Topic 7.9: Introduction to Le Chatelier's Principle

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UNIT 7 · EQUILIBRIUM

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Stress, Shift, and the Partial Undoing

A stress is any change imposed on a system at equilibrium: a species added or removed, the volume changed, the temperature changed. A shift is the system's answer: a net reaction, forward or reverse, that runs until equilibrium is restored.

The shift always opposes the stress, but only partly. It never fully cancels the change, because the net reaction stops as soon as Q returns to Kc.

During the shift the forward and reverse rates are unequal; the net reaction runs in whichever direction returns Q to Kc, and the rates settle equal again at a new equilibrium.

Adding or Removing a Species

Adding a reactant, or removing a product, pushes Q below Kc, and the system shifts right: the forward reaction runs net, consuming some of the addition or replacing the removal.

Adding a product, or removing a reactant, pushes Q above Kc, and the system shifts left: the reverse reaction runs net until Q falls back to Kc.

In every case the disturbed species ends between its disturbed value and its original equilibrium value: the change is blunted, never erased.

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Volume and Pressure Changes in Gas Systems

Halving the volume of a gas mixture doubles every concentration, but Q does not simply double: each concentration carries its coefficient as a power. The shift goes toward the side with fewer gas moles.

Count only gas moles. For $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ the count is 3 against 2, so compression shifts right; for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ it is 1 against 2, so compression shifts left.

Doubling the volume reverses the logic: the shift goes toward the side with more gas moles. When both sides hold equal gas moles, as in $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ with 2 against 2, Q is unchanged by any volume change and no shift occurs.

Temperature: The One Change That Moves Kc

Temperature is the only stress that changes Kc itself. Every other stress changes concentrations, and so Q; a temperature change moves the target.

Read heat from the equation. An exothermic reaction releases heat, so heat behaves like a product: raising the temperature shifts the system left and Kc falls. Lowering the temperature shifts it right and Kc rises.

An endothermic reaction takes in heat, so heat behaves like a reactant: raising the temperature shifts the system right and Kc rises; cooling reverses both.

Stresses That Cause No Shift

A catalyst lowers the activation energy of both directions equally, so both rates rise together: equilibrium comes sooner, but the position and Kc are unchanged.

Adding an inert gas at constant volume raises the total pressure, yet no partial pressure or concentration changes, so Q still equals Kc and nothing shifts. Added at constant pressure, the same gas expands the vessel and every concentration falls, exactly an expansion: the shift runs toward more gas moles.

Pure solids and pure liquids never appear in Q, so adding or removing them changes nothing: extra $CaCO_3(s)$ in $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ leaves $Q = [CO_2]$ untouched, with no shift, as long as some of each solid is present.

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Diluting a Solution Equilibrium

Adding solvent dilutes every dissolved species at once, and Q responds through the powers in the expression. For A(aq) ⇌ 2B(aq) with Kc = 0.40, diluting an equilibrium mixture with [A] = [B] = 0.40 mol L^{-1} to twice its volume gives [A] = [B] = 0.20 mol L^{-1} and Q = $(0.20)^2$ / 0.20 = 0.20, below Kc.

The system shifts right, toward more dissolved particles, because each forward step rebuilds B twice as fast as it consumes A, lifting Q back to Kc. Dilution is a concentration stress, judged by Q just like an addition or removal.

Worked Examples

Example 1: An addition, blunted but not cancelled. For $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, Kc = 4.0. An equilibrium mixture has $[H_2] = [I_2] = 0.50$ and [HI] = 1.00 mol L^{-1}: check $1.00^2 / (0.50 \times 0.50) = 4.0$. Hydrogen is added until $[H_2]$ = 1.50 mol L^{-1}. Now Q = $1.00^2 / (1.50 \times 0.50) = 1.33$, below Kc, so the shift is right. The shift consumes x of each reactant and makes 2x of HI; solving $(1.00 + 2x)^2 / ((1.50 - x)(0.50 - x)) = 4.0$ gives x = 0.167, and the new equilibrium is $[H_2]$ = 1.33, $[I_2]$ = 0.33 and [HI] = 1.33 mol L^{-1}. Note where $[H_2]$ ends: above 0.50, below 1.50.

Example 2: A compression. For $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, Kc = 0.40, and an equilibrium mixture has $[N_2O_4] = [NO_2]$ = 0.40 mol L^{-1}. The volume is halved, doubling both to 0.80 mol L^{-1}. Then Q = $(0.80)^2 / 0.80 = 0.80$, above Kc, so the shift is left, toward N_2O_4, the side with 1 gas mole against 2. The new equilibrium is $[N_2O_4]$ = 0.90 and $[NO_2]$ = 0.60 mol L^{-1}: check $(0.60)^2 / 0.90 = 0.40$. Doubling the volume instead would drop Q to 0.20 and run the shift right.

Example 3: Heating an exothermic equilibrium. For $2NO_2(g) \rightleftharpoons N_2O_4(g)$, ΔH < 0, so heat is effectively a product. Kc = 170 at 298 K but only about 6 at 348 K. Heating an equilibrium mixture does two things at once: Kc itself drops, and the mixture's Q, still equal to the old Kc, now sits above the new one, so the shift runs left. Brown NO_2 reforms and the mixture darkens. Cooling reverses both effects: Kc rises and the shift runs right, toward colourless N_2O_4, so the mixture lightens.

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> **Example 4: Pressure raised, nothing moves. Argon is added at constant volume to the equilibrium of Example 2. The total pressure climbs, but $[N_2O_4]$ and $[NO_2]$ are still 0.40 mol L^{-1} each, so Q = 0.40 = Kc and no shift follows. Pressure alone is not the stress: what matters is whether the concentrations inside Q have moved, and they have not.**

Traps That Cost Marks in Topic 7.9

"The shift cancels out the addition." Never fully. In Example 1 the added hydrogen ends at 1.33 mol L^{-1}, far above the original 0.50: the shift stops the moment Q returns to Kc, always before the stress is undone.

"Increasing the pressure shifts every equilibrium toward the products." Direction follows the gas mole count, not the word products. Compression shifts $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ left, toward the reactant; pressure raised by an inert gas at constant volume shifts nothing.

"Doubling every concentration doubles Kc." Kc is fixed at a given temperature. In Example 2, doubling the concentrations doubled Q, from 0.40 to 0.80, while Kc stayed 0.40: the gap between Q and Kc drove the shift.

"A catalyst increases the equilibrium yield." A catalyst changes only the time taken: both rates rise equally, so the position, Kc and the equilibrium yield are unchanged, just reached sooner.

"Adding more solid reactant pushes the reaction right." Solids are absent from Q. Adding $CaCO_3(s)$ to $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ leaves $Q = [CO_2]$ unchanged, so there is no shift.

"Heating always favours the products and raises Kc." Heating favours whichever direction absorbs heat. For an exothermic reaction that is the reverse direction: heating $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ shifts it left and Kc falls. Only endothermic reactions give more products and a larger Kc on heating.

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Key Relationships to Remember

- A stress is the imposed change; a shift is the net reaction that partially offsets it
- Adding a reactant or removing a product makes Q < Kc and shifts the system right; adding a product or removing a reactant makes Q > Kc and shifts it left
- The disturbed species ends between its disturbed value and its original equilibrium value, never back at the original
- Compression shifts toward the side with fewer gas moles; expansion shifts toward more; equal gas moles means no shift
- An inert gas at constant volume causes no shift; at constant pressure it acts as an expansion
- A catalyst speeds both directions equally: equilibrium sooner, same position, same Kc
- Pure solids and liquids do not appear in Q, so adding or removing them causes no shift
- Only temperature changes Kc: heating favours the endothermic direction, raising Kc for endothermic reactions and lowering it for exothermic ones

Continue Revising

Topic 7.9 Quiz: Introduction to Le Chatelier's Principle

Topic 7.9 Worksheet

Unit 7: All Topics

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