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Topic 9.6: Free Energy of Dissolution

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 three enthalpy steps, the two competing entropy terms, and what the sign of ΔG does and does not say. Section B practices the calculations themselves: step sums, ΔG at two temperatures with a crossover, and the two-way traffic between Ksp and ΔG°. Section C is exam style: a cold pack analysis, a precipitation verdict for calcium fluoride, and two student claims judged with numbers.

Reference facts. R = 8.314 J mol^{-1} K^{-1} throughout, and RT = 2.478 kJ mol^{-1} at 298 K. Temperatures are always in kelvin. ΔS values arrive in J mol^{-1} K^{-1} and must be divided by 1000 before they enter ΔG = ΔH − TΔS alongside kilojoule enthalpies. The solubility products used are the site's 298 K values: AgCl 1.8×10^{-10}, CaF_2 3.9×10^{-11} and PbI_2 9.8×10^{-9}.

One working habit ties the sheet together: signs first, sums second, verdict last. Classify every step and every term before adding anything. Then calculate. Finally, check: every Ksp calculated from a ΔG° is converted back to confirm the starting value, and every direction claim is made from a Q against Ksp comparison, never from the size of Ksp alone.

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) Name the three enthalpy steps that make up dissolving an ionic solid in water, and state the sign of ΔH for each. (b) Which step is the only exothermic one, and what is it called when the solvent is water? (c) Explain in one sentence why each of the other two steps must be endothermic.

A2. (a) Write ΔH_solution as a sum of the three steps. (b) A salt has lattice separation +905 kJ mol^{-1}, solvent separation +130 kJ mol^{-1} and hydration −1040 kJ mol^{-1}. Calculate ΔH_solution, and state whether the solution warms or cools as the salt dissolves. (c) State what further quantity, beyond ΔH_solution, decides whether this salt actually dissolves.

A3. (a) State the two entropy contributions when an ionic solid dissolves in water, with the sign of each. (b) For which dissolving process is ΔS most reliably and sharply negative, and why? (c) Explain how ΔS_solution can be negative for a salt built from small, highly charged ions, even though those ions become more dispersed as they dissolve.

A4. (a) State what the sign of ΔG_solution tells you, and two things it does not tell you. (b) Judge the claim: "An endothermic dissolution cannot be spontaneous." (c) Judge the claim: "If a salt dissolves quickly, its ΔG_solution must be negative."

A5. (a) Write the equilibrium equation for solid silver chloride in contact with its saturated solution, and the Ksp expression that goes with it. (b) Write the equation connecting ΔG°_solution and Ksp, defining every symbol. (c) Ksp for AgCl is 1.8×10^{-10} at 298 K. Without calculating, state the sign of ΔG°_solution and what it says about the position of the dissolution equilibrium.

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Section B: Core Practice

B1. An ionic solid has lattice separation +720 kJ mol^{-1}, solvent separation +85 kJ mol^{-1} and hydration −790 kJ mol^{-1}. (a) Calculate ΔH_solution. (b) State whether the water warms or cools as this solid dissolves. (c) A second solid shares the same lattice and solvent steps but has hydration −830 kJ mol^{-1}. Calculate its ΔH_solution, and state which solid has the more exothermic enthalpy of solution.

B2. A salt has ΔH_solution = +25 kJ mol^{-1} and ΔS_solution = +110 J mol^{-1} K^{-1}. (a) Calculate ΔG_solution at 298 K, showing the unit conversion explicitly. (b) Calculate ΔG_solution at 200 K. (c) Calculate the crossover temperature at which ΔG_solution = 0, and verify it by substitution. (d) State, with a reason, whether warming helps or hinders this salt dissolving.

B3. Silver chloride has Ksp = 1.8×10^{-10} at 298 K. (a) Calculate ΔG°_solution, showing each step. (b) Check your answer by converting your ΔG° back into Ksp. (c) Lead(II) iodide has Ksp = 9.8×10^{-9} at 298 K. Without a full calculation, state which salt has the larger ΔG°_solution, and why.

B4. Salts X and Y have the same lattice separation, +840 kJ mol^{-1}, and the same solvent separation, +110 kJ mol^{-1}. Hydration releases 960 kJ mol^{-1} for X and 810 kJ mol^{-1} for Y. (a) Calculate ΔH_solution for each salt. (b) State which salt has the more exothermic enthalpy of solution, naming the step that decides it. (c) A student says the figures must be swapped, because Y contains smaller, more highly charged cations than X. Judge the student's reasoning, and state the entropy consequence that follows for whichever salt truly hydrates more strongly.

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B5. Solid silver chloride, Ksp = 1.8×10^{-10} at 298 K, is added to two solutions. (a) Solution 1 has $[Ag^+] = [Cl^-] = 1.0 \times 10^{-5}$ mol L^{-1}. Calculate Q and state whether more AgCl can dissolve, or whether precipitation occurs. (b) Solution 2 has $[Ag^+] = [Cl^-] = 2.0 \times 10^{-5}$ mol L^{-1}. Calculate Q and state what happens. (c) State the value of Q in a saturated solution of AgCl, and the value of ΔG_solution there.

B6. Lead(II) iodide has ΔG°_solution = +45.7 kJ mol^{-1} at 298 K. (a) Calculate Ksp, showing the joule conversion. (b) Verify your answer by converting your Ksp back into ΔG°. (c) Solid PbI_2 sits in its saturated solution and pure water is added. State what happens to Q at the moment of dilution, what then occurs, and the final value of Q, assuming solid remains.

Section C: Exam Style

C1. Ammonium nitrate, NH_4NO_3, is the salt used in instant cold packs. For its dissolution, ΔH_solution = +25 kJ mol^{-1} and ΔS_solution = +110 J mol^{-1} K^{-1}. (a) Write the dissolution equation. (b) Calculate ΔG_solution at 298 K and state whether dissolving is thermodynamically favorable at that temperature. (c) Explain why the pack turns cold even though the process is favorable, naming the term that pays the enthalpy cost. (d) A separate measurement finds ΔG_solution = −7.8 kJ mol^{-1} at 298 K for this salt. Rearrange $\Delta G = \Delta H - T\Delta S$ to calculate ΔS_solution from ΔH_solution and this ΔG, converting units explicitly, and confirm that it matches the value given above.

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C2. Calcium fluoride has Ksp = 3.9×10^{-11} at 298 K. (a) Write the dissolution equilibrium and the Ksp expression. (b) Calculate ΔG°_solution at 298 K. (c) A solution contains $[Ca^{2+}] = 1.0 \times 10^{-3}$ mol L^{-1} and $[F^-] = 1.0 \times 10^{-4}$ mol L^{-1}. Calculate Q, and state whether CaF_2 precipitates from this solution or whether more could dissolve. (d) A second solution contains $[Ca^{2+}] = 1.0 \times 10^{-2}$ mol L^{-1} and $[F^-] = 2.0 \times 10^{-3}$ mol L^{-1}. Calculate Q and state what happens, and what Q becomes when the process stops.

C3. Two students make claims about dissolving. Claim 1: "If dissolving absorbs heat, it cannot happen spontaneously." Claim 2: "If dissolving releases heat, it is favorable at every temperature." Salt A has ΔH_solution = +8 kJ mol^{-1} and ΔS_solution = +45 J mol^{-1} K^{-1}. Salt B has ΔH_solution = −12 kJ mol^{-1} and ΔS_solution = −50 J mol^{-1} K^{-1}. (a) Calculate ΔG_solution for each salt at 298 K, showing the unit conversion. (b) Use your answer for salt A to judge Claim 1. (c) Calculate the temperature above which salt B is no longer favorable, verifying your value with a ΔG calculation at 200 K, and use the result to judge Claim 2.

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Answer Key

A1. (a) Lattice separation: the crystal is pulled apart into gaseous ions, ΔH positive. Solvent separation: solvent molecules are pushed apart to make room, ΔH positive. Hydration (solvation): the ions and solvent form attractions, ΔH negative. (b) Hydration, the forming step, is the only exothermic one; with water as solvent it is called hydration. (c) Both other steps break existing attractions, ion-ion in the lattice and solvent-solvent in the liquid, and breaking attractions always requires an input of energy.

A2. (a) ΔH_solution = lattice separation + solvent separation + hydration, with the first two terms positive and the third negative. (b) ΔH_solution = 905 + 130 − 1040 = −5 kJ mol^{-1}. The sum is negative, so dissolving releases a little heat overall and the solution warms slightly. (c) The entropy change, through ΔG_solution = ΔH_solution − TΔS_solution: only the sign of ΔG decides whether dissolving is favorable.

A3. (a) Dispersal of the ions through the solvent: positive, because the ions gain positions and arrangements. Ordering of water into hydration shells around the ions: negative, because the locked water molecules lose freedom of movement. (b) A gas dissolving in a liquid. Gas particles give up the large volume and microstates of the gas phase for confinement in the liquid, so the entropy falls sharply and reliably. (c) Small, highly charged ions grip water tightly and organize large, ordered hydration shells. The negative ordering term from those shells can outweigh the positive dispersal term, leaving ΔS_solution negative overall even though the ions themselves have spread out.

A4. (a) The sign of ΔG_solution states whether dissolution is thermodynamically favorable (negative) or unfavorable (positive) under the conditions in question. It does not state how fast the solid dissolves, and it does not state whether the process is exothermic or endothermic: ΔH carries that information separately. (b) False. ΔG = ΔH − TΔS can be negative with ΔH positive whenever ΔS is positive and TΔS exceeds ΔH. Ammonium nitrate dissolves endothermically and spontaneously for exactly this reason. (c) False. Rate and favorability are separate properties. A large negative ΔG says nothing about speed: a favorable dissolution can be slow, and the speed of dissolving responds to stirring, crushing and surface area, none of which appear in ΔG.

A5. (a) $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$, with $K_{sp} = [Ag^+][Cl^-]$. The solid itself does not appear in the expression: its amount does not change the position of equilibrium. (b) ΔG°_solution = −RT ln Ksp, where ΔG°_solution is the standard free energy of dissolution in J mol^{-1} while inside the equation, R = 8.314 J mol^{-1} K^{-1}, T is the temperature in kelvin, and Ksp is the solubility product at that temperature. (c) Ksp is far below 1, so ln Ksp is negative and ΔG°_solution is positive. The standard equilibrium lies far toward the solid: only a very small concentration of ions is present in the saturated solution.

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B1. (a) $\Delta H_{solution} = 720 + 85 - 790 = +15$ kJ mol^{-1}. (b) The sum is positive, so dissolving absorbs heat overall and the water cools. (c) Second solid: $\Delta H_{solution} = 720 + 85 - 830 = -25$ kJ mol^{-1}. The second solid has the more exothermic enthalpy of solution: with the two breaking steps shared, its stronger hydration release wins by 40 kJ mol^{-1}.

B2. (a) Convert first: $\Delta S_{solution} = +110$ J mol^{-1} K^{-1} $= +0.110$ kJ mol^{-1} K^{-1}. $T\Delta S = 298 \times 0.110 = 32.8$ kJ mol^{-1}. $\Delta G = \Delta H - T\Delta S = 25 - 32.8 = -7.8$ kJ mol^{-1}: favorable at 298 K. (b) $T\Delta S = 200 \times 0.110 = 22.0$ kJ mol^{-1}. $\Delta G = 25 - 22.0 = +3.0$ kJ mol^{-1}: unfavorable at 200 K. (c) $\Delta G = 0$ requires $T = \Delta H / \Delta S = 25{,}000$ J mol^{-1} / 110 J mol^{-1} K^{-1} $= 227$ K. Verification: at 227 K, $T\Delta S = 227 \times 0.110 = 25.0$ kJ mol^{-1} to three significant figures, so $\Delta G = 0$ to the precision of the data, as required. (d) Warming helps. With ΔS positive, a higher T enlarges the favorable $T\Delta S$ term, which is why the salt is unfavorable cold and favorable warm, with the changeover at 227 K.

B3. (a) $\ln K_{sp} = \ln(1.8 \times 10^{-10}) = -22.44$. $\Delta G°_{solution} = -RT \ln K_{sp} = -(8.314$ J mol^{-1} K^{-1}$)(298$ K$)(-22.44) = +55{,}600$ J mol^{-1} $= +55.6$ kJ mol^{-1}. (b) $\ln K_{sp} = -\Delta G° / RT = -55{,}600 / 2477.6 = -22.44$, so $K_{sp} = e^{-22.44} = 1.8 \times 10^{-10}$, the starting value recovered. (c) Silver chloride has the larger $\Delta G°_{solution}$. Its K_{sp} is the smaller of the two, and $\Delta G° = -RT \ln K_{sp}$ grows as K_{sp} shrinks: the smaller constant sits further from 1 on the log scale, so it returns the larger positive free energy.

B4. (a) Salt X: $\Delta H_{solution} = 840 + 110 - 960 = -10$ kJ mol^{-1}. Salt Y: $\Delta H_{solution} = 840 + 110 - 810 = +140$ kJ mol^{-1}. (b) Salt X is more exothermic, by 150 kJ mol^{-1}. The lattice and solvent steps are identical for the two salts, so the hydration step decides the comparison outright. (c) The student's chemistry is right but the conclusion does not rescue the data: smaller, more highly charged ions do hydrate more exothermically, so if Y truly held those cations, Y should show the larger hydration release. As printed, X releases more, so either the cation description or the figures must be wrong. The entropy consequence: the salt that hydrates more strongly, X on these figures, also locks its hydration water into more ordered shells, so it carries the more negative ordering contribution to $\Delta S_{solution}$.

B5. (a) $Q = [Ag^+][Cl^-] = (1.0 \times 10^{-5})(1.0 \times 10^{-5}) = 1.0 \times 10^{-10}$. $Q < K_{sp}$ $(1.0 \times 10^{-10} < 1.8 \times 10^{-10})$: the solution is unsaturated, so more AgCl can dissolve and no precipitation occurs. (b) $Q = (2.0 \times 10^{-5})(2.0 \times 10^{-5}) = 4.0 \times 10^{-10}$. $Q > K_{sp}$: the solution holds more ion product than equilibrium allows, so AgCl precipitates until Q falls back to 1.8×10^{-10}. (c) In a saturated solution $Q = K_{sp} = 1.8 \times 10^{-10}$ exactly, and $\Delta G_{solution} = 0$: dissolving and precipitating run at equal rates in dynamic equilibrium.

B6. (a) Convert first: $\Delta G°_{solution} = +45.7$ kJ mol^{-1} $= +45{,}700$ J mol^{-1}. $\ln K_{sp} = -\Delta G° / RT = -45{,}700 / 2477.6 = -18.45$, so $K_{sp} = e^{-18.45} = 9.8 \times 10^{-9}$. (b) $\Delta G° = -RT \ln K_{sp} = -(2477.6)(\ln 9.8 \times 10^{-9}) = -(2477.6)(-18.44) = +45{,}700$ J mol^{-1} $= +45.7$ kJ mol^{-1}, the starting value recovered. (c) Dilution lowers both ion concentrations, so Q drops below K_{sp} at the moment the water is added. The solution is now unsaturated, so more PbI_2 dissolves until Q climbs back to $K_{sp} = 9.8 \times 10^{-9}$, where it stops with the solution saturated again.

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C1. (a) $NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$. (b) Convert: $\Delta S_{solution} = +0.110$ kJ mol^{-1} K^{-1}. $T\Delta S = 298 \times 0.110 = 32.8$ kJ mol^{-1}. $\Delta G = 25 - 32.8 = -7.8$ kJ mol^{-1}. Negative, so dissolving is thermodynamically favorable at 298 K. (c) The pack turns cold because $\Delta H_{solution}$ is positive: the dissolving salt draws the heat it needs from the water around it. Favorability is paid for by the entropy term, $T\Delta S = 32.8$ kJ mol^{-1}, which is larger than the 25 kJ mol^{-1} enthalpy cost; enthalpy and favorability are separate ledgers, and here entropy settles the bill. (d) Rearranged: $\Delta S = (\Delta H - \Delta G) / T$. Convert to joules: $\Delta H = +25{,}000$ J mol^{-1} and $\Delta G = -7{,}800$ J mol^{-1}. $\Delta S = (25{,}000 - (-7{,}800)) / 298 = 32{,}800 / 298 = +110$ J mol^{-1} K^{-1}, matching the value given in the question.

C2. (a) $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ F^-(aq)$, with $K_{sp} = [Ca^{2+}][F^-]^2$. (b) $\ln K_{sp} = \ln(3.9 \times 10^{-11}) = -23.97$. $\Delta G°_{solution} = -RT \ln K_{sp} = -(8.314)(298)(-23.97) = +59{,}400$ J mol^{-1} $= +59.4$ kJ mol^{-1}. (c) $Q = [Ca^{2+}][F^-]^2 = (1.0 \times 10^{-3})(1.0 \times 10^{-4})^2 = 1.0 \times 10^{-11}$. $Q < K_{sp}$ ($1.0 \times 10^{-11} < 3.9 \times 10^{-11}$): no precipitate forms, and more CaF_2 could dissolve in this solution. (d) $Q = (1.0 \times 10^{-2})(2.0 \times 10^{-3})^2 = 4.0 \times 10^{-8}$. $Q > K_{sp}$ by about a factor of 1000, so CaF_2 precipitates, and precipitation continues until Q falls back to $K_{sp} = 3.9 \times 10^{-11}$.

C3. (a) Salt A: $\Delta S = +0.045$ kJ mol^{-1} K^{-1}, so $T\Delta S = 298 \times 0.045 = 13.4$ kJ mol^{-1} and $\Delta G = 8 - 13.4 = -5.4$ kJ mol^{-1}. Salt B: $\Delta S = -0.050$ kJ mol^{-1} K^{-1}, so $T\Delta S = 298 \times (-0.050) = -14.9$ kJ mol^{-1} and $\Delta G = -12 - (-14.9) = +2.9$ kJ mol^{-1}. (b) Claim 1 is false. Salt A absorbs heat, $\Delta H = +8$ kJ mol^{-1}, yet its ΔG at 298 K is negative because the positive entropy term outweighs the enthalpy cost: it dissolves spontaneously. (c) Salt B is favorable only while $T\Delta S$ stays smaller than the enthalpy payoff: $\Delta G = 0$ at $T = \Delta H / \Delta S = 12{,}000 / 50 = 240$ K. Verification at 200 K: $T\Delta S = 200 \times (-0.050) = -10.0$ kJ mol^{-1}, so $\Delta G = -12 + 10.0 = -2.0$ kJ mol^{-1}, favorable, as expected below the crossover. Above 240 K, salt B is unfavorable despite releasing heat, so Claim 2 is false: an exothermic dissolution with a negative ΔS is favorable only at low temperatures.

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