

Entropy and spontaneity

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Reactivity 1.4, Entropy and spontaneity, for the course first assessed in 2025. The whole unit is additional higher level (AHL); there is no SL counterpart. Prerequisites: enthalpy changes, balanced equations, equilibrium and logarithms. Numerical model reactions are original teaching examples, not experimental measurements or official examination questions.

AHL: Entropy and accessible arrangements

An endothermic change can occur without continuous external driving: enthalpy alone cannot predict the favoured direction. The second ingredient is **entropy**, a state property related to the ways matter and energy can be distributed among accessible microscopic arrangements. “Disorder” is a rough analogy, not a sufficient explanation. A state with more accessible arrangements has higher entropy.

Imagine four labelled, independently moving model particles, each able to occupy the left or right half of a box. There is one arrangement with all four on the left but six distinct arrangements with two on each side. A spread-out distribution is more probable because more microscopic arrangements produce it, not because particles actively seek disorder. These counts illustrate the idea; they are not a quantitative entropy calculation for a real gas.

For the same substance under comparable conditions, the gas generally has higher entropy than the liquid, and the liquid higher than the solid: particles and energy have more accessible arrangements. Melting, vaporization and expansion of a gas normally increase entropy; freezing, condensation and compression at constant temperature normally decrease it.

In a reaction, an increase in the total amount of gas often suggests a positive system entropy change. For $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$, one mole of gas becomes two, suggesting an increase. This is a useful qualitative guide, not a replacement for entropy data when gas amounts are unchanged or different substances must be compared.

A standard molar entropy S° is an entropy per mole under specified standard conditions, usually tabulated in $\text{J K}^{-1} \text{mol}^{-1}$. Unlike standard enthalpies of formation, the standard molar entropies of elements at room temperature are **not zero**. The third-law reference is a perfect crystal at 0 K, with zero entropy in that ideal limit.

AHL: Calculating a reaction entropy change

Use coefficients from the balanced equation:

$$\Delta S^\circ = \sum \nu S^\circ_{\text{products}} - \sum \nu S^\circ_{\text{reactants}}.$$

Multiply each molar entropy by its stoichiometric coefficient before subtracting. Reversing the reaction reverses the sign; doubling the equation doubles its reaction entropy change.

■ Worked example: a model dissociation

For the invented model reaction $\text{AB}(\text{g}) \rightarrow \text{A}(\text{g}) + \text{B}(\text{g})$, assign $S^\circ_{\text{AB}} = 220$, $S^\circ_{\text{A}} = 150$ and $S^\circ_{\text{B}} = 160 \text{ J K}^{-1} \text{mol}^{-1}$.

$$\Delta S^\circ = (150 + 160) - 220 = +90 \text{ J K}^{-1} \text{mol}^{-1}.$$

The positive sign agrees with the increase in gas amount. It describes the reacting **system**, not system plus surroundings. A negative system entropy change is possible when the surroundings gain sufficient entropy.

For rounded example data $S^\circ_{\text{N}_2} = 192$, $S^\circ_{\text{H}_2} = 131$ and $S^\circ_{\text{NH}_3} = 193$ in the same units, the equation $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ gives

$$\Delta S^\circ = 2(193) - [192 + 3(131)] = -199 \text{ J K}^{-1} \text{mol}^{-1}.$$

The negative sign is consistent with four moles of gas becoming two. The value refers to the equation as written, forming two moles of ammonia; it is not automatically the change per mole of ammonia.

AHL: Gibbs energy and spontaneity

Gibbs energy combines the system’s enthalpy and entropy changes. At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S.$$

Here T is absolute temperature in kelvin. Use one energy unit throughout: either all J or all kJ. If ΔH is in kJ mol^{-1} and ΔS in $\text{J K}^{-1} \text{mol}^{-1}$, divide the entropy value by 1000 before substitution.

- $\Delta G < 0$: the forward change is thermodynamically spontaneous for the **current composition and conditions**.
- $\Delta G > 0$: the reverse change is favoured; the forward direction would require coupling or external driving.
- $\Delta G = 0$: there is no net thermodynamic driving force; a reacting mixture is at equilibrium.

Spontaneous does not mean instantaneous, complete, explosive or requiring no initial activation. An activation barrier can make a favourable change extremely slow. A catalyst changes the pathway and rates, not the initial/final thermodynamic states: it does not change ΔG° or the equilibrium constant at a fixed temperature.

The criterion includes the surroundings indirectly. At constant pressure, an exothermic system transfers heat to its surroundings, increasing their entropy. The relationship $\Delta S_{\text{total}} = -\Delta G/T$ under the stated constant-temperature/pressure conditions explains why the system's entropy may decrease while the total entropy increases.

■ Worked example: an endothermic change

Assign $\Delta H^\circ = +20.0 \text{ kJ mol}^{-1}$, $\Delta S^\circ = +100 \text{ J K}^{-1} \text{ mol}^{-1}$ and $T = 300 \text{ K}$ to an invented reaction.

$$\Delta S^\circ = \frac{100}{1000} = 0.100 \text{ kJ K}^{-1} \text{ mol}^{-1}.$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 20.0 - 300(0.100) = -10.0 \text{ kJ mol}^{-1}.$$

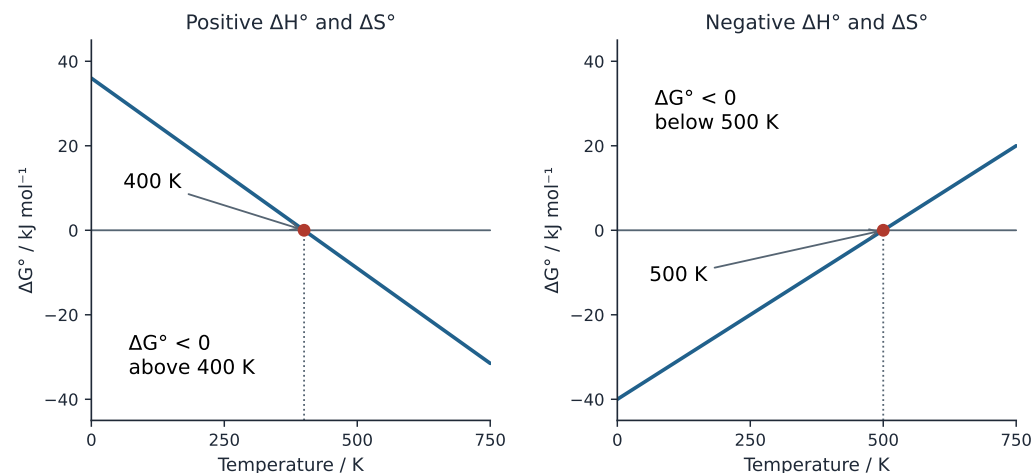
The positive entropy contribution outweighs the positive enthalpy term. The negative **standard** Gibbs energy change favours products in the equilibrium sense, but the actual direction at an arbitrary composition also depends on the reaction quotient, developed below.

AHL: Temperature thresholds

If ΔH° and ΔS° are approximately constant over a temperature range, a plot of ΔG° against T is a straight line. Its intercept is ΔH° and gradient is $-\Delta S^\circ$. Set $\Delta G^\circ = 0$ to find a crossing:

$$T_{\text{cross}} = \frac{\Delta H^\circ}{\Delta S^\circ}.$$

Convert units first. A crossing is a boundary, not an interval of negative Gibbs energy. Test a temperature on either side, or reason from the gradient, before writing an inequality.



Temperature trends assume constant enthalpy and entropy and unchanged phases over the range shown.

■ Worked comparison: opposite slopes

For model A, $\Delta H^\circ = +36.0 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = +90.0 \text{ J K}^{-1} \text{ mol}^{-1}$:

$$T_{\text{cross}} = 36.0/0.0900 = 400 \text{ K}.$$

At 300 K, $\Delta G^\circ = 36.0 - 300(0.0900) = +9.0 \text{ kJ mol}^{-1}$; at 500 K it is -9.0 kJ mol^{-1} . Thus $\Delta G^\circ < 0$ above 400 K in this model.

For model B, $\Delta H^\circ = -40.0 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -80.0 \text{ J K}^{-1} \text{ mol}^{-1}$:

$$\Delta G^\circ = -40.0 + 0.0800T, \quad T_{\text{cross}} = 500 \text{ K}.$$

At 300 K the value is $-16.0 \text{ kJ mol}^{-1}$; at 600 K it is $+8.0 \text{ kJ mol}^{-1}$. The negative-entropy model instead has $\Delta G^\circ < 0$ **below** 500 K.

Sign of ΔH°	Sign of ΔS°	When $\Delta G^\circ < 0$
—	+	all positive temperatures in the model
+	—	no positive temperature in the model
+	+	above the positive crossing
—	—	below the positive crossing

These predictions are conditional. Enthalpy and entropy vary with temperature; phase changes can invalidate a straight-line extrapolation. A mathematically calculated

threshold outside the stated range of stable phases is not proof of a real operating condition.

AHL: Composition, reaction quotient and equilibrium

Standard and actual Gibbs energy changes answer different questions. For the current mixture,

$$\Delta G = \Delta G^\circ + RT \ln Q.$$

Q is the reaction quotient, built from the current composition with stoichiometric powers. Rigorous thermodynamic Q uses dimensionless activities; school ideal-mixture calculations use concentrations or pressures relative to their standard values. Pure solids and pure liquids have activity approximately one and do not appear as variable concentration factors. Do not take a logarithm of a quantity carrying units.

For an ideal model $A(g) \rightleftharpoons B(g)$, Q is the ratio of the activities of B to A. As B accumulates relative to A, Q rises and the forward driving force becomes less negative. Equilibrium means $Q = K$ and $\Delta G = 0$, giving

$$\Delta G^\circ = -RT \ln K.$$

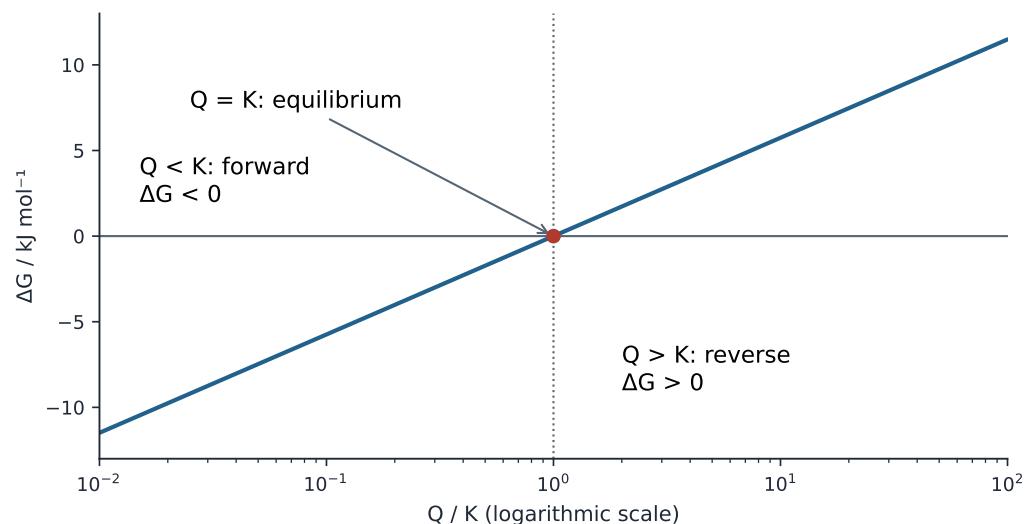
Use $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ with ΔG° in J mol^{-1} , or $R = 0.008314$ with kJ mol^{-1} . The logarithm is natural, not base ten.

- $K > 1$ means $\ln K > 0$ and $\Delta G^\circ < 0$.
- $K < 1$ means $\Delta G^\circ > 0$; reactants are favoured in the equilibrium ratio, not the exclusive species present.
- $K = 1$ means $\Delta G^\circ = 0$. It does not imply equal concentrations of every species for every possible equation.

Combining the equations gives a particularly useful direction test:

$$\Delta G = RT \ln \left(\frac{Q}{K} \right).$$

If $Q < K$, the forward change is favoured; if $Q > K$, the reverse change is favoured. At equilibrium, $\Delta G = 0$ even when ΔG° is nonzero.



The standard value can stay unchanged while composition changes the actual driving force.

■ Worked example: an unfavourable standard value, but forward change

For an invented reaction at 300 K, let $\Delta G^\circ = +6.00 \text{ kJ mol}^{-1}$ and $Q = 0.0100$.

$$\Delta G = 6.00 + 0.008314(300) \ln(0.0100) = -5.49 \text{ kJ mol}^{-1}.$$

The forward change is favoured at this composition even though the standard value is positive. Separately, $K = \exp[-6000/(8.314 \times 300)] \approx 0.0902$, so $Q < K$, confirming the direction independently. Do not replace the actual ΔG with the standard value.

Practice

All model data are invented unless identified as rounded example data. Use $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

1. Explain entropy using accessible arrangements, and explain why “particles want to become disordered” is inadequate. Compare liquid and gas of the same substance under suitable comparable conditions.
2. Predict the sign of the system entropy change for water freezing, isothermal compression of a gas, and $2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g)$. State the reasoning and one limitation of gas-amount counting.
3. Use the rounded ammonia data above to calculate ΔS° for the balanced synthesis equation. Give the value for the reversed equation and for forming one mole of ammonia.

- A student sets the standard molar entropy of nitrogen at 298 K to zero because it is an element. Correct the error and identify the relevant zero-entropy reference.
- Calculate ΔG° at 300 K for $\Delta H^\circ = +20.0 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = +100 \text{ J K}^{-1} \text{ mol}^{-1}$. Explain why an endothermic standard change can have a negative standard Gibbs energy change.
- For $\Delta H^\circ = +40.0 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = +80.0 \text{ J K}^{-1} \text{ mol}^{-1}$, find ΔG° at 400 K. Find the crossing temperature and the interval with $\Delta G^\circ < 0$ under the constant-value approximation.
- State the sign combinations giving $\Delta G^\circ < 0$ at all positive temperatures and at no positive temperature in the simple model. Explain each from $\Delta H^\circ - T\Delta S^\circ$.
- For $\Delta H^\circ = -40.0 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -80.0 \text{ J K}^{-1} \text{ mol}^{-1}$, determine the interval with $\Delta G^\circ < 0$. Check it using 300 K and 600 K.
- A model has $\Delta H^\circ = +18.0 \text{ kJ mol}^{-1}$ and $\Delta G^\circ = -6.00 \text{ kJ mol}^{-1}$ at 300 K. Calculate ΔS° in $\text{J K}^{-1} \text{ mol}^{-1}$.
- An equilibrium has $K = 1000$ at 298 K. Calculate ΔG° and explain what its sign says about K , without claiming the reaction goes to completion.
- At 300 K, $\Delta G^\circ = +6.00 \text{ kJ mol}^{-1}$ and $Q = 0.0100$. Calculate the actual ΔG . Calculate K as a separate check of the predicted direction.
- A model reaction has $K = 10.0$ at 300 K. Use $\Delta G = RT \ln(Q/K)$ to find ΔG for $Q = 0.100, 10.0$ and 100 . Identify the direction favoured in each case.
- Explain why a catalyst does not change K at fixed temperature, why a spontaneous reaction can be slow, and why a temperature crossing calculated from constant thermodynamic values may fail outside the stated range.

■ Worked answers

- Entropy relates to the number of accessible ways matter/energy can be distributed, a state property rather than an intention of particles. A gas generally has more accessible arrangements than the same substance as a liquid; qualitative “disorder” alone does not explain the microscopic counting.
- Freezing: negative, fewer accessible arrangements in the solid. Isothermal gas compression: negative, less available spatial distribution. Decomposition: positive is expected as 2 mol gas becomes 5 mol. Gas amount is a guide; compare entropy data when changes of substance or similar gas amounts make the prediction uncertain.
- $\Delta S^\circ = 2(193) - [192 + 3(131)] = -199 \text{ J K}^{-1} \text{ mol}^{-1}$ per equation as written. Reverse: $+199 \text{ J K}^{-1} \text{ mol}^{-1}$. For $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightarrow \text{NH}_3$, halve the value: $-99.5 \text{ J K}^{-1} \text{ mol}^{-1}$.
- The zero convention for elemental standard enthalpy of formation is not an entropy convention. Nitrogen gas at 298 K has nonzero molar entropy. The ideal third-law reference is a perfect crystal at 0 K.

- Convert $\Delta S^\circ = 0.100 \text{ kJ K}^{-1} \text{ mol}^{-1}$. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 20.0 - 300(0.100) = -10.0 \text{ kJ mol}^{-1}$. The positive entropy term outweighs the endothermic enthalpy term; the actual direction also depends on composition.
- $\Delta G^\circ = 40.0 - 400(0.0800) = +8.00 \text{ kJ mol}^{-1}$. $T_{\text{cross}} = 40.0/0.0800 = 500 \text{ K}$. Because the gradient is negative, $\Delta G^\circ < 0$ for $T > 500 \text{ K}$; equality at 500 K is not a negative value.
- Negative enthalpy and positive entropy: both terms make ΔG° negative at every positive T . Positive enthalpy and negative entropy: subtracting $T\Delta S^\circ$ adds a positive term, so no positive T makes it negative in this model.
- $\Delta G^\circ = -40.0 + 0.0800T$; it is negative below 500 K. At 300 K it is $-16.0 \text{ kJ mol}^{-1}$; at 600 K it is $+8.0 \text{ kJ mol}^{-1}$. The direction of the inequality differs from question 6 because ΔS° is negative.
- $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T = [18.0 - (-6.00)]/300 = 0.0800 \text{ kJ K}^{-1} \text{ mol}^{-1} = 80.0 \text{ J K}^{-1} \text{ mol}^{-1}$.
- $\Delta G^\circ = -RT \ln K = -8.314(298) \ln(1000) = -17114 \text{ J mol}^{-1}$, or $-17.1 \text{ kJ mol}^{-1}$. The negative standard value corresponds to $K > 1$; finite K does not mean all reactants disappear.
- $\Delta G = \Delta G^\circ + RT \ln Q = 6.00 + 0.008314(300) \ln(0.0100) = -5.49 \text{ kJ mol}^{-1}$: forward change is favoured. $K = \exp[-6000/(8.314 \times 300)] \approx 0.0902$; $0.0100 < K$ independently gives the same direction.
- At $Q = 0.100$, $\Delta G = 0.008314(300) \ln(0.0100) = -11.5 \text{ kJ mol}^{-1}$: forward. At $Q = 10.0$, $\Delta G = RT \ln 1 = 0$: equilibrium. At $Q = 100$, $\Delta G = 0.008314(300) \ln 10 = +5.74 \text{ kJ mol}^{-1}$: reverse.
- A catalyst lowers a kinetic barrier but does not change the Gibbs-energy difference of the states, so ΔG° and K are unchanged at fixed T . A high barrier can make a favourable process slow. Thermodynamic values change with temperature and phases can change, invalidating a constant-value extrapolation.

Exam tips

- Write T in kelvin. Convert J to kJ before combining entropy with a kJ enthalpy; keep R consistent too.
- Use products minus reactants, including all coefficients, for entropy changes. Elements at 298 K do not have zero standard molar entropy.
- A crossing needs an inequality and stated assumptions. For negative entropy, increasing temperature makes ΔG° more positive.
- Distinguish ΔG from ΔG° : equilibrium requires the first to be zero, not generally the second. Use natural logarithms and dimensionless Q and K .
- State spontaneity separately from rate and completion. A catalyst changes neither K nor the thermodynamic direction at a specified composition.

Reference: IB Chemistry guide, Reactivity 1.4.