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Topic 9.5: Free Energy and Equilibrium

Revision Notes · AP Chemistry

UNIT 9 · THERMODYNAMICS AND ELECTROCHEMISTRY

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The Bridge Between ΔG° and K

Two descriptions of the same destination. The equilibrium constant K reports the ratio of products to reactants at equilibrium. The standard free energy change ΔG° reports the free energy released, or needed, when standard state reactants convert to standard state products.

One equation connects them.

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

Here R = 8.314 J mol^{-1} K^{-1}, T is the temperature in kelvin, and ln is the natural logarithm. Neither quantity mentions speed: both describe where equilibrium lies, never how fast a reaction gets there.

Reading the Sign of ΔG°

K greater than 1: ΔG° is negative. ln K is positive, so the leading minus sign makes ΔG° negative. Products favored at equilibrium: K = 4.2 × 10^8 gives ΔG° = −49.2 kJ mol^{-1} at 298 K.

K less than 1: ΔG° is positive. ln K is negative, so ΔG° is positive and reactants are favored. ΔG° = +35 kJ mol^{-1} at 298 K corresponds to K = 7.3 × 10^{-7}: products still form, but only in traces.

K equal to 1: ΔG° is zero. ln 1 = 0, so neither side is favored. Zero does not mean nothing reacts: the equilibrium mixture holds comparable amounts of both sides.

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Units: Joules and Kelvin, Every Time

ΔG° enters the equation in joules. A ΔG° quoted as −11.4 kJ mol^{-1} must be entered as −11,400 J mol^{-1}, and results are divided by 1000 to report kJ mol^{-1}. Skipping that factor of 1000 is the commonest arithmetic failure on this topic.

T enters in kelvin. A temperature of 25 °C enters as 298 K; inserting 25 shrinks RT twelvefold.

ln, not log. The equation uses the natural logarithm. The base 10 form carries a conversion factor:

$\Delta G^\circ = -2.303\ RT \log K$

Using log in the ln equation understates every result by 2.303.

A Sense of Scale: 5.7 kJ Buys a Factor of Ten

At 298 K, the step is 5.7 kJ mol^{-1}.

$RT \ln 10 = 5.7\ \text{kJ mol}^{-1}$

Each 5.7 kJ mol^{-1} step in ΔG° multiplies or divides K by exactly 10. ΔG° = −5.7 kJ mol^{-1} means K = 10; ΔG° = −11.4 kJ mol^{-1} means K = 1.0 × 10^2; ΔG° = +5.7 kJ mol^{-1} means K = 0.10.

Estimate before calculating. Dividing ΔG° by 5.7 reads off the power of ten in K, enough to check a calculator answer.

The step size grows with temperature. The 5.7 figure belongs to 298 K.

$RT \ln 10 = 19.1\ \text{kJ mol}^{-1}$ at 1000 K

So the same energy step buys a far smaller change in K.

ΔG Is Not ΔG°

ΔG° is fixed by temperature alone. For a given reaction it has one value at one temperature. It states only which side equilibrium favors.

ΔG belongs to the actual mixture. Its sign is a direction arrow: negative means forward toward equilibrium; positive means reverse; zero means the mixture is already at equilibrium.

A negative ΔG° does not force forward motion. Load a vessel with products and ΔG turns positive even when ΔG° is strongly negative. Direction questions are always ΔG questions.

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Direction Under Real Conditions: Q Against K

The companion equation.

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

Here Q is the reaction quotient: the same products over reactants construction as K, built from current pressures or concentrations instead of equilibrium ones.

Compare Q with K. Q < K: too little product, ΔG is negative, forward. Q > K: too much product, ΔG is positive, reverse. Q = K: ΔG = 0, equilibrium. The comparison and the equation always agree.

$\Delta G = RT \ln(Q / K)$

The quiz's own case. For a reaction with K = 5.0, a mixture with Q = 20 gives $\Delta G = RT \ln(20 / 5.0) = +3.4$ kJ mol^{-1} at 298 K: positive, so the reaction proceeds in reverse.

Temperature Moves K

K belongs to a temperature. Change T and ΔG° and K change together, still locked by the bridge equation. Temperature is the only influence that moves K.

Exothermic reactions lose K as T rises. Ammonia synthesis has $\Delta H^\circ = -92$ kJ mol^{-1} and $\Delta S^\circ = -199$ J mol^{-1} K^{-1}.

$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$

At 298 K, $\Delta G^\circ = -32.7$ kJ mol^{-1} and $K = 5.4 \times 10^5$. At 700 K, $\Delta G^\circ = +47.3$ kJ mol^{-1} and $K = 3.0 \times 10^{-4}$. Le Chatelier's principle gives the same verdict: heating pushes an exothermic equilibrium back toward reactants.

The same ΔG° means a different K at a different T. $\Delta G^\circ = -8.314$ kJ mol^{-1} at 1000 K gives ln K = 1 and K = 2.7. The identical energy at 298 K gives K = 29, because RT is smaller there.

Worked Examples

> **Example 1: K from ΔG°, two ways. A reaction has $\Delta G^\circ = -11.4$ kJ mol^{-1} at 298 K. Convert first: −11,400 J mol^{-1}. Then $\ln K = -\Delta G^\circ / RT = 11{,}400 / 2477.6 = 4.60$, so $K = e^{4.60} = 1.0 \times 10^2$. Scale check: 11.4 / 5.7 = 2 powers of ten, $K = 10^2$. The two routes agree.**

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Example 2: Direction from ΔG, with numbers.

$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

This reaction has K = 0.15 at 298 K, so $\Delta G° = -RT \ln(0.15) = +4.7$ kJ mol^{-1}. A mixture at $P(N_2O_4) = 0.10$ atm and $P(NO_2) = 0.50$ atm has $Q = (0.50)^2 / 0.10 = 2.5$, far above K. Then $\Delta G = \Delta G° + RT \ln Q = +4.70 + (2.478)(\ln 2.5) = +7.0$ kJ mol^{-1}. Positive: the mixture proceeds in reverse until Q falls to 0.15.

Example 3: ΔG° from a small K. K = 0.020 at 298 K gives ln K = −3.91, so ΔG° = −RT ln K = −(2477.6)(−3.91) = +9690 J mol^{-1} = +9.7 kJ mol^{-1}. Positive, as K < 1 requires, and reactants are favored.

Example 4: The same energy at 1000 K. ΔG° = −8.314 kJ mol^{-1} at 1000 K gives ln K = 8314 / 8314 = 1.00, so K = e^1 = 2.7. At 298 K the same ΔG° gives ln K = 3.36 and K = 29: the same energy is worth more at the lower temperature.

Traps That Cost Marks in Topic 9.5

Answering a direction question with ΔG°. ΔG° names the destination; ΔG, or a Q against K comparison, names the direction of travel.

Feeding kilojoules into a joules equation. −RT ln K works in joules because R does. Convert ΔG° at the start, or the answer lands a factor of 1000 adrift.

Using Celsius, or log for ln. T must be kelvin, and log base 10 needs its 2.303 factor.

Reading K < 1 as "no products". Reactants are favored, not exclusive: K = 7.3×10^{-7} still places some product at equilibrium.

Doubling ΔG° and expecting K to double. K depends exponentially on ΔG°. Doubling a ΔG° of −16.3 kJ mol^{-1} at 500 K, where K = 50, squares the constant: K becomes 2500, not 100.

Claiming a catalyst or a concentration change alters K. Only temperature does; the others move Q only.

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Key Relationships to Remember

- $\Delta G^\circ = -RT \ln K$, with $R = 8.314$ J mol^{-1} K^{-1}, T in kelvin, and ΔG° in joules while inside the equation
- $K > 1$ pairs with $\Delta G^\circ < 0$ (products favored); $K < 1$ pairs with $\Delta G^\circ > 0$ (reactants favored); $K = 1$ pairs with $\Delta G^\circ = 0$
- At 298 K, every 5.7 kJ mol^{-1} of ΔG° is one factor of 10 in K; the step is $RT \ln 10$ and grows with temperature
- The more negative ΔG° is at a given temperature, the larger K is; doubling ΔG° squares K rather than doubling it
- $\Delta G = \Delta G^\circ + RT \ln Q = RT \ln(Q / K)$: its sign, not the sign of ΔG°, sets the direction a real mixture moves
- $Q < K$ means forward, $Q > K$ means reverse, $Q = K$ means equilibrium with $\Delta G = 0$
- ΔG° and K depend only on temperature for a given reaction; concentrations, pressures and catalysts change Q and ΔG, never K
- For an exothermic reaction K falls as temperature rises; for an endothermic reaction K rises, as $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ requires

Continue Revising

Topic 9.5 Quiz: Free Energy and Equilibrium

Topic 9.5 Worksheet

Unit 9: All Topics

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