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AP Chemistry Unit 9 - Advanced FRQ Practice

Unit 9: Applications of Thermodynamics

Challenging **Time: 150 minutes (15 min/question)**

From "I Don't Get It" to "I Ace It" - Master Thermodynamics for AP Success! 🎯

📋 Instructions:

- Show ALL work clearly for full credit consideration
- Include proper units in all calculations (kJ, J/(mol·K), K for temperature)
- Use appropriate significant figures based on given data
- Convert temperatures to Kelvin for all thermodynamic calculations
- Explain reasoning for conceptual questions using complete sentences
- Interpret signs correctly: negative ΔG° indicates spontaneity
- Reference the provided thermodynamic data tables when applicable

📊 Reference Information & Constants:

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

Gibbs Free Energy: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Non-standard conditions: $\Delta G = \Delta G^\circ + RT \ln(Q)$

Equilibrium relationship: $\Delta G^\circ = -RT \ln(K)$

Entropy change: $\Delta S^\circ\text{rxn} = \Sigma n S^\circ(\text{products}) - \Sigma n S^\circ(\text{reactants})$

Enthalpy change: $\Delta H^\circ\text{rxn} = \Sigma n \Delta H^\circ f(\text{products}) - \Sigma n \Delta H^\circ f(\text{reactants})$

Temperature conversion: $T(\text{K}) = T(^\circ\text{C}) + 273.15$

Phase transition: $\Delta S = \Delta H\_\text{transition} / T$

Question 1: Entropy Prediction and Calculation (14 points)

Consider the following chemical reaction at 25°C:

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$$

Standard Molar Entropy Values at 25°C:

- $S°[H_2(g)] = 130.7$ J/(mol·K)
- $S°[O_2(g)] = 205.2$ J/(mol·K)
- $S°[H_2O(l)] = 69.9$ J/(mol·K)

(a) Predict the sign of ΔS° for this reaction without doing any calculations. Justify your prediction based on the physical states of reactants and products. (2 points)

(b) Calculate the standard entropy change (ΔS°) for this reaction at 25°C. (3 points)

(c) Explain at the molecular level why the entropy of $H_2O(l)$ is less than the entropy of $H_2(g)$, even though H_2O is a more complex molecule. (2 points)

(d) If the reaction were instead: $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$, with $S°[H_2O(g)] = 188.8$ J/(mol·K), calculate the new ΔS° and explain why it differs from your answer in part (b). (4 points)

(e) Rank the following substances in order of increasing standard molar entropy at 25°C and justify your ranking: $CH_4(g)$, $CH_3OH(l)$, C(s, graphite). (3 points)

Question 2: Gibbs Free Energy and Spontaneity (16 points)

The decomposition of calcium carbonate is represented by the equation:

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

Thermodynamic Data at 25°C:

Substance	ΔH°f (kJ/mol)	S° [J/(mol·K)]
$CaCO_3(s)$	−1206.9	92.9
$CaO(s)$	−635.1	38.1
$CO_2(g)$	−393.5	213.8

(a) Calculate the standard enthalpy change (ΔH°) for this reaction. (2 points)

(b) Calculate the standard entropy change (ΔS°) for this reaction. (2 points)

(c) Calculate the standard Gibbs free energy change (ΔG°) at 25°C (298 K). (3 points)

(d) Based on your ΔG° value, is this reaction spontaneous at 25°C? Explain your answer. (2 points)

(e) Calculate the temperature at which ΔG° = 0 (the equilibrium temperature). Express your answer in both Kelvin and Celsius. (4 points)

(f) Explain why calcium carbonate decomposes when heated to high temperatures, even though the reaction is non-spontaneous at room temperature. Use the terms enthalpy, entropy, and Gibbs free energy in your explanation. (3 points)

Question 3: Temperature Dependence of Spontaneity (14 points)

For a particular chemical reaction, the thermodynamic values are:

Reaction Data:

- $\Delta H° = +92.2$ kJ/mol (endothermic)
- $\Delta S° = +198.8$ J/(mol·K) (entropy increases)

(a) Without doing detailed calculations, predict whether this reaction will be spontaneous at low temperatures, high temperatures, both, or neither. Justify your prediction using the Gibbs free energy equation. (3 points)

(b) Calculate $\Delta G°$ at 25°C (298 K). Is the reaction spontaneous at this temperature? (3 points)

(c) Calculate $\Delta G°$ at 500 K. Is the reaction spontaneous at this temperature? (3 points)

(d) Calculate the temperature at which the reaction becomes spontaneous (where $\Delta G° = 0$). (3 points)

(e) Sketch a graph of $\Delta G°$ versus temperature for this reaction, clearly labeling the axes, the spontaneous and non-spontaneous regions, and the temperature at which $\Delta G° = 0$. (2 points)

Question 4: Free Energy and Equilibrium (15 points)

Consider the following gas-phase equilibrium at 298 K:

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

Given Information:

- $\Delta G° = +4.8$ kJ/mol at 298 K
- $R = 8.314$ J/(mol·K)
- At a certain moment, a reaction vessel contains $P(N_2O_4) = 1.5$ atm and $P(NO_2) = 0.50$ atm

(a) Calculate the equilibrium constant K_p for this reaction at 298 K using the relationship $\Delta G° = -RT \ln(K)$. (3 points)

(b) Based on the sign of ΔG°, does the equilibrium favor reactants or products? Explain your reasoning. (2 points)

(c) Calculate the reaction quotient Q for the conditions given ($P(N_2O_4) = 1.5$ atm, $P(NO_2) = 0.50$ atm). (2 points)

(d) Calculate ΔG (not ΔG°) under these non-standard conditions using $\Delta G = \Delta G° + RT \ln(Q)$. (3 points)

(e) Based on your ΔG value from part (d), predict the direction in which the reaction will proceed to reach equilibrium. Explain your reasoning. (2 points)

(f) At equilibrium, what is the value of ΔG? Explain the relationship between ΔG, ΔG°, and equilibrium. (3 points)

Question 5: Phase Transitions and Entropy (13 points)

Water undergoes a phase transition from liquid to vapor at its boiling point.

Phase Transition Data:
- Normal boiling point of water: 100°C (373 K)
- $\Delta H°_{vap}$ = 40.7 kJ/mol
- Molar mass of H_2O = 18.02 g/mol

(a) Calculate the entropy change ($\Delta S°_{vap}$) for the vaporization of water at its boiling point using the relationship $\Delta S = \Delta H/T$. (3 points)

(b) Explain at the molecular level why the entropy increases when liquid water vaporizes. (2 points)

(c) Calculate ΔG° for the vaporization of water at exactly 100°C (373 K). Explain the significance of this value. (3 points)

(d) Predict whether the vaporization of water is spontaneous at 25°C and at 150°C. Justify your predictions without detailed calculations. (3 points)

(e) Calculate the entropy change for vaporizing 36.0 g of water at 100°C. (2 points)

Question 6: Coupled Reactions and Biological Systems (15 points)

In biological systems, thermodynamically unfavorable reactions are often coupled to the hydrolysis of ATP.

Reaction Data at 37°C (310 K):

Reaction 1 (unfavorable): A → B
$\Delta G°_1 = +15.5$ kJ/mol

Reaction 2 (ATP hydrolysis): $ATP + H_2O \rightarrow ADP + P_i$
$\Delta G°_2 = -30.5$ kJ/mol

(a) Explain why Reaction 1 does not occur spontaneously under standard conditions. (1 point)

(b) Write the overall equation for the coupled reaction where Reaction 2 drives Reaction 1. (1 point)

(c) Calculate ΔG° for the overall coupled reaction. (2 points)

(d) Based on your answer to part (c), is the coupled reaction spontaneous under standard conditions? Explain. (2 points)

(e) Calculate the equilibrium constant K for the coupled reaction at 37°C (310 K). (3 points)

(f) If the ΔG° for Reaction 1 were instead +35.0 kJ/mol, would coupling it to ATP hydrolysis still make it spontaneous? Show your calculation. (3 points)

(g) Explain why cells use ATP hydrolysis to drive unfavorable biosynthetic reactions rather than relying on other energy sources. (3 points)

Question 7: Thermodynamic Favorability Analysis (14 points)

Four different reactions have the following thermodynamic parameters at 298 K:

Reaction	ΔH° (kJ/mol)	ΔS° [J/(mol·K)]
A	−125	+85
B	+95	−120
C	−45	−135
D	+55	+210

(a) For each reaction, calculate ΔG° at 298 K. (4 points)

(b) Determine which reactions are spontaneous at 298 K. (1 point)

(c) Classify each reaction into one of the four thermodynamic categories and predict the temperature dependence of spontaneity:

- Type 1: Spontaneous at all temperatures
- Type 2: Non-spontaneous at all temperatures
- Type 3: Spontaneous at low T, non-spontaneous at high T
- Type 4: Non-spontaneous at low T, spontaneous at high T

(4 points)

(d) For Reaction C, calculate the temperature above which the reaction becomes non-spontaneous. (3 points)

(e) For Reaction D, calculate the temperature above which the reaction becomes spontaneous. (2 points)

Question 8: Thermodynamic and Kinetic Control (12 points)

Consider the conversion of diamond to graphite at 25°C and 1 atm:

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C(s, diamond) → C(s, graphite)
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Thermodynamic Data at 25°C:

- ΔH°_f[C(s, diamond)] = +1.89 kJ/mol
- ΔH°_f[C(s, graphite)] = 0 kJ/mol (by definition)
- S°[C(s, diamond)] = 2.38 J/(mol·K)
- S°[C(s, graphite)] = 5.74 J/(mol·K)

(a) Calculate ΔH° for the conversion of diamond to graphite. (1 point)

(b) Calculate ΔS° for this conversion. (2 points)

(c) Calculate ΔG° for this conversion at 25°C (298 K). (2 points)

(d) Based on the sign of ΔG°, is graphite or diamond the thermodynamically stable form of carbon at 25°C and 1 atm? (1 point)

(e) Diamonds are stable for extremely long periods at room temperature despite being thermodynamically unstable relative to graphite. Explain this observation using the concepts of thermodynamic favorability versus kinetic accessibility. (3 points)

(f) Distinguish between a reaction that is "thermodynamically favorable" and one that is "kinetically favorable." Provide an example of a reaction that is thermodynamically favorable but kinetically slow. (3 points)

Question 9: Entropy and the Third Law (13 points)

The Third Law of Thermodynamics states that the entropy of a perfect crystal at absolute zero (0 K) is zero.

Standard Molar Entropy Data at 298 K:
- S°[$H_2O(s)$] = 41.3 J/(mol·K)
- S°[$H_2O(l)$] = 69.9 J/(mol·K)
- S°[$H_2O(g)$] = 188.8 J/(mol·K)
- ΔH°fus = 6.01 kJ/mol at 273 K
- ΔH°vap = 40.7 kJ/mol at 373 K

(a) Explain the physical meaning of the Third Law and why entropy approaches zero at absolute zero. (2 points)

(b) Explain the trend in molar entropy values: S°(ice) < S°(liquid water) < S°(water vapor). Include molecular-level reasoning. (3 points)

(c) Calculate the entropy change when ice melts at 0°C (273 K). (2 points)

(d) Calculate the entropy change when liquid water vaporizes at 100°C (373 K). (2 points)

(e) Compare the ΔS values for melting and vaporization. Explain why the entropy change for vaporization is much larger than for melting. (2 points)

(f) Which process represents a greater increase in molecular disorder: melting 1 mole of ice or vaporizing 1 mole of liquid water? Justify your answer using your calculated entropy changes. (2 points)

Question 10: Comprehensive Thermodynamics Integration (16 points)

The Haber process for ammonia synthesis is one of the most important industrial reactions:

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

Thermodynamic Data at 298 K:

Substance	ΔH°f (kJ/mol)	S° [J/(mol·K)]
$N_2(g)$	0	191.6
$H_2(g)$	0	130.7
$NH_3(g)$	−45.9	192.8

(a) Calculate ΔH° for the synthesis of ammonia. (2 points)

(b) Calculate ΔS° for this reaction. (2 points)

(c) Calculate ΔG° at 298 K. Is the reaction spontaneous under standard conditions at this temperature? (3 points)

(d) Calculate the equilibrium constant K_p at 298 K. (2 points)

(e) The Haber process is typically run at temperatures around 500°C (773 K) even though the reaction is exothermic. Calculate ΔG° at 773 K (assume ΔH° and ΔS° are temperature-independent). (3 points)

(f) Based on your calculations, explain the thermodynamic trade-off in the Haber process: Why does increasing temperature decrease the thermodynamic favorability (make

ΔG° less negative or more positive)? (2 points)

(g) Industrial chemists run the Haber process at high temperatures despite unfavorable thermodynamics. Explain this choice by discussing the difference between thermodynamic favorability and reaction rate (kinetics). Why is a catalyst essential? (2 points)

Unit 9 Thermodynamics Mastery Tips:

- **Temperature MUST be in Kelvin:** Always convert °C to K by adding 273.15 for all ΔG calculations
- **Unit Consistency:** Match energy units—if ΔH° is in kJ, convert ΔS° from J/(mol·K) to kJ/(mol·K) by dividing by 1000
- **Sign Interpretation:** Negative ΔG° = spontaneous; positive ΔG° = non-spontaneous; ΔG° = 0 at equilibrium
- **Four Thermodynamic Cases:** $\Delta H° < 0$, $\Delta S° > 0$ (always spontaneous); $\Delta H° > 0$, $\Delta S° < 0$ (never spontaneous); others depend on T
- **Entropy Predictions:** S increases: gases form, particles increase, dissolution, temperature rises; S decreases: opposite
- **Equilibrium Connection:** $\Delta G° = -RT \ln(K)$; when $K > 1$, $\Delta G° < 0$ (products favored); $K < 1$, $\Delta G° > 0$ (reactants favored)
- **Standard vs Non-standard:** Use $\Delta G° = \Delta H° - T\Delta S°$ for standard; use $\Delta G = \Delta G° + RT \ln(Q)$ for non-standard conditions
- **Phase Transitions:** At phase change temperature, $\Delta G = 0$, so $\Delta S = \Delta H/T$
- **Coupled Reactions:** Add ΔG° values when reactions are coupled; unfavorable reaction can proceed if coupled to favorable one
- **Thermodynamic vs Kinetic:** ΔG tells IF reaction is spontaneous; activation energy Ea tells HOW FAST; diamonds are kinetically stable but thermodynamically unstable!

🎯 ANSWER KEY & DETAILED SOLUTIONS

Question 1: Entropy Prediction and Calculation - Complete Solution (14 points)

(a) Predict sign of ΔS° (2 points)

Prediction: ΔS° will be NEGATIVE

Justification: The reaction converts 3 moles of gas (2 H_2 + 1 O_2) into 2 moles of liquid (2 H_2O). Gases have much higher entropy than liquids because gas molecules have greater freedom of motion and occupy much larger volumes. The decrease in the number of gas molecules and the phase change from gas to liquid both contribute to a decrease in entropy (disorder).

Scoring (2 points): 1 point for correct prediction (negative); 1 point for proper justification involving gas → liquid and/or number of particles

(b) Calculate ΔS° (3 points)

Formula: $\Delta S°_{rxn} = \Sigma nS°(\text{products}) - \Sigma nS°(\text{reactants})$

Calculation:
$\Delta S° = [2 \times S°(H_2O(l))] - [2 \times S°(H_2(g)) + 1 \times S°(O_2(g))]$

$\Delta S° = [2 \times 69.9] - [2 \times 130.7 + 1 \times 205.2]$

$\Delta S° = 139.8 - [261.4 + 205.2]$

$\Delta S° = 139.8 - 466.6 =$ **-326.8 J/(mol·K)**

The negative value confirms our prediction that entropy decreases.

Scoring (3 points): 1 point for correct formula; 1 point for correct substitution with stoichiometry; 1 point for correct answer with units

(c) Molecular explanation (2 points)

Even though H_2O is more complex molecularly than H_2, its entropy is lower because **phase state dominates over molecular complexity**. In $H_2(g)$, molecules move freely throughout the container volume with high kinetic energy and positional disorder. In $H_2O(l)$, molecules are constrained by hydrogen bonding to stay close together with limited positional freedom, despite having more internal degrees of freedom (vibrations, rotations) due to being triatomic. The enormous decrease in positional entropy from gas to liquid outweighs any increase from molecular complexity.

Scoring (2 points): 1 point for identifying phase difference as dominant factor; 1 point for explaining molecular motion/freedom differences

(d) Calculate new ΔS° for gaseous product (4 points)

New Calculation:
$\Delta S^\circ = [2 \times S^\circ(H_2O(g))] - [2 \times S^\circ(H_2(g)) + 1 \times S^\circ(O_2(g))]$

$\Delta S^\circ = [2 \times 188.8] - [2 \times 130.7 + 205.2]$

$\Delta S^\circ = 377.6 - 466.6 = \mathbf{-89.0\ J/(mol \cdot K)}$

Comparison and Explanation:
The new ΔS° (−89.0 J/(mol·K)) is much less negative than the original (−326.8 J/(mol·K)). This is because water remains in

the gas phase, so the large entropy decrease associated with gas → liquid transition is avoided. The entropy still decreases because the number of gas molecules decreases from 3 to 2, reducing the total positional disorder, but this effect is much smaller than the phase change effect. The difference between the two ΔS° values (−326.8 − (−89.0) = −237.8 J/(mol·K)) represents the entropy decrease specifically due to condensation of 2 moles of water vapor.

Scoring (4 points): 1 point for correct calculation setup; 1 point for correct numerical answer; 2 points for thorough explanation of difference

(e) Rank substances by entropy (3 points)

Ranking (increasing S°): C(s, graphite) < CH_3OH(l) < CH_4(g)

Justification:

- **C(s, graphite)** has the lowest entropy: It's a solid with atoms in fixed positions in a crystalline lattice, allowing minimal molecular motion.

- **CH_3OH(l)** has intermediate entropy: It's a liquid, so molecules can move more freely than in a solid but are still constrained by intermolecular forces (especially hydrogen bonding). The molecule is more complex than C or CH_4, adding some internal degrees of freedom.

- **CH_4(g)** has the highest entropy: It's a gas, so molecules move freely throughout the container with high kinetic energy and maximum positional disorder. Gas-phase entropy dominates over other factors.

Scoring (3 points): 1 point for correct ranking; 2 points for justification involving phase states and molecular motion

Question 2: Gibbs Free Energy and Spontaneity - Complete Solution (16 points)

(a) Calculate ΔH° (2 points)

$\Delta H^\circ_{rxn} = \Sigma n\Delta H^\circ_f(\text{products}) - \Sigma n\Delta H^\circ_f(\text{reactants})$

$\Delta H^\circ = [\Delta H^\circ_f(CaO) + \Delta H^\circ_f(CO_2)] - [\Delta H^\circ_f(CaCO_3)]$

$\Delta H^\circ = [(-635.1) + (-393.5)] - [-1206.9]$

$\Delta H^\circ = -1028.6 - (-1206.9) =$ **+178.3 kJ/mol**

The reaction is endothermic.

Scoring (2 points): 1 point for correct setup; 1 point for correct answer

(b) Calculate ΔS° (2 points)

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

$\Delta S^\circ = [S^\circ(CaO) + S^\circ(CO_2)] - [S^\circ(CaCO_3)]$

$\Delta S^\circ = [38.1 + 213.8] - [92.9]$

$\Delta S^\circ = 251.9 - 92.9 =$ **+159.0 J/(mol·K)**

Entropy increases (positive) because a gas (CO_2) is produced from a solid.

Scoring (2 points): 1 point for correct setup; 1 point for correct answer with units

(c) Calculate ΔG° at 298 K (3 points)

$\Delta G° = \Delta H° - T\Delta S°$

Unit conversion: $\Delta S° = 159.0$ J/(mol·K) $= 0.1590$ kJ/(mol·K)

$\Delta G° = 178.3$ kJ/mol $- (298$ K$)(0.1590$ kJ/(mol·K)$)$

$\Delta G° = 178.3 - 47.4 =$ **+130.9 kJ/mol**

Scoring (3 points): 1 point for correct equation; 1 point for proper unit conversion; 1 point for correct answer

(d) Spontaneity determination (2 points)

Answer: The reaction is NOT spontaneous at 25°C.

Explanation: $\Delta G° = +130.9$ kJ/mol is positive, which means the reaction is thermodynamically unfavorable under standard conditions at this temperature. For a reaction to be spontaneous, $\Delta G°$ must be negative.

Scoring (2 points): 1 point for correct determination; 1 point for explanation based on sign of $\Delta G°$

(e) Calculate equilibrium temperature (4 points)

At equilibrium, $\Delta G° = 0$, so:

$0 = \Delta H° - T\Delta S°$

$T\Delta S° = \Delta H°$

$T = \Delta H° / \Delta S°$

$T = 178.3$ kJ/mol $/ 0.1590$ kJ/(mol·K)

T = **1121 K**

Convert to Celsius:
T(°C) = 1121 − 273.15 = **848°C**

Above this temperature, the reaction becomes spontaneous.

Scoring (4 points): 1 point for setting ΔG° = 0; 1 point for correct algebraic manipulation; 1 point for answer in Kelvin; 1 point for conversion to Celsius

(f) Conceptual explanation (3 points)

Calcium carbonate decomposes at high temperatures because the reaction is **endothermic (ΔH° > 0) with positive entropy change (ΔS° > 0)**.

According to the Gibbs equation ΔG° = ΔH° − TΔS°:

- At low temperatures (room temperature), the positive ΔH° term dominates, making ΔG° positive (non-spontaneous)

- At high temperatures, the TΔS° term becomes large enough to overcome the unfavorable ΔH°, making ΔG° negative (spontaneous)

- The entropy increase (gas formation from solid) is thermodynamically favored at high T because the TΔS° term grows with temperature

This is why limestone ($CaCO_3$) must be heated to high temperatures (~850°C) in kilns to produce lime (CaO) for cement production.

Scoring (3 points): 1 point for identifying endothermic + entropy increase; 1 point for explaining temperature effect on TΔS° term; 1 point for connecting to spontaneity change

Question 3: Temperature Dependence - Solutions Summary (14 points)

(a) Prediction: Reaction will be spontaneous at HIGH temperatures only.
Reasoning: ΔH° > 0 (unfavorable) but ΔS° > 0 (favorable). At low T, positive ΔH° dominates, making ΔG° > 0. At high T, the TΔS° term becomes large, making ΔG° < 0. This is Type 4: endothermic with entropy increase.

(b) ΔG° at 298 K:
$\Delta G° = 92.2 \text{ kJ/mol} - (298 \text{ K})(0.1988 \text{ kJ/(mol·K)})$
$\Delta G° = 92.2 - 59.2 =$ **$+33.0$ kJ/mol**
NOT spontaneous at 298 K ($\Delta G° > 0$)

(c) ΔG° at 500 K:
$\Delta G° = 92.2 - (500)(0.1988) = 92.2 - 99.4 =$ **-7.2 kJ/mol**
SPONTANEOUS at 500 K ($\Delta G° < 0$)

(d) Temperature where ΔG° = 0:
$T = \Delta H°/\Delta S° = 92.2 \text{ kJ/mol} / 0.1988 \text{ kJ/(mol·K)} =$ **464 K**
Above 464 K, reaction becomes spontaneous

(e) Graph should show:
- x-axis: Temperature (K); y-axis: ΔG° (kJ/mol)
- Linear line with negative slope ($-\Delta S°$)
- y-intercept at $\Delta H° = +92.2$ kJ/mol
- Crosses x-axis at $T = 464$ K
- Region above line ($T < 464$ K): $\Delta G° > 0$, non-spontaneous
- Region below line ($T > 464$ K): $\Delta G° < 0$, spontaneous

Question 4: Free Energy and Equilibrium - Solutions Summary (15 points)

(a) Calculate K_p:
$\Delta G° = -RT \ln(K)$
4.8 kJ/mol $= 4800$ J/mol $= -(8.314)(298) \ln(K_p)$
$\ln(K_p) = -4800/2477.6 = -1.938$
$K_p = e^{-1.938} = \mathbf{0.144}$

(b) Since $\Delta G° > 0$ (positive) and $K < 1$, equilibrium favors REACTANTS (N_2O_4).

(c) $Q = P^2(NO_2) / P(N_2O_4) = (0.50)^2 / 1.5 = 0.25 / 1.5 =$ **0.167**

(d) $\Delta G = \Delta G° + RT \ln(Q)$
$\Delta G = 4800 + (8.314)(298) \ln(0.167)$
$\Delta G = 4800 + 2477.6(-1.790) = 4800 - 4435 =$ **+365 J/mol = +0.37 kJ/mol**

(e) Since $\Delta G > 0$ (positive), the reaction will proceed in the REVERSE direction (toward N_2O_4) to reach equilibrium. Also, Q (0.167) > K (0.144), so reaction shifts left to decrease Q to K.

(f) At equilibrium, $\Delta G = 0$ (always). This occurs when $Q = K$. The relationship is:
- $\Delta G°$ relates to standard conditions (all species at 1 atm/1 M)
- ΔG applies to any conditions
- At equilibrium: $Q = K$, so $\Delta G = \Delta G° + RT \ln(K) = 0$ (by definition of equilibrium)

Question 5: Phase Transitions - Solutions Summary (13 points)

(a) $\Delta S°_{vap} = \Delta H°_{vap} / T$ = 40.7 kJ/mol / 373 K = 0.109 kJ/(mol·K) = **109 J/(mol·K)**

(b) Entropy increases during vaporization because liquid molecules with limited motion due to intermolecular forces become gas molecules with complete freedom of motion throughout a much larger volume. Positional disorder increases dramatically.

(c) At boiling point (100°C):
$\Delta G° = \Delta H° - T\Delta S°$ = 40.7 − (373)(0.109) = 40.7 − 40.7 = **0 kJ/mol**
Significance: At phase transition temperature, $\Delta G° = 0$, meaning liquid and vapor are in equilibrium. Neither phase is thermodynamically favored.

(d) At 25°C: Vaporization is NOT spontaneous (water doesn't spontaneously boil at room temperature; $\Delta G° > 0$)
At 150°C: Vaporization IS spontaneous (water spontaneously boils above 100°C; $\Delta G° < 0$)
The crossover temperature is 100°C (normal boiling point).

(e) For 36.0 g H_2O:
Moles = 36.0 g / 18.02 g/mol = 2.00 mol
ΔS = 2.00 mol × 109 J/(mol·K) = **218 J/K**

Question 6: Coupled Reactions - Solutions Summary (15 points)

(a) Reaction 1 is non-spontaneous because $\Delta G°_1 = +15.5$ kJ/mol is positive.

(b) Overall coupled reaction:
$A + ATP + H_2O \rightarrow B + ADP + Pi$

(c) $\Delta G°\text{overall} = \Delta G°_1 + \Delta G°_2 = (+15.5) + (-30.5) =$ **−15.0 kJ/mol**

(d) Yes, coupled reaction IS spontaneous ($\Delta G° < 0$). The favorable ATP hydrolysis "drives" the unfavorable biosynthetic reaction.

(e) K at 310 K:
$\Delta G° = -RT \ln(K)$
$-15000 = -(8.314)(310) \ln(K)$
$\ln(K) = 15000 / 2577.3 = 5.82$
$K = e^{5.82} =$ **336** (strongly favors products)

(f) If $\Delta G°_1 = +35.0$ kJ/mol:
$\Delta G°\text{overall} = 35.0 + (-30.5) = +4.5$ kJ/mol (positive)
NO, coupling would NOT make it spontaneous. The unfavorable reaction exceeds ATP's driving force.

(g) Cells use ATP because:
- ATP hydrolysis releases significant free energy (−30.5 kJ/mol)
- ATP is readily available and constantly regenerated
- Enzymes couple ATP hydrolysis to specific reactions efficiently
- Provides controlled, regulated energy release (unlike combustion)

Question 7: Thermodynamic Favorability - Solutions Summary (14 points)

(a) Calculate ΔG° for each (T = 298 K):
A: ΔG° = −125 − (298)(0.085) = −125 − 25.3 = **−150.3 kJ/mol**
B: ΔG° = +95 − (298)(−0.120) = 95 + 35.8 = **+130.8 kJ/mol**
C: ΔG° = −45 − (298)(−0.135) = −45 + 40.2 = **−4.8 kJ/mol**
D: ΔG° = +55 − (298)(0.210) = 55 − 62.6 = **−7.6 kJ/mol**

(b) Spontaneous at 298 K: A, C, D (all have ΔG° < 0)

(c) Classifications:
- Reaction A: Type 1 (ΔH° < 0, ΔS° > 0) — spontaneous at all T
- Reaction B: Type 2 (ΔH° > 0, ΔS° < 0) — non-spontaneous at all T
- Reaction C: Type 3 (ΔH° < 0, ΔS° < 0) — spontaneous at low T only
- Reaction D: Type 4 (ΔH° > 0, ΔS° > 0) — spontaneous at high T only

(d) For C (becomes non-spontaneous above):
T = ΔH°/ΔS° = 45 kJ/mol / 0.135 kJ/(mol·K) = **333 K (60°C)**
Below 333 K: spontaneous; above 333 K: non-spontaneous

(e) For D (becomes spontaneous above):
T = 55 / 0.210 = **262 K (−11°C)**
Above 262 K: spontaneous

Question 8: Thermodynamic vs Kinetic Control - Solutions Summary (12 points)

(a) $\Delta H° = \Delta H°_f(\text{graphite}) - \Delta H°_f(\text{diamond}) = 0 - 1.89 =$ **-1.89 kJ/mol**

(b) $\Delta S° = S°(\text{graphite}) - S°(\text{diamond}) = 5.74 - 2.38 =$ **$+3.36$ J/(mol·K)**

(c) $\Delta G° = -1.89 - (298)(0.00336) = -1.89 - 1.00 =$ **-2.89 kJ/mol**

(d) Graphite is thermodynamically stable ($\Delta G° < 0$ for diamond → graphite).

(e) Diamonds persist despite being thermodynamically unstable because the conversion has an extremely high activation energy (E_a). The reaction is **thermodynamically favorable but kinetically hindered**. Breaking and rearranging the strong C–C bonds in diamond's 3D network structure requires enormous energy input. At room temperature, there's insufficient thermal energy to overcome this barrier, so the reaction rate is essentially zero even though $\Delta G° < 0$. This is why "diamonds are forever"—they're kinetically stable.

(f) • **Thermodynamically favorable:** $\Delta G < 0$; reaction CAN occur (energetically downhill)
• **Kinetically favorable:** Low E_a; reaction DOES occur rapidly
Example: Combustion of paper ($C + O_2 \rightarrow CO_2$) is thermodynamically favorable (large negative $\Delta G°$) but kinetically slow at room temperature. A match (energy input) overcomes activation barrier, then reaction proceeds rapidly.

Question 9: Entropy and Third Law - Solutions Summary (13 points)

(a) The Third Law states that at absolute zero (0 K), a perfect crystal has zero entropy because all particles occupy the lowest energy state with perfect order—only one microstate exists ($W = 1$), so $S = k \ln(1) = 0$.

(b) Trend S°(ice) < S°(liquid) < S°(vapor):
• Ice: molecules in fixed positions in crystalline lattice; minimal motion
• Liquid: molecules can move/flow but remain close together; intermediate disorder
• Vapor: molecules move freely throughout container; maximum positional disorder
Phase state dominates: greater molecular freedom = higher entropy

(c) Melting: $\Delta S = \Delta H_{fus}/T = 6.01$ kJ/mol / 273 K = 0.0220 kJ/(mol·K) = **22.0 J/(mol·K)**

(d) Vaporization: $\Delta S = \Delta H_{vap}/T = 40.7 / 373 = 0.109$ kJ/(mol·K) = **109 J/(mol·K)**

(e) ΔS(vaporization) >> ΔS(melting) because:
• Liquid → gas involves much greater volume increase than solid → liquid
• Gas molecules have vastly more positional freedom than liquid molecules
• The entropy increase is ~5× larger for vaporization

(f) Vaporization represents greater disorder increase (109 vs 22 J/(mol·K)). The gas phase has enormously higher entropy than either condensed phase.

Question 10: Comprehensive Thermodynamics - Solutions Summary (16 points)

(a) $\Delta H° = 2(-45.9) - [0 + 3(0)] =$ **-91.8 kJ/mol** (exothermic)

(b) $\Delta S° = 2(192.8) - [191.6 + 3(130.7)] = 385.6 - 583.7 =$ **-198.1 J/(mol·K)** (decrease)

(c) $\Delta G°$ at 298 K:
$\Delta G° = -91.8 - (298)(-0.1981) = -91.8 + 59.0 =$ **-32.8 kJ/mol**
YES, spontaneous at 298 K ($\Delta G° < 0$)

(d) K_p at 298 K:
$\Delta G° = -RT \ln(K)$
$-32800 = -(8.314)(298) \ln(K)$
$\ln(K) = 13.23$
$K_p = e^{13.23} =$ **5.6×10^5** (strongly favors products)

(e) $\Delta G°$ at 773 K:
$\Delta G° = -91.8 - (773)(-0.1981) = -91.8 + 153.1 =$ **$+61.3$ kJ/mol**
Non-spontaneous at high temperature!

(f) The reaction is exothermic with entropy decrease (Type 3). According to $\Delta G° = \Delta H° - T\Delta S°$, when $\Delta S° < 0$, the $-T\Delta S°$ term becomes increasingly positive as T increases. At high T, this positive term overwhelms the negative $\Delta H°$, making $\Delta G°$ positive. Thermodynamically, the reaction becomes LESS favorable at high temperature.

(g) Despite unfavorable thermodynamics, high temperature is used because:
- Reaction rate increases exponentially with T (Arrhenius equation)
- At low T, reaction is too slow to be practical industrially

> • Catalyst (iron) lowers activation energy but doesn't change ΔG°
> • Industrial process accepts lower equilibrium yield for acceptable reaction rate
> • High pressure (200 atm) helps shift equilibrium toward products (Le Châtelier)
> This is the classic thermodynamic-kinetic trade-off in industrial chemistry.

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