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Topic 7.14: Free Energy of Dissolution

Worksheet · AP Chemistry

UNIT 7 · EQUILIBRIUM

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How to Use This Worksheet

Work in order. Section A checks the definitions and the sign rules that connect Ksp and ΔG°. Section B practises the skills: finding ΔG° from Ksp, finding Ksp from ΔG°, and using ΔG° = ΔH° − TΔS° to predict how temperature changes solubility. Section C is exam style: judging claims and two full scenarios.

Reference facts. ΔG° = −RT ln Ksp, with R = 8.314 J mol^{-1} K^{-1} and T in kelvin. At 298 K, RT = 2,478 J/mol; at 350 K, RT = 2,910 J/mol; at 400 K, RT = 3,326 J/mol. Also ΔG° = ΔH° − TΔS°. Three landmark values: Ksp = 1 gives ΔG° = 0; Ksp above 1 gives a negative ΔG° and a favoured dissolution; Ksp below 1 gives a positive ΔG° and an unfavoured dissolution. A useful benchmark is Ksp = 1.0×10^{-3}, which gives ΔG° = +17.1 kJ/mol at 298 K. Useful values at 298 K: AgCl, Ksp = 1.8×10^{-10}, ΔG° = +55.6 kJ/mol; $Mg(OH)_2$, Ksp = 5.6×10^{-12}, ΔG° = +64.2 kJ/mol; PbI_2, Ksp = 9.8×10^{-9}, ΔG° = +45.7 kJ/mol; CaF_2, Ksp = 3.9×10^{-11}, ΔG° = +59.4 kJ/mol; $BaSO_4$, Ksp = 1.1×10^{-10}, ΔG° = +56.8 kJ/mol; $Fe(OH)_3$, Ksp = 2.8×10^{-39}, ΔG° = +220 kJ/mol; $Ca(OH)_2$, Ksp = 5.5×10^{-6}, ΔG° = +30.0 kJ/mol; Ag_2CrO_4, Ksp = 1.1×10^{-12}, ΔG° = +68.2 kJ/mol.

Three habits protect every answer. Use the natural logarithm, ln, never $\log_{10}$, in ΔG° = −RT ln Ksp. Convert kJ to J before any subtraction in ΔG° = ΔH° − TΔS°. And use kelvin, never Celsius, for T.

Do not look at the answer key until you have attempted every question.

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Section A: Recall and Concepts

A1. (a) Define the standard free energy of dissolution, ΔG°, in one sentence. (b) State what a negative ΔG° means for a dissolution. (c) State what a positive ΔG° means for a dissolution. (d) State what $\Delta G^\circ = 0$ means for a dissolution.

A2. (a) Write the equation that links ΔG° and Ksp. (b) State the value and units of R. (c) Calculate RT at 298 K, showing the multiplication. (d) State why ln Ksp is negative for a sparingly soluble salt. (e) State the value of ln Ksp when Ksp = 1, and state what ΔG° is then.

A3. (a) State the value of ΔG° when Ksp = 1. (b) State the sign of ΔG° when Ksp is greater than 1, and state what that sign means. (c) State the sign of ΔG° when Ksp is less than 1, and state what that sign means. (d) A salt has Ksp = 1.0×10^{-3} and ln Ksp = -6.91. Calculate ΔG° at 298 K.

A4. Four salts have these Ksp values at 298 K: $Ca(OH)_2$, 5.5×10^{-6}; PbI_2, 9.8×10^{-9}; AgCl, 1.8×10^{-10}; $Fe(OH)_3$, 2.8×10^{-39}. (a) State which salt dissolves most favourably. (b) State which salt dissolves least favourably. (c) State the order of the four salts from most to least favourable. (d) State whether the most favourable salt has the largest or the smallest ΔG°, and explain why in one sentence.

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A5. (a) Write the equation that splits ΔG° into enthalpy and entropy. (b) State the usual sign of ΔS° for a dissolution, and explain why in one sentence. (c) State what happens to ΔG° when the temperature rises, if ΔS° is positive. (d) State the condition under which warming lowers the solubility of a salt. (e) A salt has ΔH° = −10.0 kJ/mol and ΔS° = +40 J mol^{-1} K^{-1}. Calculate ΔG° at 298 K, and state whether its dissolution is favoured under standard conditions.

Section B: Core Practice

B1. AgCl has Ksp = 1.8 × 10^{-10} at 298 K, with ln Ksp = −22.44. (a) State the value of RT at 298 K. (b) Calculate ΔG° for the dissolution of AgCl, showing the multiplication. (c) State the sign of ΔG° and what it means. (d) $Mg(OH)_2$ has ΔG° = +64.2 kJ/mol. State the difference between the two ΔG° values. (e) State which salt, AgCl or $Mg(OH)_2$, dissolves more favourably, and explain why in one sentence. (f) $Mg(OH)_2$ has ln Ksp = −25.91. State whether this is more or less negative than the ln Ksp of AgCl, and explain why in one sentence.

B2. $Mg(OH)_2$ has Ksp = 5.6 × 10^{-12} at 298 K, with ln Ksp = −25.91. (a) Calculate ΔG° for the dissolution of $Mg(OH)_2$. (b) State why ΔG° for $Mg(OH)_2$ is larger than ΔG° for AgCl, using the two Ksp values. (c) Calculate the ratio of the Ksp of AgCl to the Ksp of $Mg(OH)_2$. (d) State which salt has the larger Ksp, and which has the smaller ΔG°. (e) State whether a larger Ksp always means a smaller ΔG°, and justify your answer in one sentence.

B3. CaF_2 has ΔG° = +59.4 kJ/mol at 298 K. (a) Calculate ln Ksp from ΔG°. (b) Calculate Ksp. (c) State whether your answer matches the known Ksp of CaF_2, 3.9 × 10^{-11}, and explain what a match shows. (d) State whether CaF_2 or AgCl dissolves more favourably, using the two ΔG° values.

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B4. PbI_2 has ΔG° = +45.7 kJ/mol at 298 K. (a) Calculate ln Ksp from ΔG°. (b) Calculate Ksp. (c) State whether PbI_2 or CaF_2 dissolves more favourably, and give the difference between their ΔG° values. (d) State whether PbI_2 or AgCl has the larger Ksp, and state the two Ksp values. (e) Explain in one sentence why PbI_2 is the most favourable of the three salts AgCl, CaF_2 and PbI_2. (f) Ag_2CrO_4 has ΔG° = +68.2 kJ/mol. State whether it dissolves more or less favourably than PbI_2, and give the difference between the two ΔG° values.

B5. A salt has ΔH° = +30.0 kJ/mol and ΔS° = +60 J mol^{-1} K^{-1}. (a) Calculate ΔG° at 298 K, showing the subtraction. (b) Calculate Ksp at 298 K. (c) Calculate ΔG° at 350 K. (d) Calculate Ksp at 350 K, using RT = 2,910 J/mol. (e) State the factor by which Ksp rose on warming, and state whether the dissolution is endothermic or exothermic.

B6. A salt has ΔH° = +20.0 kJ/mol and ΔS° = +50 J mol^{-1} K^{-1}. (a) Calculate ΔG° at 298 K. (b) Calculate Ksp at 298 K. (c) Calculate ΔG° at 350 K. (d) Calculate Ksp at 350 K, using RT = 2,910 J/mol. (e) State the factor by which Ksp rose on warming, and state whether this salt or the salt in B5 is more soluble at 298 K.

Section C: Exam Style

C1. Judge each claim, supporting each verdict with the definition or the rule it depends on. (a) "A salt with Ksp = 2.0 has a positive ΔG°." (b) "Using $\log_{10}$ Ksp instead of ln Ksp gives the same ΔG°." (c) "A salt with ΔG° = +220 kJ/mol is the least soluble salt in this unit." (d) "Warming always raises the solubility of a salt." (e) "A salt with Ksp = 1.0×10^{-6} has ΔG° = +34.2 kJ/mol at 298 K."

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C2. A salt has ΔH° = +45.0 kJ/mol and ΔS° = +100 J mol^{-1} K^{-1}. (a) Calculate ΔG° at 298 K, and calculate Ksp at 298 K. (b) Calculate ΔG° at 400 K, and calculate Ksp at 400 K, using RT = 3,326 J/mol. (c) State the factor by which Ksp rose on warming from 298 K to 400 K. (d) Explain in one sentence why warming raised Ksp for this salt. (e) State whether the dissolution is favoured under standard conditions at either temperature, and justify your answer with the two ΔG° values. (f) Calculate the temperature at which ΔG° would reach zero for this salt, and state what that temperature means.

C3. Three salts have these ΔG° values at 298 K: $BaSO_4$, +56.8 kJ/mol; CaF_2, +59.4 kJ/mol; Ag_2CrO_4, +68.2 kJ/mol. (a) Rank the three salts from most to least favourable dissolution. (b) State which salt has the largest Ksp, and which has the smallest Ksp. (c) Calculate the Ksp of $BaSO_4$ from its ΔG°, and state whether your answer matches the known value of 1.1×10^{-10}. (d) Calculate the Ksp of Ag_2CrO_4 from its ΔG°, and state whether your answer matches the known value of 1.1×10^{-12}. (e) Explain in one sentence why Ag_2CrO_4 is the least favourable of the three. (f) $Ca(OH)_2$ has ΔG° = +30.0 kJ/mol. State whether it dissolves more or less favourably than all three salts in this question, and explain why in one sentence.

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Answer Key

A1. (a) ΔG° is the free energy change when one mole of solid dissolves to form a 1 mol/L solution under standard conditions. (b) A negative ΔG° means dissolution is thermodynamically favoured. (c) A positive ΔG° means dissolution is unfavoured, so very little solid dissolves. (d) $\Delta G^\circ = 0$ means the solid and its dissolved ions are equally stable under standard conditions.

A2. (a) $\Delta G^\circ = -RT \ln K_{sp}$. (b) $R = 8.314$ J mol^{-1} K^{-1}. (c) $RT = 8.314 \times 298 = 2{,}478$ J/mol. (d) A sparingly soluble salt has Ksp below 1, and the natural logarithm of a number below 1 is negative. (e) $\ln 1 = 0$, so $\Delta G^\circ = -RT \times 0 = 0$.

A3. (a) $\Delta G^\circ = 0$, because $\ln 1 = 0$. (b) Negative, which means dissolution is favoured under standard conditions. (c) Positive, which means dissolution is unfavoured under standard conditions. (d) $\Delta G^\circ = -(2{,}478)(-6.91) = +17{,}100$ J/mol = +17.1 kJ/mol.

A4. (a) $Ca(OH)_2$, with the largest Ksp, 5.5×10^{-6}. (b) $Fe(OH)_3$, with the smallest Ksp, 2.8×10^{-39}. (c) $Ca(OH)_2$, then PbI_2, then AgCl, then $Fe(OH)_3$. (d) The largest: the most favourable salt has the least negative $\ln K_{sp}$, so $\Delta G^\circ = -RT \ln K_{sp}$ is the smallest.

A5. (a) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. (b) Positive, because ordered ions in a crystal become free-moving ions in solution, which increases disorder. (c) ΔG° falls, because the $-T\Delta S^\circ$ term becomes more negative. (d) Warming lowers solubility when the dissolution is exothermic, when ΔH° is negative, whatever the sign of ΔS°. (e) $\Delta G^\circ = -10{,}000 - (298)(40) = -10{,}000 - 11{,}920 = -21{,}920$ J/mol = −21.9 kJ/mol. The dissolution is favoured, because ΔG° is negative.

B1. (a) $RT = 2{,}478$ J/mol. (b) $\Delta G^\circ = -(2{,}478)(-22.44) = +55{,}600$ J/mol = +55.6 kJ/mol. (c) Positive, which means dissolution is unfavoured under standard conditions. (d) 64.2 − 55.6 = 8.6 kJ/mol. (e) AgCl dissolves more favourably, because its ΔG° is smaller by 8.6 kJ/mol. (f) More negative: $Mg(OH)_2$ has the smaller Ksp, 5.6×10^{-12} against 1.8×10^{-10}, so its natural logarithm is further below zero.

B2. (a) $\Delta G^\circ = -(2{,}478)(-25.91) = +64{,}200$ J/mol = +64.2 kJ/mol. (b) $Mg(OH)_2$ has the smaller Ksp, 5.6×10^{-12} against 1.8×10^{-10}, so its $\ln K_{sp}$ is more negative and $\Delta G^\circ = -RT \ln K_{sp}$ is larger. (c) $(1.8 \times 10^{-10})/(5.6 \times 10^{-12}) = 32$, so the Ksp of AgCl is about 32 times the Ksp of $Mg(OH)_2$. (d) AgCl has the larger Ksp and the smaller ΔG°. (e) Yes: a larger Ksp means a less negative $\ln K_{sp}$, so $\Delta G^\circ = -RT \ln K_{sp}$ is smaller.

B3. (a) $\ln K_{sp} = -\Delta G^\circ/RT = -59{,}400/2{,}478 = -23.97$. (b) $K_{sp} = e^{(-23.97)} = 3.9 \times 10^{-11}$. (c) Yes, it matches: the round trip from Ksp to ΔG° and back returns the same Ksp, which checks the arithmetic. (d) AgCl dissolves more favourably, because its ΔG° of +55.6 kJ/mol is smaller than +59.4 kJ/mol for CaF_2.

B4. (a) $\ln K_{sp} = -\Delta G^\circ/RT = -45{,}700/2{,}478 = -18.44$. (b) $K_{sp} = e^{(-18.44)} = 9.8 \times 10^{-9}$. (c) PbI_2 dissolves more favourably: 59.4 − 45.7 = 13.7 kJ/mol lower than CaF_2. (d) PbI_2 has the larger Ksp: 9.8×10^{-9} against 1.8×10^{-10} for AgCl. (e) PbI_2 has the largest Ksp of the three, so its $\ln K_{sp}$ is the

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least negative and its ΔG° is the smallest. (f) Less favourably: 68.2 − 45.7 = 22.5 kJ/mol larger than the ΔG° of PbI_2.

B5. (a) ΔG° = 30,000 − (298)(60) = 30,000 − 17,880 = +12,120 J/mol = +12.1 kJ/mol. (b) Ksp = e^(−12,120/2,478) = 0.0075. (c) ΔG° = 30,000 − (350)(60) = 30,000 − 21,000 = +9,000 J/mol = +9.0 kJ/mol. (d) Ksp = e^(−9,000/2,910) = 0.045. (e) 0.045/0.0075 = 6, a factor of six; the dissolution is endothermic, because ΔH° is positive.

B6. (a) ΔG° = 20,000 − (298)(50) = 20,000 − 14,900 = +5,100 J/mol = +5.1 kJ/mol. (b) Ksp = e^(−5,100/2,478) = 0.13. (c) ΔG° = 20,000 − (350)(50) = 20,000 − 17,500 = +2,500 J/mol = +2.5 kJ/mol. (d) Ksp = e^(−2,500/2,910) = 0.42. (e) 0.42/0.13 = 3.2, a factor of about three; this salt is more soluble at 298 K, with Ksp = 0.13 against 0.0075 for the salt in B5.

C1. (a) False. Ksp above 1 gives a positive ln Ksp, so ΔG° = −RT ln Ksp is negative. (b) False. The equation needs the natural logarithm: for AgCl, $\log_{10}$ Ksp is −9.74 while ln Ksp is −22.44, and mixing them up changes ΔG° by a factor of 2.303. (c) True. ΔG° = +220 kJ/mol is the value for $Fe(OH)_3$, whose Ksp of 2.8×10^{-39} is the smallest in this unit. (d) False. Warming raises solubility when the dissolution is endothermic, ΔH° positive, whatever the sign of ΔS°; it lowers solubility when the dissolution is exothermic, ΔH° negative. (e) True. ln(1.0×10^{-6}) = −13.82, so ΔG° = −(2,478)(−13.82) = +34,200 J/mol = +34.2 kJ/mol.

C2. (a) ΔG° = 45,000 − (298)(100) = 45,000 − 29,800 = +15,200 J/mol = +15.2 kJ/mol. Ksp = e^(−15,200/2,478) = 0.0022. (b) ΔG° = 45,000 − (400)(100) = 45,000 − 40,000 = +5,000 J/mol = +5.0 kJ/mol. Ksp = e^(−5,000/3,326) = 0.22. (c) 0.22/0.0022 = 100, a factor of one hundred. (d) The dissolution is endothermic with positive entropy, so warming makes the −TΔS° term more negative, ΔG° falls, and Ksp rises. (e) No: ΔG° is positive at both temperatures, +15.2 kJ/mol at 298 K and +5.0 kJ/mol at 400 K, so dissolution is unfavoured at both, though less unfavoured at 400 K. (f) Set ΔG° = 0: 45,000 − 100T = 0, so T = 450 K. At 450 K the dissolution is exactly at the boundary between favoured and unfavoured; above 450 K, ΔG° is negative and dissolution is favoured.

C3. (a) $BaSO_4$, then CaF_2, then Ag_2CrO_4. (b) $BaSO_4$ has the largest Ksp and Ag_2CrO_4 has the smallest Ksp. (c) ln Ksp = −56,800/2,478 = −22.92, so Ksp = e^(−22.92) = 1.1×10^{-10}, which matches the known value. (d) ln Ksp = −68,200/2,478 = −27.52, so Ksp = e^(−27.52) = 1.1×10^{-12}, which matches the known value. (e) Ag_2CrO_4 has the largest ΔG°, +68.2 kJ/mol, which means its ln Ksp is the most negative and its Ksp is the smallest of the three. (f) More favourably: its ΔG° of +30.0 kJ/mol is smaller than all three values in this question, so its ln Ksp is the least negative and its Ksp is the largest.

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