07 Chemical Energetics II



7 Spontaneity and Entropy

Spontaneous reaction: a reaction that is energetically feasible, i.e. _____. Once started, it proceeds on its own _____ of energy from the surroundings.

NOTE Spontaneous says nothing about **rate**: a spontaneous reaction can be very slow.

7.1 Entropy

DEFINITION **Entropy, S**: a measure of the _____ in a system. The more disordered a system, the greater the number of ways for particles and energy to be _____, therefore the larger is the entropy.

$\Delta S = S_{final} - S_{initial}$

units: J mol^{-1} K^{-1}

8 Factors Affecting Entropy

Temperature ↑

$\Delta S > 0$: particles have more average _____ and there are more ways to distribute the larger number of quanta of energy.

Change in phase

S: solid < liquid ≪ gas. Melting: particles no longer in _____ → more ways to arrange particles and distribute energy. Boiling: particles move randomly, large ↑ in volume.

More gas particles

$\Delta S > 0$: disorder increases as the number of moles of _____ _____ increases, e.g. $2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$. No change in moles of gas → $\Delta S \approx 0$.

Predict ΔS	Sign	Reason
$2N_2O(g) + O_2(g) \rightarrow 4NO(g)$	+	moles of gas ↑ (3 → 4) → more ways to distribute particles and energy
$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$	_____	a gas forms from liquids
$3O_2(g) \rightarrow 2O_3(g)$	_____	moles of gas ↓ (3 → 2)
$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	−	moles of gas ↓ (3 → 2) → fewer ways to distribute

NOTE **Dissolving an ionic solid**: two opposing effects: ions become free to move (S ↑), but water molecules become more _____ around the ions (S ↓). Usually the first wins, e.g. $NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$, $\Delta S > 0$.

9 Gibbs Free Energy

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

T in kelvin, convert ΔS to _____ before use

DEFINITION The **standard Gibbs free energy, $\Delta G^\ominus$**, is used to predict the _____ of a reaction.

ΔG < 0	ΔG = 0	ΔG > 0
spontaneous, K > 1, products favoured	at equilibrium (e.g. at m.p. or b.p.)	non-spontaneous, spontaneous in reverse

$$\Delta G_r = \Sigma \Delta G_f(\text{products}) - \Sigma \Delta G_f(\text{reactants})$$

WORKED EXAMPLE: RUSTING Iron rusts in air:

$$2Fe(s) + \frac{3}{2} O_2(g) \rightarrow Fe_2O_3(s)$$

$\Delta H = -825$ kJ mol^{-1} and $\Delta S = -272$ J mol^{-1} K^{-1}. Is rusting spontaneous at 298 K?

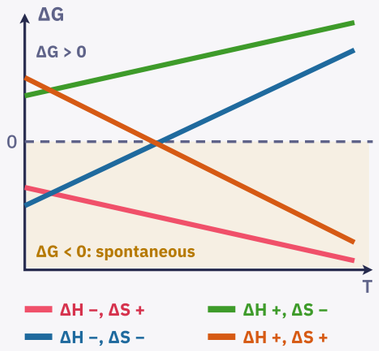
1. Convert ΔS to kJ: −272 J mol^{-1} K^{-1} = _____ kJ mol^{-1} K^{-1}
2. $\Delta G = \Delta H - T\Delta S = -825 - 298 \times (-0.272)$
3. ΔG = _____
4. $\Delta G < 0$ → spontaneous at 298 K

WORKED EXAMPLE: MELTING ICE Ice melts at 273 K. The enthalpy change of fusion is +6.0 kJ mol^{-1}. Find ΔS for melting.

1. At the m.p., ice and water are at equilibrium → $\Delta G = 0$
2. $0 = \Delta H - T\Delta S \rightarrow \Delta S = \Delta H \div T$
3. $\Delta S = 6000 \div 273$ = _____

10 Effect of Temperature on Spontaneity

ΔH	ΔS	Spontaneity
–	+	Since ΔS > 0, −TΔS < 0 → ΔG negative at _____: always spontaneous
+	–	Since ΔS < 0, −TΔS > 0 → ΔG positive at all temperatures: _____ spontaneous
–	–	Since ΔS < 0, −TΔS > 0. As T ↑, −TΔS becomes more positive → ΔG positive eventually: spontaneous only at _____
+	+	Since ΔS > 0, −TΔS < 0. As T ↑, −TΔS becomes more negative → ΔG negative eventually: spontaneous at _____



Case	Examples
ΔH –, ΔS +	combustion of octane, decomposition of nitroglycerine
ΔH +, ΔS –	photosynthesis: must be driven by a continuous energy input (sunlight)
ΔH –, ΔS –	precipitation of AgCl, condensation, freezing (enthalpy driven)
ΔH +, ΔS +	melting, boiling, decomposition of Group 2 carbonates (entropy driven)

WORKED EXAMPLE: MINIMUM TEMPERATURE

In a blast furnace:
$C(s) + CO_2(g) \rightarrow 2CO(g)$
ΔH = +172.5 kJ mol^{-1} and ΔS = +176.2 J mol^{-1} K^{-1}. Find the minimum temperature for the reaction to be spontaneous.

1. At 298 K: ΔG = 172.5 − 298 × 0.1762 = +120 kJ mol^{-1} > 0 → not spontaneous
2. Spontaneous when ΔG < 0: ΔH − TΔS < 0 → T > ΔH ÷ ΔS
3. T > 172.5 ÷ 0.1762 = _____

WORKED EXAMPLE Baking powder releases CO_2 on heating:
$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$
ΔH = +130 kJ mol^{-1} and ΔS = +335 J mol^{-1} K^{-1}. Above what temperature is this spontaneous?

1. At 298 K: ΔG = 130 − 298 × 0.335 = +30.2 kJ mol^{-1} > 0 → not spontaneous
2. Spontaneous when ΔG < 0 → T > ΔH ÷ ΔS
3. T > 130 ÷ 0.335 = _____

Likewise $MgCO_3$ decomposes above 576 K but $BaCO_3$ only above 1566 K: ΔH($MgCO_3$) is _____, ΔS similar.

11 Limitations of $\Delta G^{\ominus}$

11.1 Standard states

$\Delta G^{\ominus}$ is worked out for _____ only (1 bar, 1 mol dm^{-3}). Real conditions are often different, so $\Delta G^{\ominus}$ can give the wrong prediction.

e.g. $H_2O(l) \rightarrow H_2O(g)$ at 298 K: $\Delta G^{\ominus} = 44.0 - 298 \times 0.118 = +8.84$ kJ mol^{-1}, so water should not boil. Yet at a low enough pressure, water does boil at 298 K.

11.2 Temperature

Using ΔG = ΔH − TΔS at a new temperature assumes ΔH and ΔS stay _____ as T changes. This is not true if a substance _____ in between, as ΔH and ΔS then change a lot.

e.g. $H_2 + I_2 \rightarrow 2HI$: ΔG = +3.5 kJ mol^{-1} at 298 K (I_2 solid) but −20.0 kJ mol^{-1} at 500 K (I_2 gas), so 298 K data cannot predict ΔG at 500 K.

11.3 Kinetics

ΔG only tells us whether a reaction is energetically feasible, **not how fast** it goes.

C(diamond) → C(graphite) has ΔG < 0, so it is spontaneous. But its _____ is very high, so almost no particles have enough energy to react at room temperature, and the change is far too slow to observe.

→ Diamond is energetically unstable but _____ _____ relative to graphite.

