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Topic 9.7: Coupled Reactions

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 addition rule, the size condition on the driver, the shared intermediate that makes coupling real, and the line between coupling and catalysis. Section B practices the calculations themselves: totals, a missing driver recovered from the sum, scaling a driver until the total turns negative, and the full equation arithmetic of ATP-driven glucose phosphorylation. Section C is exam style: a mechanism judged, a nonstandard total defended, and an ATP design problem with a catalyst proposal to evaluate.

Reference facts. ΔG° values are in kJ mol^{-1} throughout. Cell reactions use the biological standard free energy $\Delta G^{\circ\prime}$, prime marking the biological standard state at pH 7, and ATP hydrolysis is $\Delta G^{\circ\prime} = -30.5$ kJ mol^{-1} wherever it appears. Pi means inorganic phosphate. Values given for a reaction are for the reaction exactly as written: reverse it and the sign flips, scale it and the value scales.

One working habit ties the sheet together: signs first, link second, verdict last. Write every ΔG with its sign and count the driver's copies before adding anything. Then confirm the two steps share an intermediate that cancels. Only then read the verdict off the sign of the total. Finally, check: every total is recomputed by rearranging the sum, driver = overall − driven, to catch any sign slip.

The answer key gives the full working for every part. Do not look at the answer key until you have attempted every question.

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Section A: Recall and Concepts

A1. (a) State the condition on ΔG°(overall) for a coupled process to be thermodynamically favorable. (b) A pair of steps sums to exactly 0 kJ mol^{-1}. State what that means for the coupled process. (c) State the second requirement, beyond the sign of the total, for one reaction to drive another in practice.

A2. (a) Define a shared intermediate in a coupled pair of reactions. (b) In the sequence X → Y (ΔG° = −40 kJ mol^{-1}) and Y → Z (ΔG° = +25 kJ mol^{-1}), name the shared intermediate, write the overall equation, and calculate ΔG°(overall). (c) Two reactions whose ΔG° values sum to −30 kJ mol^{-1} share no species and run in separate vessels. Can one drive the other? Justify your answer.

A3. (a) Write the equation for the hydrolysis of ATP and give its ΔG°′. (b) Explain what the prime symbol in ΔG°′ signifies. (c) A student says ATP drives unfavorable reactions by lowering their activation energy. Correct the statement.

A4. (a) A student couples a step at +10 kJ mol^{-1} to one at −10 kJ mol^{-1} and claims the process is favorable. Judge the claim, giving the total. (b) State the effect on a step's ΔG° of reversing the step, and of tripling the step. (c) A coupled pair has overall ΔG° < 0. State the consequence for the pair's overall equilibrium constant, and state what coupling has done to the driven step's own equilibrium constant.

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A5. (a) Judge the claim: "Adding a catalyst to an unfavorable reaction does the same job as coupling it to ATP hydrolysis." (b) Judge the claim: "Once an unfavorable reaction is coupled to a favorable one, its own ΔG° becomes negative." (c) State what an enzyme changes in a coupled process, and two things it leaves untouched.

Section B: Core Practice

B1. Calculate ΔG°(overall) for each pairing and state whether the coupled process is favorable. (a) A driven step at +45 kJ mol^{-1} with a driver at −80 kJ mol^{-1}. (b) A driven step at +28 kJ mol^{-1} with a driver at −20 kJ mol^{-1}. (c) A driven step at +50 kJ mol^{-1} with a driver at −70 kJ mol^{-1}.

B2. A coupled pair has an overall ΔG° of −12 kJ mol^{-1}. The unfavorable component has ΔG° = +33 kJ mol^{-1}. (a) Calculate the ΔG° of the favorable component, showing the rearrangement. (b) Check your answer by adding the two components. (c) State, with a reason, whether a driver of −30 kJ mol^{-1} could have produced the same overall total with this driven step.

B3. A step P → Q has ΔG° = +18 kJ mol^{-1}. A driver R → S has ΔG° = −12 kJ mol^{-1}. (a) Calculate the total when Q's step is coupled to one copy of the driver, and give the verdict. (b) Calculate the total with two copies of the driver, and give the verdict. (c) State the minimum whole number of driver copies that makes the process favorable, and the rule you used. (d) A student instead couples three copies of P → Q to one copy of the driver. Calculate that total and give the verdict.

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B4. Glucose phosphorylation in glycolysis runs as two coupled steps. Driven step: glucose + Pi → glucose-6-phosphate + H_2O, $\Delta G^{\circ\prime} = +13.8$ kJ mol^{-1}. Driver step: ATP + H_2O → ADP + Pi, $\Delta G^{\circ\prime} = -30.5$ kJ mol^{-1}. (a) Identify the shared intermediate and the other species that cancels. (b) Write the overall equation. (c) Calculate $\Delta G^{\circ\prime}$(overall) and state the verdict. (d) In ionic form the species are glucose $C_6H_{12}O_6$, ATP^{4-} = $C_{10}H_{12}N_5O_{13}P_3^{4-}$, glucose-6-phosphate^{2-} = $C_6H_{11}O_9P^{2-}$, ADP^{3-} = $C_{10}H_{12}N_5O_{10}P_2^{3-}$ and H^+, and the overall equation is glucose + ATP^{4-} → glucose-6-phosphate^{2-} + ADP^{3-} + H^+. Verify that this equation balances for atoms and for charge.

B5. A biosynthetic reaction has $\Delta G^{\circ\prime} = +22$ kJ mol^{-1}. For each proposed driver, calculate the coupled total and state whether it can drive the reaction. (a) $\Delta G^{\circ\prime} = -23$ kJ mol^{-1}. (b) $\Delta G^{\circ\prime} = -19$ kJ mol^{-1}. (c) $\Delta G^{\circ\prime} = -30$ kJ mol^{-1}.

B6. The synthesis of sucrose from glucose and fructose has $\Delta G^{\circ\prime} = +23$ kJ mol^{-1}. In cells it is coupled to the hydrolysis of UTP to UDP, $\Delta G^{\circ\prime} = -30.5$ kJ mol^{-1}. (a) Calculate the coupled $\Delta G^{\circ\prime}$ and state the verdict. (b) Judge the claim: "The coupling has increased the equilibrium constant of sucrose synthesis itself." (c) Judge the claim: "At equilibrium, the coupled process favors its products," giving the reason in terms of the sign of the coupled $\Delta G^{\circ\prime}$.

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Section C: Exam Style

C1. Reaction 1, A → B, has $\Delta G^\circ = -60$ kJ mol^{-1}. Reaction 2, C → D, has $\Delta G^\circ = +45$ kJ mol^{-1}. A coupled mechanism forms an intermediate E that is shared by both reactions. (a) Calculate the ΔG° of the coupled process and state whether reaction 1 can drive reaction 2. (b) A student argues that the coupling would work equally well with no shared intermediate, because the sum of the ΔG° values is negative. Judge the argument. (c) The coupled process is observed to run very slowly. Explain why that observation does not contradict the thermodynamics, and state what could be changed to speed the process up without altering any ΔG°.

C2. At nonstandard conditions, a driven step P → Q has $\Delta G = +8$ kJ mol^{-1} and a coupled driver has $\Delta G = -15$ kJ mol^{-1}. (a) Calculate the ΔG of the coupled process and state the direction it runs. (b) The concentration of P is tripled, with all else unchanged. A student concludes that the coupled process must now be unfavorable. Judge the conclusion, referring to the coupled total. (c) State a change in the two ΔG values that would make the coupled process genuinely unfavorable.

C3. A cell needs to drive a reaction with $\Delta G^{\circ\prime} = +48$ kJ mol^{-1} and can couple it only to ATP hydrolysis, $\Delta G^{\circ\prime} = -30.5$ kJ mol^{-1} per ATP. (a) Show that one ATP is not sufficient, and find the minimum whole number of ATP molecules needed, giving the coupled total for that number. (b) An engineer proposes a different fix: add a catalyst chosen to make the reaction's $\Delta G^{\circ\prime}$ negative, so no ATP is needed. Judge the proposal. (c) For the successfully coupled process in part (a), state whether reactants or products are favored at equilibrium, with a reason.

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Answer Key

A1. (a) The sum of the steps' ΔG° values must be negative: ΔG°(overall) = ΔG°(driven) + ΔG°(driver) < 0. (b) A total of exactly zero means the coupled process is at equilibrium: there is no net drive toward products or toward reactants, so the coupling has not made the process favorable. Favorability requires a strictly negative total. (c) The two reactions must be mechanistically linked through a shared intermediate, a species produced by one step and consumed by the other, so the free energy released is actually transferred to the driven step.

A2. (a) A shared intermediate is a species that appears as a product of one step and as a reactant of the other, so that when the step equations are added it cancels out of the overall equation. (b) The intermediate is Y. Overall equation: X → Z. ΔG°(overall) = (−40) + (+25) = −15 kJ mol^{-1}. (c) No. A negative sum is necessary but not sufficient: with no shared species there is no mechanism by which the favorable reaction's free energy reaches the unfavorable one. Each reaction simply settles at its own equilibrium, and the unfavorable reaction is not driven.

A3. (a) ATP + H_2O → ADP + Pi, with ΔG°′ = −30.5 kJ mol^{-1}. (b) The prime marks the biological standard state: pH 7, so $[H_3O^+]$ = 1.0 × 10^{-7} mol L^{-1}, in place of the ordinary standard $[H_3O^+]$ = 1 mol L^{-1}. ΔG°′ values are added in coupling sums exactly as ΔG° values are. (c) ATP does not change any activation energy. It drives the reaction thermodynamically: its hydrolysis is mechanistically linked to the driven step through shared species, and the negative ΔG°′ of hydrolysis outweighs the positive ΔG°′ of the driven step, making the coupled total negative. Lowering activation energies is what catalysts and enzymes do, and it changes rates only.

A4. (a) The claim fails. The total is (+10) + (−10) = 0 kJ mol^{-1}, and zero is equilibrium, not favorable: the coupled process has no net drive toward products. (b) Reversing a step flips the sign of its ΔG°: a step at +25 kJ mol^{-1} reversed carries −25 kJ mol^{-1}. Tripling a step multiplies its ΔG° by 3: three copies of a −12 kJ mol^{-1} step contribute −36 kJ mol^{-1}. (c) A negative overall ΔG° means the coupled pair's overall equilibrium constant is greater than 1, so the overall products are favored at equilibrium. The driven step's own equilibrium constant is unchanged: coupling creates a new overall process with its own K and leaves each step's thermodynamics exactly as it was.

A5. (a) False. A catalyst lowers activation energy and speeds a reaction toward its equilibrium, but it never changes ΔG, so it cannot make an unfavorable reaction favorable. Coupling works precisely because it changes the overall ΔG by adding a favorable reaction's free energy change; no catalyst can substitute for that. (b) False. Coupling changes the overall process, never the step itself. The driven step keeps its positive ΔG°; it proceeds because it is one half of a combined process whose total is negative, not because its own value was rewritten. (c) An enzyme changes the rate at which the coupled process runs, by lowering the activation energy of steps it catalyzes. It leaves untouched the ΔG° of every step and the position of the overall equilibrium, equivalently the overall ΔG° and K.

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B1. (a) $\Delta G°$(overall) = (+45) + (−80) = −35 kJ mol^{-1}. Negative, so the coupled process is favorable. (b) $\Delta G°$(overall) = (+28) + (−20) = +8 kJ mol^{-1}. Positive, so the coupling fails: the driver releases less than the driven step costs, and the process remains unfavorable. (c) $\Delta G°$(overall) = (+50) + (−70) = −20 kJ mol^{-1}. Negative, so the coupled process is favorable.

B2. (a) Overall = driven + driver, so driver = overall − driven = (−12) − (+33) = −45 kJ mol^{-1}. (b) Check: (+33) + (−45) = −12 kJ mol^{-1}, the stated overall total, recovered. (c) No. With a −30 kJ mol^{-1} driver the total would be (+33) + (−30) = +3 kJ mol^{-1}, positive, so that pairing would not even be favorable, let alone reach −12 kJ mol^{-1}. The driver must supply the full −45 kJ mol^{-1} to produce the stated total.

B3. (a) Total = (+18) + (−12) = +6 kJ mol^{-1}. Positive, so one copy is not enough and the process is unfavorable. (b) Total = (+18) + 2(−12) = (+18) + (−24) = −6 kJ mol^{-1}. Negative, so two copies make the process favorable. (c) The minimum is 2 copies. Rule: use the smallest whole number of copies for which the total first becomes negative. (d) Total = 3(+18) + (−12) = (+54) + (−12) = +42 kJ mol^{-1}. Positive, so this arrangement is strongly unfavorable: scaling the driven step scales its cost, and one driver copy comes nowhere near paying it.

B4. (a) The shared intermediate is Pi, inorganic phosphate: the driver step produces it and the driven step consumes it. H_2O also cancels, consumed by the driver and produced by the driven step. (b) Adding the steps and cancelling Pi and H_2O: glucose + ATP → glucose-6-phosphate + ADP. (c) $\Delta G°'$(overall) = (+13.8) + (−30.5) = −16.7 kJ mol^{-1}. Negative, so the coupled phosphorylation is thermodynamically favorable and proceeds. (d) Atoms, left: C 6 + 10 = 16; H 12 + 12 = 24; N 5; O 6 + 13 = 19; P 3. Atoms, right: C 6 + 10 = 16; H 11 + 12 + 1 = 24; N 5; O 9 + 10 = 19; P 1 + 2 = 3. Every element matches. Charge, left: 0 + (−4) = −4. Charge, right: (−2) + (−3) + (+1) = −4. The equation balances for atoms and for charge.

B5. (a) Total = (+22) + (−23) = −1 kJ mol^{-1}. Negative: this driver can drive the reaction, though with only 1 kJ mol^{-1} to spare. (b) Total = (+22) + (−19) = +3 kJ mol^{-1}. Positive: this driver cannot drive the reaction; it releases less than the step costs. (c) Total = (+22) + (−30) = −8 kJ mol^{-1}. Negative: this driver can drive the reaction comfortably.

B6. (a) $\Delta G°'$(overall) = (+23) + (−30.5) = −7.5 kJ mol^{-1}. Negative, so the coupled synthesis is thermodynamically favorable: UTP hydrolysis more than pays the cost of building sucrose. (b) The claim is false. Coupling does not touch the synthesis reaction itself: sucrose synthesis keeps $\Delta G°'$ = +23 kJ mol^{-1} and keeps its own equilibrium constant. What exists is a new overall process, synthesis plus hydrolysis, with its own combined $\Delta G°'$ and its own K. (c) The claim is true. The coupled $\Delta G°'$ is negative, and a negative $\Delta G°'$ corresponds to an overall equilibrium constant greater than 1, so at equilibrium the products of the overall process are favored over its reactants.

C1. (a) $\Delta G°$(coupled) = (−60) + (+45) = −15 kJ mol^{-1}. Negative, so yes: through the shared intermediate E, reaction 1 releases more than reaction 2 costs and can drive it. (b) The argument fails. A negative sum is only the thermodynamic half of the requirement. Without a shared

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intermediate there is no pathway by which the free energy released by reaction 1 is transferred to reaction 2; the two reactions are independent, each reaches its own equilibrium, and reaction 2 is not driven. (c) There is no contradiction, because ΔG° reports direction and equilibrium position only, never rate: a favorable process with a high activation energy runs slowly. Adding a suitable catalyst, an enzyme in a cell, lowers the activation energy and speeds the process up while leaving every ΔG°, and the overall equilibrium, unchanged.

C2. (a) $\Delta G(\text{coupled}) = (+8) + (-15) = -7$ kJ mol^{-1}. The total is negative, so the coupled process runs forward, toward the products of the overall process. (b) The conclusion does not follow. The verdict rests on the coupled total, and on the values given that total is -7 kJ mol^{-1}, still negative, so the process stays favorable. A concentration change can shift individual ΔG values, but it changes no ΔG° and it does not by itself overturn the sign of the sum stated here. (c) The process becomes unfavorable when the sum turns positive: for example, if the driver's ΔG rose from -15 to -5 kJ mol^{-1}, giving $(+8) + (-5) = +3$ kJ mol^{-1}, or if the driven step's ΔG rose above $+15$ kJ mol^{-1} against the same driver. The driver must stop outweighing the cost.

C3. (a) One ATP: $(+48) + (-30.5) = +17.5$ kJ mol^{-1}, still positive, so one ATP is not sufficient. Two ATP: $(+48) + 2(-30.5) = (+48) + (-61) = -13$ kJ mol^{-1}, negative. The minimum is 2 ATP molecules per reaction event, with a coupled total of -13 kJ mol^{-1}. (b) The proposal is impossible. A catalyst lowers activation energy and changes only how fast equilibrium is approached; it cannot change any ΔG, so it cannot make the reaction's $\Delta G^{\circ\prime}$ negative. The only way to drive this step is to change the overall thermodynamics, which is what coupling to ATP hydrolysis does. (c) Products are favored. The coupled total is negative, $\Delta G^{\circ\prime} = -13$ kJ mol^{-1}, and a negative overall $\Delta G^{\circ\prime}$ means the overall equilibrium constant is greater than 1, so the equilibrium mixture is dominated by the products of the coupled process.

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