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# Topic 7.9: Introduction to Le Chatelier's Principle

Worksheet · AP Chemistry

UNIT 7 · EQUILIBRIUM

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## How to Use This Worksheet

Work in order. Section A checks the vocabulary and the quick judgements: what a stress is, which stresses cause no shift, gas mole counting, and the temperature rules. Section B practises the full routine on real numbers: write Q after the stress, compare it with Kc, then find or bound the new equilibrium. Section C is exam style: a removal solved in full, a five-change comparison, and a temperature change read through colour.

Reference facts. A stress changes Q; the system shifts until Q equals Kc again. Adding a reactant or removing a product makes Q less than Kc and shifts the system right; adding a product or removing a reactant makes Q greater than Kc and shifts it left. Compression shifts toward fewer gas moles, expansion toward more; equal gas moles means no shift. Only temperature changes Kc: heating favours the endothermic direction. A catalyst, a pure solid or liquid, and an inert gas at constant volume cause no shift.

Conventions: every vessel is closed and the temperature is constant unless a question says otherwise. Concentrations are in mol $L^{-1}$. A shift right means a net forward reaction; a shift left means a net reverse reaction. Where a question asks for a new equilibrium, the answer must satisfy Kc exactly and conserve atoms.

Do not look at the answer key until you have attempted every question.

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## Section A: Recall and Concepts

**A1.** (a) Define the terms stress and shift. (b) State whether a shift ever fully cancels the stress that caused it, and explain your answer using Q and Kc.

**A2.** Judge each statement, giving the reason. (a) "Adding a catalyst to an equilibrium mixture increases Kc." (b) "Adding argon at constant volume raises the total pressure, so $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ shifts right." (c) "Adding more $CaCO_3(s)$ to $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ shifts the system right."

**A3.** For each reaction, count the moles of gas on each side and state the direction of shift when the equilibrium mixture is compressed at constant temperature. (i) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. (ii) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. (iii) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$.

**A4.** (a) For the exothermic reaction $A(g) \rightleftharpoons B(g)$ + heat, state the effect of heating, and separately of cooling, on the position of equilibrium and on Kc. (b) For the endothermic reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, $\Delta H > 0$, state the effect of heating on the position and on Kc.

**A5.** For $A(aq) \rightleftharpoons 2B(aq)$, Kc = 0.40. An equilibrium mixture has [A] = 0.90 and [B] = 0.60 mol $L^{-1}$. (a) Verify that the mixture is at equilibrium. (b) The solution is diluted to twice its volume. Calculate Q immediately after the dilution and state the direction of the shift, explaining it in terms of particles.

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## Section B: Core Practice

**B1.** For $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, Kc = 4.0. An equilibrium mixture has $[H_2] = [I_2] = 0.40$ and $[HI] = 0.80$ mol $L^{-1}$. Hydrogen is added until $[H_2] = 1.20$ mol $L^{-1}$. (a) Calculate Q immediately after the addition and state the direction of the shift. (b) Calculate the new equilibrium concentrations. (c) State where the final $[H_2]$ sits relative to its original and disturbed values, and name the general rule this illustrates.

**B2.** For $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, Kc = 0.40. An equilibrium mixture has $[N_2O_4] = [NO_2] = 0.40$ mol $L^{-1}$. (a) The volume is suddenly halved. State both concentrations immediately afterwards, calculate Q, and state the direction of the shift with the gas mole counts. (b) Starting again from the same equilibrium mixture, the volume is instead doubled. Calculate Q and state the direction of the shift. (c) State the value of Kc in (a) and in (b).

**B3.** A concentration-time graph for $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ flattens at $[SO_2] = 0.40$, $[O_2] = 0.20$ and $[SO_3] = 0.60$ mol $L^{-1}$. Some $SO_3$ is then removed, dropping $[SO_3]$ to 0.20 mol $L^{-1}$ while the other concentrations are unchanged at that instant. (a) Calculate Kc from the plateau values. (b) Calculate Q immediately after the removal and state the direction of the shift. (c) Solving for the new equilibrium gives $[SO_3] \approx 0.33$ mol $L^{-1}$. State the two values between which it must lie, and explain why it cannot reach the higher of them. (d) State the value of Kc at the new equilibrium.

**B4.** For $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta H = -198$ kJ $mol^{-1}$. Kc = $2.5 \times 10^2$ at 800 K and Kc = 4.0 at 1000 K. An equilibrium mixture at 800 K is heated to 1000 K. (a) State the direction of the shift, explaining your answer by treating heat as a product. (b) State what happens to the equilibrium concentration of $SO_3$. (c) The mixture is then cooled back to 800 K. State the value of Kc and the direction of the shift. (d) Explain why temperature changed Kc here while the stresses in B1 to B3 did not.

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**B5.** For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, Kc = 8.0. An equilibrium mixture has $[N_2] = 0.25$, $[H_2] = 0.50$ and $[NH_3] = 0.50$ mol $L^{-1}$. (a) Argon is added at constant volume. State the value of Q and whether the system shifts, with the reason. (b) In a second vessel, argon is added at constant pressure and the volume doubles, halving every concentration. Calculate Q and state the direction of the shift, giving the gas mole counts on each side.

**B6.** For $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, Kc = $[CO_2] = 0.010$, and a vessel at equilibrium holds both solids with $[CO_2] = 0.010$ mol $L^{-1}$. (a) More $CaCO_3(s)$ is added. State the effect on the position of equilibrium and on $[CO_2]$, with the reason. (b) More CaO(s) is added instead. State the effect. (c) $CO_2(g)$ is pumped in until $[CO_2] = 0.030$ mol $L^{-1}$. Calculate Q, state the shift direction, and state the final $[CO_2]$ once equilibrium is restored, explaining how this case differs from the partial offset in B1.

## Section C: Exam Style

**C1.** 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 $L^{-1}$. Some HI is removed, dropping [HI] to 0.20 mol $L^{-1}$ at that instant. (a) Calculate Q and state the direction of the shift. (b) Calculate the new equilibrium concentrations. (c) Show that the new [HI] is only a partial replacement of what was removed. (d) State Kc at the new equilibrium.

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**C2.** For $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta H < 0$, five changes are made, each separately, to a mixture at equilibrium. For each change state the shift direction, the effect on Kc, and the effect on the equilibrium concentration of $SO_3$. (i) The vessel is compressed at constant temperature. (ii) A catalyst is added. (iii) The temperature is raised. (iv) Argon is added at constant volume. (v) Some $SO_2$ is removed at constant temperature.

**C3.** For $2NO_2(g) \rightleftharpoons N_2O_4(g)$ the forward reaction is exothermic. At 350 K, Kc = 8.0, and an equilibrium mixture has $[NO_2] = 0.50$ and $[N_2O_4] = 2.0$ mol $L^{-1}$. The mixture is heated to a temperature at which Kc = 0.50. $NO_2$ is brown and $N_2O_4$ is colourless. (a) Verify that the starting mixture is at equilibrium. (b) Compare Q just after heating with the new Kc and state the direction of the shift. (c) State how the colour changes and why. (d) State whether $[NO_2]$ at the new equilibrium is higher or lower than 0.50 mol $L^{-1}$, and give the value of Kc there.

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## Answer Key

**A1.** (a) A stress is a change imposed on a system at equilibrium, such as adding or removing a species, changing the volume, or changing the temperature. A shift is the system's response: a net forward or net reverse reaction that runs until equilibrium is restored. (b) No. The net reaction runs only until Q returns to Kc. Because the disturbed species appears in Q, Q reaches Kc while part of the imposed change is still in place, so the shift stops early: the stress is partly offset, never fully cancelled and never overshot.

**A2.** (a) False. A catalyst speeds the forward and reverse reactions equally, so equilibrium is reached faster, but the position and Kc are unchanged; Kc changes only with temperature. (b) False. At constant volume the argon raises the total pressure but changes no partial pressure and no concentration, so Q still equals Kc and there is no shift. (c) False. $CaCO_3$ is a pure solid and does not appear in Q, which is simply $[CO_2]$; adding more of it leaves Q unchanged, so there is no shift.

**A3.** (i) Reactants: 1 + 3 = 4 gas moles; products: 2 gas moles. Compression shifts right, toward fewer gas moles. (ii) Reactants: 2 gas moles; products: 2 gas moles. The counts are equal, so Q is unchanged and there is no shift. (iii) Reactants: 1 gas mole; products: 1 + 1 = 2 gas moles. Compression shifts left, toward the single gas mole.

**A4.** (a) Heating: heat is a product of the forward reaction, so the system shifts left to consume heat, the position moves toward A, and Kc decreases. Cooling: the system shifts right to replace the lost heat, the yield of B rises, and Kc increases. (b) Heating adds the reactant-like heat, so the system shifts right toward NO, and Kc increases.

**A5.** (a) $Q = [B]^2 / [A] = (0.60)^2 / 0.90 = 0.36 / 0.90 = 0.40 = Kc$, so the mixture is at equilibrium. (b) Dilution halves both concentrations: [A] = 0.45 and [B] = 0.30 mol $L^{-1}$. $Q = (0.30)^2 / 0.45 = 0.09 / 0.45 = 0.20$, below Kc = 0.40, so the shift is right. Each forward step turns one dissolved particle into two, so the forward reaction rebuilds B twice as fast as it consumes A and lifts Q back to Kc: the system shifts toward the side with more dissolved particles.

**B1.** (a) $Q = [HI]^2 / ([H_2][I_2]) = (0.80)^2 / (1.20 \times 0.40) = 0.64 / 0.48 = 1.33$. $Q < Kc = 4.0$, so the shift is right, toward HI. (b) Let the shift consume x of $H_2$ and of $I_2$ and form 2x of HI: $[H_2] = 1.20 - x$, $[I_2] = 0.40 - x$, $[HI] = 0.80 + 2x$. Setting $(0.80 + 2x)^2 / ((1.20 - x)(0.40 - x)) = 4.0$ gives x = 0.133. The new equilibrium is $[H_2] = 1.067$, $[I_2] = 0.267$ and $[HI] = 1.067$ mol $L^{-1}$. Check: $(1.067)^2 / (1.067 \times 0.267) = 4.0$. (c) The final $[H_2]$, 1.067 mol $L^{-1}$, lies between the disturbed value 1.20 and the original 0.40: the system consumed part of the addition but not all of it. This is the partial offset: a shift blunts a stress without cancelling it.

**B2.** (a) Both concentrations double: $[N_2O_4] = [NO_2] = 0.80$ mol $L^{-1}$. $Q = (0.80)^2 / 0.80 = 0.80$, above Kc = 0.40, so the shift is left, toward $N_2O_4$, the side with 1 gas mole against 2. (b) Both concentrations halve: $[N_2O_4] = [NO_2] = 0.20$ mol $L^{-1}$. $Q = (0.20)^2 / 0.20 = 0.20$, below Kc, so the shift is right, toward

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$NO_2$, the side with more gas moles. (c) Kc = 0.40 in both cases. Volume changes move Q, never Kc; only temperature changes Kc.

**B3.** (a) $K_c = [SO_3]^2 / ([SO_2]^2[O_2]) = (0.60)^2 / ((0.40)^2 \times 0.20) = 0.36 / 0.032 = 11.25$, about 11. (b) $Q = (0.20)^2 / ((0.40)^2 \times 0.20) = 0.04 / 0.032 = 1.25$, well below Kc, so the shift is right: the forward reaction runs net and remakes $SO_3$. (c) It must lie between 0.20 and 0.60 mol $L^{-1}$. It rises above 0.20 because the shift produces $SO_3$, and Q climbs back to Kc at about 0.33, with $[SO_2] \approx 0.27$ and $[O_2] \approx 0.13$ mol $L^{-1}$. It cannot reach 0.60: the removal carried sulfur and oxygen out of the vessel, so gas-phase sulfur now totals 0.60 mol $L^{-1}$ instead of the original 1.00, and the original mixture cannot be rebuilt from what remains. (d) Kc is unchanged at 11.25: the temperature did not change.

**B4.** (a) The forward reaction releases heat, so heat acts as a product. Heating adds to the product side, and the system shifts left, consuming heat by converting $SO_3$ back into $SO_2$ and $O_2$, until Q matches the new, smaller Kc. (b) The equilibrium $[SO_3]$ falls: Kc drops from 250 to 4.0, and the leftward shift lowers the equilibrium amount of $SO_3$. (c) Kc returns to $2.5 \times 10^2$, because Kc depends only on temperature, and the shift runs right as $SO_3$ forms again. (d) The stresses in B1 to B3 changed concentrations, and so Q, at a fixed temperature. Temperature is different: Kc is a constant for a stated temperature, so changing the temperature gives the constant itself a new value, and Q must chase a new target.

**B5.** (a) Q is unchanged at 8.0, equal to Kc, so there is no shift. The argon raises the total pressure, but at constant volume the amounts and the volume are unchanged, so every concentration, and every partial pressure, is exactly as before. (b) The concentrations halve: $[N_2] = 0.125$, $[H_2] = 0.25$ and $[NH_3] = 0.25$ mol $L^{-1}$. $Q = (0.25)^2 / (0.125 \times (0.25)^3) = 32$. $Q > K_c = 8.0$, so the shift is left, toward the side with more gas moles: 4 moles of gas (1 $N_2$ + 3 $H_2$) against 2 of $NH_3$. Adding an inert gas at constant pressure behaves exactly like doubling the volume.

**B6.** (a) No effect. $CaCO_3$ is a pure solid and does not appear in $Q = [CO_2]$; Q stays 0.010 = Kc, so there is no shift and $[CO_2]$ stays 0.010 mol $L^{-1}$. (b) No effect, for the same reason: CaO is also a pure solid absent from Q. (c) $Q = [CO_2] = 0.030$, above $K_c = 0.010$, so the shift is left: $CO_2$ reacts with CaO to form $CaCO_3$ until $[CO_2]$ falls back to exactly 0.010 mol $L^{-1}$. This differs from B1 because the solids act as a reservoir: while both solids are present, the equilibrium $[CO_2]$ is pinned at the Kc value, so the added gas is fully absorbed rather than partly offset. In B1 every species sat inside the expression, so the new equilibrium had to settle between the disturbed value and the original.

**C1.** (a) $Q = (0.20)^2 / (0.50 \times 0.50) = 0.04 / 0.25 = 0.16$, far below $K_c = 4.0$, so the shift is right: the forward reaction runs net to replace the removed HI. (b) Let the shift consume x of each reactant and form 2x of HI: $[H_2] = [I_2] = 0.50 - x$ and $[HI] = 0.20 + 2x$. Setting $(0.20 + 2x)^2 / (0.50 - x)^2 = 4.0$ and taking the square root gives $(0.20 + 2x) / (0.50 - x) = 2$, so $0.20 + 2x = 1.00 - 2x$ and $x = 0.20$. The new equilibrium is $[H_2] = [I_2] = 0.30$ and $[HI] = 0.60$ mol $L^{-1}$. Check: $(0.60)^2 / (0.30 \times 0.30) = 0.36 / 0.09 = 4.0$. (c) [HI] rose from the disturbed 0.20 to 0.60 mol $L^{-1}$, recovering 0.40 of the 0.80 mol $L^{-1}$

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that was removed, but it stays below the original 1.00 mol $L^{-1}$: a partial replacement, as the partial offset rule requires. (d) Kc = 4.0, unchanged: the temperature never changed.

**C2.** (i) Compression: shift right, toward 2 gas moles of $SO_3$ against 3 of reactants; Kc unchanged; the equilibrium $[SO_3]$ rises. (ii) Catalyst: no shift; Kc unchanged; $[SO_3]$ unchanged, only reached faster. (iii) Temperature raised: shift left, because the forward reaction is exothermic and heat acts as a product; Kc decreases; $[SO_3]$ falls. (iv) Argon at constant volume: no shift; Kc unchanged; $[SO_3]$ unchanged, because no concentration or partial pressure changes. (v) $SO_2$ removed: removing a reactant raises Q above Kc, so the shift is left; Kc unchanged; $[SO_3]$ falls as some $SO_3$ converts back to replace part of the lost $SO_2$.

**C3.** (a) $Kc = [N_2O_4] / [NO_2]^2 = 2.0 / (0.50)^2 = 2.0 / 0.25 = 8.0$, matching the stated Kc, so the mixture is at equilibrium. (b) Just after heating, the concentrations have not yet changed, so Q is still 8.0, but Kc is now 0.50. Q > Kc, so the shift is left, toward $NO_2$. (c) The mixture darkens: the leftward shift converts colourless $N_2O_4$ into brown $NO_2$, so the brown colour deepens. (d) $[NO_2]$ at the new equilibrium is higher than 0.50 mol $L^{-1}$, because the net reverse reaction produces $NO_2$ throughout the shift; Kc there is 0.50, the value set by the new temperature.

**Continue Revising**

Topic 7.9 Revision Notes

Topic 7.9 Quiz: Introduction to Le Chatelier's Principle

Previous Worksheet: Topic 7.8 Representations of Equilibrium

Next Worksheet: Topic 7.10 Reaction Quotient and Le Chatelier's Principle

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