  2 mol gas (decreased freedom); Negative  $\Delta S$  means spontaneity decreases as T increases (T $\Delta S$  term becomes more positive).

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