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Topic 9.3: Gibbs Free Energy and Thermodynamic Favorability

Worksheet · AP Chemistry

UNIT 9 · THERMODYNAMICS AND ELECTROCHEMISTRY

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How to Use This Worksheet

Work in order. Section A checks the ideas: the sign criterion, the Gibbs equation and its units, the four sign combinations, and the crossover temperature. Section B practices the calculation itself: six problems built on converting units, finding $\Delta G°$ at a stated temperature, locating crossovers, predicting the sign of $\Delta S°$, diagnosing a unit blunder, and adding free energies for a coupled pair. Section C is exam style: a full classification problem, a phase change whose crossover is a melting point, and two reactions with the same signs but different crossovers.

Reference facts: every value you need is printed inside the question that uses it. $\Delta H°$ values are in kJ mol^{-1} and $\Delta S°$ values in J mol^{-1} K^{-1} throughout, and the same ($\Delta H°$, $\Delta S°$) pairs recur across the sheet: (−120, −150), (−45, +120), (−80, −200) and (+40, +80), with (+90, +300) joining them in Section C. Temperatures are always in kelvin. Where a question gives $\Delta H°$ and $\Delta S°$, treat both as constant over the temperature range studied.

One working habit ties the sheet together: signs first, units second, arithmetic third. Read the two signs and name the case before calculating anything, because the case often answers the question on its own. Then convert $\Delta S°$ to kJ mol^{-1} K^{-1}. Then calculate. Finally, check: a crossover temperature, substituted back into $\Delta G° = \Delta H° - T\Delta S°$, must return exactly zero, and a $\Delta G°$ sign must match the verdict the case predicted for that side of the crossover.

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The answer key gives the full working for every part. Attempt every question before looking at it.

Section A: Recall and Concepts

A1. (a) State what the sign of ΔG° tells us about a reaction under standard conditions, for each of the three cases ΔG° < 0, ΔG° > 0 and ΔG° = 0. (b) A reaction has ΔG° = +45 kJ mol^{-1}. State which side, reactants or products, is favored at equilibrium. (c) A second reaction has ΔG° = −45 kJ mol^{-1}, yet it is observed to proceed extremely slowly. Explain why the slow rate does not contradict the ΔG° value.

A2. (a) Write the Gibbs equation, defining every symbol and giving the unit of each quantity as it must be used in the equation. (b) State the units in which ΔS° is tabulated, and the conversion that must be applied before it is combined with a ΔH° value in kJ mol^{-1}. (c) A temperature is given as 25 °C. State the value that enters the Gibbs equation, and why it is not 25.

A3. For each sign combination, state whether the reaction is favorable at all temperatures, at low temperatures only, at high temperatures only, or at no temperature: (a) ΔH° < 0, ΔS° > 0. (b) ΔH° > 0, ΔS° < 0. (c) ΔH° < 0, ΔS° < 0. (d) ΔH° > 0, ΔS° > 0.

A4. Judge each claim, giving a reason. (a) "ΔG° = 0 means no reaction is occurring." (b) "An exothermic reaction is favorable at every temperature." (c) "Using ΔS° in J mol^{-1} K^{-1} directly beside ΔH° in kJ mol^{-1} makes the entropy term 1000 times too small." (d) "A reaction with ΔH° > 0 and ΔS° > 0 is favorable below its crossover temperature."

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A5. (a) Define the crossover temperature of a reaction. (b) State the condition on the signs of ΔH° and ΔS° for a crossover temperature to exist, and explain what the formula $T = \Delta H^\circ / \Delta S^\circ$ returns when the condition is not met. (c) For the melting of a solid, state what the crossover temperature is physically, and what is true of the two phases at that temperature.

Section B: Core Practice

B1. A reaction has $\Delta H^\circ = -120$ kJ mol^{-1} and $\Delta S^\circ = -150$ J mol^{-1} K^{-1}. (a) Convert ΔS° to kJ mol^{-1} K^{-1}. (b) Calculate ΔG° at 298 K, showing every step. (c) State whether the reaction is thermodynamically favorable at 298 K.

B2. A reaction has $\Delta H^\circ = -45$ kJ mol^{-1} and $\Delta S^\circ = +120$ J mol^{-1} K^{-1}. (a) Using the signs alone, with no calculation, state at which temperatures the reaction is favorable. (b) Calculate ΔG° at 500 K. (c) Calculate ΔG° at 100 K, and state whether the result agrees with your answer to (a).

B3. A reaction has $\Delta H^\circ = -80$ kJ mol^{-1} and $\Delta S^\circ = -200$ J mol^{-1} K^{-1}. (a) Calculate the crossover temperature. (b) Calculate ΔG° at 350 K and at 450 K. (c) State the temperature range over which the reaction is thermodynamically favorable.

B4. A reaction has $\Delta H^\circ = +40$ kJ mol^{-1} and $\Delta S^\circ = +80$ J mol^{-1} K^{-1}. (a) Calculate the crossover temperature. (b) A student claims the reaction is favorable at 200 K "because ΔS° is positive". Calculate ΔG° at 200 K and judge the claim. (c) Calculate ΔG° at 600 K, and state whether the reaction is favorable there.

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B5. Predict the sign of ΔS° for each process, giving the reason in each case. (a) $2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g)$. (b) $CO_2(s) \rightarrow CO_2(g)$, dry ice subliming. (c) $H_2O(g) \rightarrow H_2O(l)$, water vapor condensing. (d) $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$. (e) The reaction in (a) is exothermic. State which of the four sign combinations it belongs to, and the temperatures at which it is favorable.

B6. (a) A student repeats the calculation of B1 but uses $\Delta S^\circ = -150$ directly, as though it were in kJ mol^{-1} K^{-1}, and obtains $\Delta G^\circ = +44{,}580$ kJ mol^{-1}. Identify the error, and state by what factor the entropy term in the student's working is wrong. (b) Process X has $\Delta G^\circ = +30$ kJ mol^{-1} and process Y has $\Delta G^\circ = -50$ kJ mol^{-1}. The two processes are coupled into a single overall process. Calculate the overall ΔG°, and state whether the combined process is thermodynamically favorable.

Section C: Exam Style

C1. A reaction has $\Delta H^\circ = -200$ kJ mol^{-1} and $\Delta S^\circ = -400$ J mol^{-1} K^{-1}. (a) Classify the reaction into one of the four sign combinations, and state what the classification predicts about temperature and favorability. (b) Calculate ΔG° at 298 K. (c) Calculate the crossover temperature, and verify it by substituting it back into the Gibbs equation. (d) A student claims that heating the reaction mixture will eventually make the reaction more favorable. Judge the claim, supporting your judgement with the value of ΔG° at 600 K.

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C2. For the melting of a solid, $\Delta H^\circ = +12.0$ kJ mol^{-1} and $\Delta S^\circ = +40.0$ J mol^{-1} K^{-1}, both taken as constant over the range studied. (a) Calculate the crossover temperature for the melting process. (b) Explain why this temperature is the melting point of the solid. (c) Calculate ΔG° for melting at 280 K, and state which phase, solid or liquid, is stable at that temperature. (d) Calculate ΔG° for melting at 320 K, and state what happens to a sample of the solid held at that temperature.

C3. Reaction P has $\Delta H^\circ = +90$ kJ mol^{-1} and $\Delta S^\circ = +300$ J mol^{-1} K^{-1}. Reaction Q has $\Delta H^\circ = +40$ kJ mol^{-1} and $\Delta S^\circ = +80$ J mol^{-1} K^{-1}. (a) Calculate the crossover temperature of each reaction. (b) Calculate ΔG° of each reaction at 400 K, and state which reaction, if either, is favorable at 400 K. (c) A student argues: "Both reactions are endothermic with $\Delta S^\circ > 0$, so any temperature that makes one of them favorable makes the other favorable too." Judge the argument, using your answers to (a) and (b). (d) Calculate ΔG° of each reaction at 250 K, and state whether either reaction is favorable at 250 K.

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Answer Key

A1. (a) $\Delta G° < 0$: the reaction as written is thermodynamically favorable, and products are favored at equilibrium. $\Delta G° > 0$: the reaction as written is unfavorable, and reactants are favored at equilibrium. $\Delta G° = 0$: the system is at equilibrium, with forward and reverse reactions running at equal rates. (b) Reactants are favored: a positive $\Delta G°$ places the equilibrium on the reactant side. (c) $\Delta G°$ judges favorability only: whether the reaction can proceed and which side equilibrium favors. It contains no information about rate, so a thermodynamically favorable reaction can still be extremely slow. The two statements describe different properties and cannot contradict each other.

A2. (a) $\Delta G° = \Delta H° - T\Delta S°$, where $\Delta G°$ is the standard Gibbs free energy change in kJ mol^{-1}, $\Delta H°$ is the standard enthalpy change in kJ mol^{-1}, T is the absolute temperature in kelvin, and $\Delta S°$ is the standard entropy change, which must be in kJ mol^{-1} K^{-1} inside this equation. (b) $\Delta S°$ is tabulated in J mol^{-1} K^{-1}. It must be divided by 1000 to convert it to kJ mol^{-1} K^{-1} before it can be combined with $\Delta H°$. (c) 298 K. The equation is built on absolute temperature, so the Celsius value must first be converted: 25 + 273 = 298 K. Inserting 25 would shrink the $T\Delta S°$ term to a fraction of its true size.

A3. (a) Favorable at all temperatures: both terms in the equation push $\Delta G°$ negative. (b) Favorable at no temperature: both terms push $\Delta G°$ positive. (c) Favorable at low temperatures only: enthalpy favors the reaction, entropy opposes it, and the entropy term wins only once T is large. (d) Favorable at high temperatures only: entropy favors the reaction, enthalpy opposes it, and the entropy term must grow with T before it can win.

A4. (a) False. $\Delta G° = 0$ means the system is at equilibrium: the forward and reverse reactions both continue, at equal rates, so the composition no longer changes. (b) False. An exothermic reaction with $\Delta S° < 0$, for example one that consumes gas, is favorable at low temperatures only; at high temperature the $-T\Delta S°$ term is positive and large enough to make $\Delta G°$ positive. (c) False, and the direction of the error matters: the entropy term becomes 1000 times too large, not too small. A $\Delta S°$ of −150 J mol^{-1} K^{-1} used unconverted enters the equation as though it were −150 kJ mol^{-1} K^{-1}, a value 1000 times bigger. (d) False. With $\Delta H° > 0$ and $\Delta S° > 0$ the reaction is favorable above its crossover temperature, where $T\Delta S°$ has grown large enough to outweigh $\Delta H°$. Below the crossover, $\Delta G°$ is still positive.

A5. (a) The crossover temperature is the temperature at which $\Delta G° = 0$ for the reaction: the system sits exactly at equilibrium there, and the reaction changes from favorable to unfavorable, or the reverse, as the temperature passes through it. (b) $\Delta H°$ and $\Delta S°$ must have the same sign. When they have opposite signs, $T = \Delta H° / \Delta S°$ returns a negative temperature, which is physically impossible in kelvin; it is the signal that the reaction is favorable at all temperatures or at none, so no crossover exists. (c) It is the melting point of the solid. At that temperature the solid and liquid phases coexist in equilibrium, with melting and freezing running at equal rates.

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B1. (a) $\Delta S^\circ = -150$ J mol^{-1} K^{-1} ÷ 1000 = −0.150 kJ mol^{-1} K^{-1}. (b) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -120 - (298)(-0.150) = -120 + 44.7 = -75.3$ kJ mol^{-1}. (c) Favorable: ΔG° is negative at 298 K.

B2. (a) Favorable at all temperatures. $\Delta H^\circ < 0$ contributes a negative term, and with $\Delta S^\circ > 0$ the subtracted term, $-T\Delta S^\circ$, is also negative at every temperature, so ΔG° can never reach zero or turn positive. (b) Convert: $\Delta S^\circ = +0.120$ kJ mol^{-1} K^{-1}. $\Delta G^\circ = -45 - (500)(0.120) = -45 - 60 = -105$ kJ mol^{-1}. (c) $\Delta G^\circ = -45 - (100)(0.120) = -45 - 12 = -57$ kJ mol^{-1}. Negative, as (a) requires: the two values bracket room temperature and both are favorable, as they must be for a reaction favorable at every temperature.

B3. (a) At the crossover $\Delta G^\circ = 0$, so $T = \Delta H^\circ / \Delta S^\circ = 80 / 0.200 = 400$ K, using $\Delta S^\circ = -0.200$ kJ mol^{-1} K^{-1} and the sizes of the two quantities. (b) At 350 K: $\Delta G^\circ = -80 - (350)(-0.200) = -80 + 70 = -10$ kJ mol^{-1}. At 450 K: $\Delta G^\circ = -80 - (450)(-0.200) = -80 + 90 = +10$ kJ mol^{-1}. (c) Favorable below 400 K, the low-temperature side, as the two values in (b) confirm: negative at 350 K, positive at 450 K, and zero at the 400 K crossover between them.

B4. (a) $T = \Delta H^\circ / \Delta S^\circ = 40 / 0.080 = 500$ K. (b) Convert: $\Delta S^\circ = +0.080$ kJ mol^{-1} K^{-1}. $\Delta G^\circ = 40 - (200)(0.080) = 40 - 16 = +24$ kJ mol^{-1}. Positive, so the reaction is not favorable at 200 K and the claim fails. A positive ΔS° helps only through the $T\Delta S^\circ$ term, and at 200 K that term, 16 kJ mol^{-1}, has not yet grown to match ΔH°; that happens only at the 500 K crossover. (c) $\Delta G^\circ = 40 - (600)(0.080) = 40 - 48 = -8$ kJ mol^{-1}. Negative, so the reaction is favorable at 600 K, above its crossover.

B5. (a) Negative. Three moles of gas become two, $\Delta n(\text{gas}) = -1$, so the gas particles lose dispersal. (b) Positive. A solid passes directly to a gas, the largest single jump in dispersal a phase change can give. (c) Negative. A gas condenses to a liquid, confining its particles to a far smaller volume. (d) Negative. Four moles of gas become two, $\Delta n(\text{gas}) = -2$. (e) $\Delta H^\circ < 0$ with $\Delta S^\circ < 0$: the third combination, favorable at low temperatures only, while the enthalpy term still outweighs the entropy penalty.

B6. (a) The student skipped the unit conversion, using ΔS° in joules as though it were in kilojoules. The value entered, −150, is 1000 times the correct −0.150 kJ mol^{-1} K^{-1}, so the entropy term is 1000 times too large and overwhelms ΔH° in the sum. Converted properly, the same data give $\Delta G^\circ = -75.3$ kJ mol^{-1}, as in B1. (b) Overall $\Delta G^\circ = +30 + (-50) = -20$ kJ mol^{-1}. Negative, so the combined process is thermodynamically favorable, even though process X on its own is not.

C1. (a) $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$: the third combination. Enthalpy favors the reaction and entropy opposes it, so it is favorable at low temperatures only, with a crossover temperature where the verdict changes. (b) Convert: $\Delta S^\circ = -0.400$ kJ mol^{-1} K^{-1}. $\Delta G^\circ = -200 - (298)(-0.400) = -200 + 119.2 = -80.8$ kJ mol^{-1}, so the reaction is favorable at 298 K. (c) $T = \Delta H^\circ / \Delta S^\circ = 200 / 0.400 = 500$ K. Verification: $\Delta G^\circ = -200 - (500)(-0.400) = -200 + 200 = 0$ kJ mol^{-1}, exactly zero as the crossover requires. (d) The claim is false. At 600 K, $\Delta G^\circ = -200 - (600)(-0.400) = -200 + 240 = +40$ kJ mol^{-1}: positive, so the reaction is unfavorable at 600 K. For this sign combination the $-T\Delta S^\circ$ term is

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positive and grows with temperature, so heating steadily damages favorability, and the reaction is favorable only below its 500 K crossover.

C2. (a) Convert: $\Delta S^\circ = +0.040$ kJ mol^{-1} K^{-1}. $T = \Delta H^\circ / \Delta S^\circ = 12.0 / 0.040 = 300$ K. (b) At the crossover temperature $\Delta G^\circ = 0$, so melting and freezing are exactly balanced and the two phases coexist in equilibrium. A temperature at which a solid and its liquid coexist in equilibrium is, by definition, the melting point at that pressure. (c) $\Delta G^\circ = 12.0 - (280)(0.040) = 12.0 - 11.2 = +0.8$ kJ mol^{-1}. Melting is unfavorable at 280 K, so the solid is the stable phase there; the favorable direction is freezing. (d) $\Delta G^\circ = 12.0 - (320)(0.040) = 12.0 - 12.8 = -0.8$ kJ mol^{-1}. Melting is favorable at 320 K, so the sample melts.

C3. (a) Reaction P: $T = 90 / 0.300 = 300$ K. Reaction Q: $T = 40 / 0.080 = 500$ K. (b) Reaction P: $\Delta G^\circ = 90 - (400)(0.300) = 90 - 120 = -30$ kJ mol^{-1}, favorable at 400 K. Reaction Q: $\Delta G^\circ = 40 - (400)(0.080) = 40 - 32 = +8$ kJ mol^{-1}, not favorable at 400 K. Only reaction P is favorable. (c) The argument is false. Sharing a sign combination settles only the shape of the behavior, favorable above the crossover; it does not fix where the crossover sits. Reaction P crosses at 300 K and reaction Q at 500 K, so at 400 K one is already favorable and the other is not, as (b) shows. (d) Reaction P: $\Delta G^\circ = 90 - (250)(0.300) = 90 - 75 = +15$ kJ mol^{-1}. Reaction Q: $\Delta G^\circ = 40 - (250)(0.080) = 40 - 20 = +20$ kJ mol^{-1}. Both are positive, so neither reaction is favorable at 250 K, which is consistent with both crossover temperatures, 300 K and 500 K, lying above 250 K.

Continue Revising

Topic 9.3 Revision Notes

Topic 9.3 Quiz: Gibbs Free Energy and Thermodynamic Favorability

Previous Worksheet: Topic 9.2 Absolute Entropy and Entropy Change

Next Worksheet: Topic 9.4 Thermodynamic and Kinetic Control

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