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# Topic 9.3: Gibbs Free Energy and Thermodynamic Favorability

Revision Notes · AP Chemistry

UNIT 9 · THERMODYNAMICS AND ELECTROCHEMISTRY

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## One Number Settles Favorability

**ΔG° is the verdict.** Enthalpy and entropy pull in their own directions, and neither settles the question alone. The Gibbs free energy change combines them into one quantity whose sign decides whether a reaction is favorable under standard conditions.

**Negative means favorable.** $\Delta G^\circ < 0$: the reaction as written is favorable, and products are favored at equilibrium. $\Delta G^\circ > 0$: it is unfavorable as written, and reactants are favored at equilibrium.

**Zero means equilibrium.** The value below marks the balance point: forward and reverse reactions run at equal rates and the composition stops changing. Zero is not "nothing happening."

$$\Delta G^\circ = 0$$

**Favorability is not speed.** A strongly negative ΔG° says a reaction can proceed, not that it proceeds quickly.

**Free energies add.** Combined processes add their ΔG° values: a step at +30 kJ $mol^{-1}$ coupled to one at −50 kJ $mol^{-1}$ gives an overall ΔG° of −20 kJ $mol^{-1}$.

## The Gibbs Equation

**The Gibbs equation.** ΔH° is the enthalpy change, in kJ $mol^{-1}$. T is the absolute temperature, in kelvin: a Celsius temperature must have 273 added before use. ΔS° is the entropy change, in J $mol^{-1}$ $K^{-1}$, multiplied by T and subtracted.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

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**Read the minus sign carefully, and respect T.** Because the entropy term is subtracted, a positive ΔS° pulls ΔG° down toward favorability while a negative ΔS° pushes it up, and either effect grows with temperature. At low temperature TΔS° is small and enthalpy decides; at high temperature it can outweigh ΔH° entirely.

## Convert the Units First

**The two terms arrive in different units.** ΔH° is tabulated in kJ $mol^{-1}$, ΔS° in J $mol^{-1}$ $K^{-1}$. Divide ΔS° by 1000 before the two can be combined.

**The planted error.** Leaving ΔS° in joules makes the TΔS° term 1000 times too large. For ΔH° = −120 kJ $mol^{-1}$ and ΔS° = −150 J $mol^{-1}$ $K^{-1}$ at 298 K, unconverted working gives ΔG° = +44,580 kJ $mol^{-1}$; converted, ΔS° = −0.150 kJ $mol^{-1}$ $K^{-1}$ gives −75.3 kJ $mol^{-1}$.

## The Four Sign Combinations

**ΔH° negative, ΔS° positive: favorable at all temperatures.** Both terms push ΔG° negative, so no temperature rescues the reverse reaction. With ΔH° = −45 kJ $mol^{-1}$ and ΔS° = +120 J $mol^{-1}$ $K^{-1}$, ΔG° is −57 kJ $mol^{-1}$ at 100 K and −165 kJ $mol^{-1}$ at 1000 K.

**ΔH° positive, ΔS° negative: favorable at no temperature.** Both terms push ΔG° positive. With ΔH° = +40 kJ $mol^{-1}$ and ΔS° = −60 J $mol^{-1}$ $K^{-1}$, ΔG° is +46 kJ $mol^{-1}$ at 100 K and +100 kJ $mol^{-1}$ at 1000 K.

**ΔH° negative, ΔS° negative: favorable at low temperatures only.** Enthalpy favors, entropy opposes. The enthalpy term wins while T is small; as T climbs the subtracted term grows until ΔG° crosses zero. With ΔH° = −120 kJ $mol^{-1}$ and ΔS° = −150 J $mol^{-1}$ $K^{-1}$, ΔG° is −105 kJ $mol^{-1}$ at 100 K but +30 kJ $mol^{-1}$ at 1000 K.

**ΔH° positive, ΔS° positive: favorable at high temperatures only.** Entropy favors, enthalpy opposes, so the reaction waits until TΔS° outgrows ΔH°. With ΔH° = +90 kJ $mol^{-1}$ and ΔS° = +300 J $mol^{-1}$ $K^{-1}$, ΔG° is +60 kJ $mol^{-1}$ at 100 K and −210 kJ $mol^{-1}$ at 1000 K.

## The Crossover Temperature

**The crossover temperature.** Setting the Gibbs equation to zero gives the one temperature at which a same-sign reaction sits exactly at equilibrium, with ΔS° in kJ $mol^{-1}$ $K^{-1}$ to match ΔH°; substituting it back returns ΔG° = 0 exactly.

$T = \Delta H^\circ / \Delta S^\circ$

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**A crossover exists only when the signs match.** With opposite signs the ratio ΔH° / ΔS° is negative, and a negative kelvin temperature is impossible. That marks the always-favorable or never-favorable cases.

**Which side is favorable depends on the case.** Both negative: favorable below the crossover, as with ΔH° = −80 kJ mol$^{-1}$ and ΔS° = −200 J mol$^{-1}$ K$^{-1}$, favorable below 400 K. Both positive: favorable above it, as with ΔH° = +90 kJ mol$^{-1}$ and ΔS° = +300 J mol$^{-1}$ K$^{-1}$, favorable above 300 K.

**For a phase change, the crossover is the transition temperature.** Melting has ΔH° > 0 and ΔS° > 0, so solid and liquid are in equilibrium at one temperature under standard pressure: the melting point. Below it freezing is favorable; above it, melting is.

## Predict the Sign of ΔS° First

**Count gas moles.** Gases carry far more entropy than liquids or solids, so the gas count settles most sign questions. In the reaction below, three moles of gas become two, so ΔS° is negative before any data is consulted. Producing gas from condensed phases gives ΔS° positive; burying gas gives it negative.

$2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g)$

**Phase changes speak plainly.** Sublimation, solid to gas, has a positive entropy change: dry ice subliming is the standard example. Condensation and freezing have negative ones. With the sign of ΔH°, these predictions place a reaction in one of the four cases before any number is used.

## Worked Examples

**Example 1: ΔH° = −120 kJ mol$^{-1}$, ΔS° = −150 J mol$^{-1}$ K$^{-1}$. Convert first: ΔS° = −0.150 kJ mol$^{-1}$ K$^{-1}$. At 298 K, ΔG° = −120 − (298)(−0.150) = −120 + 44.7 = −75.3 kJ mol$^{-1}$, so the reaction is favorable at 298 K. Both quantities are negative, so a crossover exists: T = 120 / 0.150 = 800 K.**

**Example 2: ΔH° = +90 kJ mol$^{-1}$, ΔS° = +300 J mol$^{-1}$ K$^{-1}$. Convert: ΔS° = +0.300 kJ mol$^{-1}$ K$^{-1}$. Both positive, so find the crossover: T = 90 / 0.300 = 300 K. Check either side: at 250 K, ΔG° = 90 − (250)(0.300) = +15 kJ mol$^{-1}$, unfavorable; at 350 K, ΔG° = 90 − (350)(0.300) = −15 kJ mol$^{-1}$, favorable.**

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**Example 3: $\Delta H^\circ = -45$ kJ mol$^{-1}$, $\Delta S^\circ = +120$ J mol$^{-1}$ K$^{-1}$. Convert: $\Delta S^\circ = +0.120$ kJ mol$^{-1}$ K$^{-1}$. At 500 K, $\Delta G^\circ = -45 - (500)(0.120) = -105$ kJ mol$^{-1}$. At 100 K, $\Delta G^\circ = -45 - (100)(0.120) = -57$ kJ mol$^{-1}$. Both are negative, as the signs alone require.**

**Example 4: $\Delta H^\circ = -80$ kJ mol$^{-1}$, $\Delta S^\circ = -200$ J mol$^{-1}$ K$^{-1}$. Convert: $\Delta S^\circ = -0.200$ kJ mol$^{-1}$ K$^{-1}$. The crossover is T = 80 / 0.200 = 400 K. At 350 K, $\Delta G^\circ = -80 - (350)(-0.200) = -10$ kJ mol$^{-1}$, favorable; at 450 K, $\Delta G^\circ = -80 - (450)(-0.200) = +10$ kJ mol$^{-1}$, unfavorable.**

## Traps That Cost Marks in Topic 9.3

**Using Celsius in the equation.** The Gibbs equation takes kelvin. Running a calculation at "25" instead of 298 K shrinks the entropy term almost to nothing.

**Skipping the unit conversion.** $\Delta S^\circ$ in joules beside $\Delta H^\circ$ in kilojoules makes the entropy term 1000 times too large, as the +44,580 kJ mol$^{-1}$ blunder shows.

**Reading $\Delta G^\circ = 0$ as "no reaction".** Zero means equilibrium, with forward and reverse reactions continuing at equal rates.

**Reading "favorable" as "fast".** $\Delta G^\circ$ judges whether a reaction can proceed and which side equilibrium favors, never how quickly.

**Reporting a crossover for opposite signs.** Opposite signs make $T = \Delta H^\circ / \Delta S^\circ$ negative. That is the signal to reclassify the reaction as always or never favorable.

**Assuming exothermic means always favorable.** An exothermic reaction with $\Delta S^\circ < 0$ loses at high temperature once the entropy penalty outgrows the heat released.

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### Key Relationships to Remember

- $\Delta G° = \Delta H° - T\Delta S°$, with T in kelvin and $\Delta S°$ converted to kJ $mol^{-1}$ $K^{-1}$ before use
- $\Delta G° < 0$ means thermodynamically favorable as written, with products favored at equilibrium
- $\Delta G° > 0$ means unfavorable as written, with reactants favored at equilibrium; $\Delta G° = 0$ means equilibrium
- $\Delta H° < 0$ with $\Delta S° > 0$ is favorable at all temperatures; $\Delta H° > 0$ with $\Delta S° < 0$ is favorable at none
- $\Delta H° < 0$ with $\Delta S° < 0$ is favorable at low temperatures; $\Delta H° > 0$ with $\Delta S° > 0$ is favorable at high temperatures
- Same-sign pairs have a crossover temperature $T = \Delta H° / \Delta S°$ where $\Delta G° = 0$; opposite-sign pairs have none
- For a phase change under standard pressure, the crossover temperature is the melting or boiling point
- Reversing a reaction flips the sign of $\Delta G°$; combined processes add: overall $\Delta G°$ is the sum of the steps' $\Delta G°$ values

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