Entropy and spontaneity

Reactivity 1.4 · AHL only

Can an endothermic change be favourable?

An enthalpy sign is only part of the explanation

Entropy, temperature and current composition also affect the thermodynamic direction.

This whole unit is AHL: Reactivity 1.4. Use balanced equations, enthalpy, equilibrium and natural logarithms.

Numerical models and questions are original teaching examples. A favourable direction does not establish a fast rate.

Count arrangements, not intentions

Particles on left	Distinct arrangements
0	1
1	4
2	6
3	4
4	1

Four labelled model particles: each independently occupies the left or right half of the box.

What entropy describes

Matter and energy have accessible arrangements

Entropy is a state property related to the accessible microscopic arrangements of matter and energy. Particles do not “want disorder”.

For the same substance under suitable comparable conditions, gas generally has higher entropy than liquid, and liquid higher than solid.

Melting, vaporization and gas expansion generally increase entropy. Freezing, condensation and isothermal compression generally decrease it.

A trend is not a substitute for data

Use gas amount as a qualitative clue

$\mathrm{N_2O_4(g)} \rightarrow \mathrm{2NO_2(g)}$: one mole gas becomes two, suggesting increased system entropy.

When gas amounts are unchanged or different substances complicate the comparison, use entropy data.

Elements at 298 K do not have zero standard molar entropy. The ideal zero reference is a perfect crystal at 0 K.

Entropy from solid to gas

entropy increases: $\Delta S > 0$



Entropy rises with the number of possible arrangements

Products minus reactants, with coefficients

1. **Relationship.** $\Delta S^\circ = \sum \nu S^\circ_{\text{products}} - \sum \nu S^\circ_{\text{reactants}}$.
2. **Invented model.** $\mathrm{AB(g)} \rightarrow \mathrm{A(g)} + \mathrm{B(g)}$: assigned molar entropies 220, 150 and 160 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$.
3. **Calculation.** $\Delta S^\circ = (150 + 160) - 220 = +90$ J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$.

Decision

This is the system entropy change. It is not the total change including the surroundings.

Check the coefficient trap

Rounded example data

$\mathrm{N_2} + 3\mathrm{H_2} \rightarrow 2\mathrm{NH_3}$, all gases. Molar entropies: $\mathrm{N_2}$ 192, $\mathrm{H_2}$ 131 and $\mathrm{NH_3}$ 193 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$.

Calculate the standard reaction entropy change. Then reverse the equation and halve the original equation.

The entropy value belongs to the written equation

1. **Original equation.** $\Delta S^\circ = 2(193) - [192 + 3(131)] = -199$ J K^{-1} mol^{-1}.
2. **Reversed.** Change the sign: $+199$ J K^{-1} mol^{-1}.
3. **One mole ammonia.** Halve the original equation and value: -99.5 J K^{-1} mol^{-1}.

Decision

Four moles of gas become two; the negative sign fits the qualitative prediction.

One equation, one energy unit

1. **Relationship.** $\Delta G = \Delta H - T\Delta S$ at constant temperature and pressure.
2. **Temperature.** Use kelvin, never Celsius, in the product $T\Delta S$.
3. **Energy units.** If enthalpy is in kJ mol^{-1}, convert entropy from J to kJ K^{-1} mol^{-1} before substitution.

Decision

Gibbs energy incorporates the system entropy and the effect of heat transfer on the surroundings.

Interpret the actual Gibbs energy change

Actual value	**Thermodynamic meaning**
$\Delta G < 0$	Forward change favoured
$\Delta G > 0$	Reverse change favoured
$\Delta G = 0$	No net driving force: equilibrium

An endothermic standard change with negative Gibbs energy

1. **Invented data.** $\Delta H^\circ = +20.0$ kJ mol^{-1}; $\Delta S^\circ = +100$ J K^{-1} mol^{-1}; $T = 300$ K.
2. **Convert.** $\Delta S^\circ = 100/1000 = 0.100$ kJ K^{-1} mol^{-1}.
3. **Calculate.** $\Delta G^\circ = 20.0 - 300(0.100) = -10.0$ kJ mol^{-1}.

Decision

The entropy term outweighs the positive enthalpy. Actual direction at other compositions also depends on Q.

A favourable change can remain slow

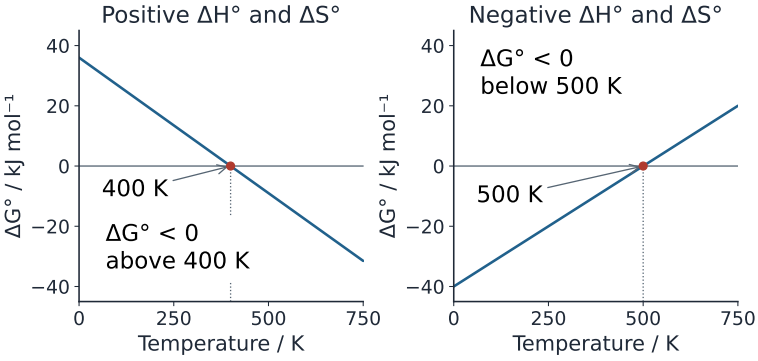
A barrier is a kinetic question

Spontaneous does not mean instantaneous or complete. An activation barrier can make a favourable change very slow.

A catalyst changes the pathway and rates, not the initial/final thermodynamic states. At fixed temperature it changes neither standard Gibbs energy nor K.

The system entropy may decrease if the surroundings gain enough entropy: with only pressure–volume work at constant T and p, $\Delta S_{\mathrm{total}} = -\Delta G/T$.

A crossing needs an inequality



Invented constant-value models: a positive entropy gives a negative gradient, and vice versa.

Positive enthalpy and positive entropy

1. **Model A.** $\Delta H^\circ = +36.0$ kJ mol^{-1}; $\Delta S^\circ = +0.0900$ kJ K^{-1} mol^{-1}.
2. **Crossing.** $\Delta G^\circ = 0$ gives $T = \Delta H^\circ / \Delta S^\circ = 400$ K.
3. **Test both sides.** At 300 K: $+9.0$ kJ mol^{-1}. At 500 K: -9.0 kJ mol^{-1}.

Decision

The standard **Gibbs energy** change is negative above 400 K, under the constant-value approximation.

Negative entropy reverses the temperature trend

1. **Model B.** $\Delta H^\circ = -40.0$ kJ mol^{-1}; $\Delta S^\circ = -0.0800$ kJ K^{-1} mol^{-1}.
2. **Rearrange.** $\Delta G^\circ = -40.0 + 0.0800\,T$; crossing at 500 K.
3. **Test.** At 300 K: -16.0 kJ mol^{-1}. At 600 K: $+8.0$ kJ mol^{-1}.

Decision

Negative below 500 K. Do not copy the inequality from a positive-entropy example.

Four sign combinations

Enthalpy sign	Entropy sign	Negative standard ΔG
$-$	$+$	All positive T in model
$+$	$-$	No positive T in model
$+$	$+$	Above positive crossing
$-$	$-$	Below positive crossing

When the straight-line model fails

State the range of the conclusion

Enthalpy and entropy vary with temperature. A phase change can invalidate a constant-value extrapolation.

The intercept of the mathematical line is enthalpy and its gradient is minus entropy; an extrapolated 0 K intercept is not a measured reaction at absolute zero.

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

Standard and actual are different quantities

1. **Current mixture.** $\Delta G = \Delta G^\circ + RT \ln Q$.
2. **Quotient.** Build Q from current dimensionless activities with stoichiometric powers; pure solid/liquid activities are approximately one.
3. **Units and logarithm.** Use natural log. With R = 8.314 J K^{-1} mol^{-1}, use Gibbs energies in J mol^{-1}.

Decision

A negative standard **Gibbs energy** does not guarantee a negative actual value at every composition.

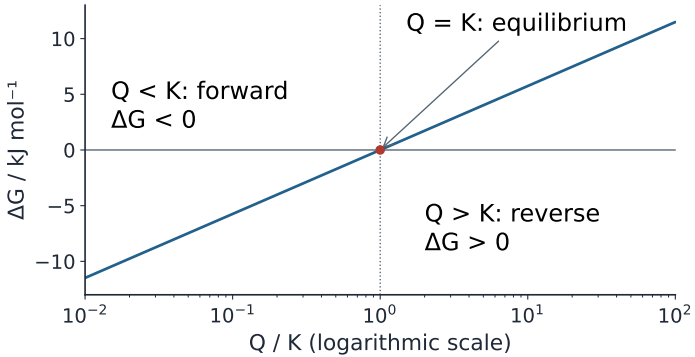
Derive the equilibrium relationship

1. **At equilibrium.** $\Delta G = 0$ and $Q = K$.
2. **Substitute.** $0 = \Delta G^\circ + RT\ln K$, so $\Delta G^\circ = -RT\ln K$.
3. **Combine.** $\Delta G = RT\ln(Q/K)$ gives direction from the current quotient relative to K.

Decision

At equilibrium actual ΔG is zero; the standard value need not be zero.

Composition changes the driving force



At 300 K: $Q < K$ favours forward change; $Q > K$ favours reverse change; $Q = K$ is equilibrium.

Positive standard value, forward actual change

1. **Invented data.** $\Delta G^\circ = +6.00$ kJ mol^{-1}; $T = 300$ K; $Q = 0.0100$.
2. **Actual value.** $\Delta G = 6.00 + 0.008314(300)\ln(0.0100) = -5.49$ kJ mol^{-1}.
3. **Independent check.** $K = \exp[-6000/(8.314 \times 300)] \approx 0.0902$; Q is smaller than K.

Decision

The current composition favours the forward direction despite a positive standard value.

A finite equilibrium constant is not completion

1. **Given.** $K = 1000$ at 298 K.
2. **Calculate.** $\Delta G^\circ = -RT\ln K = -8.314(298)\ln(1000) \approx -17.1$ kJ mol^{-1}.
3. **Interpret.** K $>$ 1 corresponds to a negative standard value. A finite K does not mean all reactants disappear.

Decision

K $=$ 1 implies zero standard ΔG, not equal concentrations for every possible balanced equation.

Try a composition change

Work before revealing

A model has K = 10.0 at 300 K. Find actual ΔG for Q = 0.100, 10.0 and 100.

Use $\Delta G = RT\ln(Q/K)$ and R = 0.008314 kJ K^{-1} mol^{-1}. State a direction for each result.

Then attempt the handout's 13 questions, including temperature inequalities and entropy coefficients.

Composition-change reasoning

1. **Q = 0.100.** $\Delta G = 0.008314(300)\ln(0.0100) = -11.5$ kJ mol^{-1}: forward.
2. **Q = 10.0.** $\Delta G = RT\ln 1 = 0$: equilibrium.
3. **Q = 100.** $\Delta G = 0.008314(300)\ln 10 = +5.74$ kJ mol^{-1}: reverse.

Check yourself

Read the symbol as carefully as the number

Products minus reactants, with coefficients, for entropy. Kelvin and one energy unit for Gibbs calculations.

A crossing needs a temperature inequality and assumptions. Distinguish standard ΔG from the actual driving force.

Natural logarithms; dimensionless Q and K. Spontaneity, speed and completion are separate conclusions.