Unit 8 · Chemical Equilibrium

HARDER PRACTICE QUESTIONS · ANSWER KEY

Full marks 34

Give the marks for the points in the marking scheme; an answer in other words that says the same is right.

1 Which way will a mixture go?

ANSWER HA · 8

Tests: whether a mixture moves forward or backward depends on the mixture compared with K, not on the size of K; K is made of equilibrium concentrations; "the same equilibrium from either side" holds only for the same atoms.

a. Work out the starting ratio $\frac{[HI]^2}{[H_2][I_2]}$ and compare it with K, because at the end it must equal K. Flask B: $\frac{0.100^2}{0.0100 \times 0.0100} = 100$, more than 54. There is too much HI for equilibrium, so the backward reaction runs faster until the ratio falls to 54: **HI falls**. Flask C: $\frac{0.147^2}{0.0400 \times 0.0100} = 54.0$, already K: **it stays the same**, since the flask is at equilibrium from the start.

b. A: $\frac{0.0314^2}{0.00428^2} = 53.8 \approx 54$. B: $\frac{0.0943^2}{0.0128^2} = 54.3 \approx 54$. Both equal K within the rounding of the data, so both are at equilibrium. In B, $[H_2]$ and $[I_2]$ each rose by 0.0028 while [HI] fell by $0.100 - 0.0943 = 0.0057$, twice as much: the 1 : 1 : 2 of the equation, run backward.

c. **Flask B**: there HI is used up, not made. A large K says the equilibrium mixture is mostly HI; it doesn't say which way a given mixture moves. That depends on whether the mixture's ratio is below K (forward) or above it (backward). B starts with more HI than even an equilibrium with K = 54 allows.

d. Both contain the same atoms in the same volume: D's 0.0400 mol/L of HI holds the hydrogen and iodine of 0.0200 mol/L each of H_2 and I_2, exactly A's start. A reaction only rearranges these atoms; whichever way the flask has to go to make the ratio equal 54, there is only one mixture of those atoms with that ratio, so both arrive at it (A by the forward reaction, D by the backward one).

e. E has three times as much hydrogen as iodine. Every HI made uses one H_2 and one I_2, so E's $[H_2]$ and $[I_2]$ fall by the same amount, and $[H_2]$ stays 0.0200 mol/L more than $[I_2]$ at the end. In A's end mixture $[H_2]$ and $[I_2]$ are equal, so E can't end at A's mixture. (The tempting answer is Kushal's: "same K, same mixture". K is the same, but it fixes only the ratio, and E has different atoms to share.) Even if every iodine went into HI, E could make at most 0.0200 mol/L of HI, less than 0.0314.

MARKING SCHEME

- ✓ B: starting ratio 100 > 54, so it goes backward and HI falls.
- ✓ C: starting ratio 54 = K, so nothing changes.
- ✓ A and B end ratios both ≈ 54: at equilibrium.
- ✓ B's changes: H_2 and I_2 +0.0028, HI −0.0057, the 1 : 1 : 2 ratio.
- ✓ Flask B; the direction depends on the mixture's ratio compared with K, not on K's size.
- ✓ A and D contain the same atoms (D's HI is A's H_2 and I_2 combined).
- ✓ Only one mixture of those atoms has the ratio 54, reached from either side.
- ✓ E has unequal H_2 and I_2 that stay unequal (or: at most 0.0200 of HI), so it can't reach A's mixture.

2 Squeezing a brown gas

ANSWER

Tests: Le Chatelier's principle only partly undoes a change, and "the equilibrium shifts left" is about amounts, not concentrations; the color follows $[NO_2]$; an inert gas acts through the reacting gases' concentrations. ($K_c = 4.0 \times 10^{-3}$ mol/L is a round value chosen for the problem, of the size measured near room temperature; the concentrations follow from it.)

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a. Just after the push, $\frac{[NO_2]^2}{[N_2O_4]} = \frac{0.0400^2}{0.200} = 8.0 \times 10^{-3}$, twice K_c. Halving the volume doubled every concentration, but the square on top doubled the top twice. To bring the ratio back down to K, NO_2 must be used up and N_2O_4 made: it reacts **backward (to the left)**, towards fewer gas molecules, as Le Chatelier's principle says.

b. $\frac{0.0287^2}{0.206} = 4.0 \times 10^{-3}$ mol/L $= K_c$.

c. **No.** The color depends on the concentration of NO_2. It doubled at the push (the same gas crowded into half the space: the color darkened at once), then fell back only part of the way, to 0.0287 mol/L, which is still **more than** the 0.0200 mol/L before the push. So the settled gas is **darker** than at the start, though paler than just after the push. What Le Chatelier got right is the amount: before, $0.0200 \times 1.00 = 0.0200$ mol of NO_2; settled, $0.0287 \times 0.500 = 0.0144$ mol. Some NO_2 really did become N_2O_4. (The tempting answer, Shristi's, reads "shifts towards N_2O_4" as "less NO_2 per liter".)

d. At a fixed temperature the pressure is proportional to the total concentration of gas: before, $0.100 + 0.0200 = 0.120$ mol/L; settled, $0.206 + 0.0287 = 0.235$ mol/L. The pressure rose $0.235 \div 0.120 =$ **1.96 times**. With no reaction it would have risen exactly 2 times (Boyle's law). The shift to fewer molecules brought it down only a little: an equilibrium partly undoes a change, never completely.

e. i. **No shift, no change of color.** At constant volume the argon raises the total pressure, but the amounts of N_2O_4 and NO_2 in the same volume, so their concentrations, don't change, and the ratio is still K. ii. The volume grows, so both concentrations fall, as if the mixture had been expanded. The top of the ratio, squared, falls faster, so the ratio drops below K and the equilibrium **shifts to the right, making more NO_2 molecules**; yet the gas is **paler**, because the NO_2 is now spread through a bigger volume (the shift only partly makes up for the spreading).

MARKING SCHEME

- ✓ Ratio just after $= 8.0 \times 10^{-3}$, more than K.
- ✓ So it must react backward, $NO_2 \rightarrow N_2O_4$.
- ✓ Settled ratio $= 4.0 \times 10^{-3} =$ K.
- ✓ She is wrong: $[NO_2]$ settles at 0.0287, more than 0.0200, so the gas ends darker.
- ✓ The amount of NO_2 fell (0.0200 → 0.0144 mol): the shift Le Chatelier predicts.
- ✓ Pressure rose 1.96 times, less than 2: the change is only partly undone.
- ✓ Argon at constant volume: no shift, no color change.
- ✓ Argon at constant pressure: shift right (more NO_2 molecules), but paler.

3 Limestone in a closed vessel

ANSWER

Tests: pure solids drop out of K, so the gas pressure over them is fixed at a given temperature whatever the amount of solid; an equilibrium needs some of every substance in it; an open system can't reach equilibrium. (0.22 atm at 1073 K is a value chosen for the problem, of the size measured for limestone near 800 °C.)

a. $CaCO_3$ and CaO are pure solids, with active mass 1, so $K_p = p_{CO_2}$. At 1073 K the CO_2 pressure at equilibrium must be 0.22 atm, however much solid there is. (Tempting: "more reactant, so the equilibrium shifts right and gives more CO_2". Adding a pure solid doesn't change its active mass, so it shifts nothing.) Y simply has more $CaCO_3$ left over.

b. $n_{CO_2} = \frac{pV}{RT} = \frac{0.22 \times 5.0}{0.0821 \times 1073} = \frac{1.10}{88.1} = 0.0125$ mol, and each mole of CO_2 comes from one mole of $CaCO_3$: $0.0125 \times 100 =$ **1.25 g** decomposed (8.75 g is left).

c. 1.00 g is 0.0100 mol of $CaCO_3$, so at most 0.0100 mol of CO_2: $p = \frac{nRT}{V} = \frac{0.0100 \times 88.1}{100} = 0.0088$ atm, the pressure measured. So all of it decomposed. Z is **not** at equilibrium: there is no $CaCO_3$ left, so no backward reaction can balance the forward one, and the CO_2 pressure is below 0.22 atm.

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d. To reach equilibrium, Z's 100 L must hold CO_2 at 0.22 atm: $n = \frac{pV}{RT} = \frac{0.22 \times 100}{88.1} = 0.25$ mol, from 0.25 mol of $CaCO_3$, **25 g**; with exactly 25 g it would just run out as the pressure reached 0.22 atm, so it needs **more than 25 g**, to have some left over. So the amount of solid doesn't change the equilibrium pressure (part a), but there must be enough of it to fill the space with gas at that pressure and still have some left; with less, it all decomposes and there is no equilibrium. (The same is why an open lime kiln turns all its limestone into lime: its CO_2 goes up the chimney, so the space to fill never ends.)

MARKING SCHEME

- ✓ $K_p = p_{CO_2}$ (the solids left out), so the pressure is fixed, whatever the amount of solid.
- ✓ X: 0.0125 mol of CO_2, so 1.25 g of $CaCO_3$ decomposed.
- ✓ Z: 0.0100 mol of $CaCO_3$ gives 0.0088 atm, so all of it decomposed.
- ✓ Z is not at equilibrium: no $CaCO_3$ is left and the pressure is below K.
- ✓ At least 0.25 mol, 25 g, to fill 100 L at 0.22 atm; the solid must be enough to fill the space and still be left over.

4 Making ammonia: how far against how fast

ANSWER

Tests: temperature moves the equilibrium yield and the rate in opposite directions; a catalyst changes how fast, never how far; the compromise read from data, with the tempting wrong ideas "reaching equilibrium is the goal" and "a better catalyst raises the equilibrium yield".

a. **Rising part (350–475 °C):** at low temperatures equilibrium would give a lot of ammonia, but the reaction is so slow that in a few seconds the gas gets only a small part of the way there (0.7% against 51.9% at 350 °C). Warming it speeds the reaction a lot, so more is made in the time.
Falling part (above about 500 °C): the forward reaction is exothermic, so a rise in temperature shifts the equilibrium in the endothermic direction, backward: K gets smaller and the middle column falls. Now the reaction is fast enough to get the gas close to equilibrium (18.6 of 19.0% at 500 °C, all the way at 550 °C), so the yield is set by equilibrium, which falls with temperature. The best lies between, where neither the rate nor the equilibrium alone limits it: about 475–500 °C in this model. (The middle column comes from the measured equilibrium constant, Gillespie and Beattie's fit, the one the unit's ammonia widget uses; the last column is that widget's made-up model of one converter. Where its best lies depends on how fast the model's made-up catalyst is: with three times as long on the catalyst the model's best would be about 450 °C. Real plants run at the unit's 400–450 °C; don't carry the model's 475–500 °C away as a fact.)

b. The gas starts with no ammonia and moves towards equilibrium; it can get closer, or reach it, but a mixture moving towards equilibrium never passes it (once there, the two rates are equal and nothing more changes).

c. **No.** Reaching equilibrium isn't the aim; making as much ammonia as possible per pass is. At 550 °C the gas leaves with 13.0%, less than the 19.2% at 475 °C, which hasn't reached equilibrium but is closer to a higher one. (Nor is more than 80% of the gas leaving unreacted a waste: the ammonia is cooled to a liquid and drained off, and the unreacted nitrogen and hydrogen are sent round the converter again.)

d. **No** at 450 °C: more time only brings the gas closer to equilibrium, and a mixture moving towards equilibrium never passes it, so 27.5% is the ceiling (the model gives 21.8%). The longer time helps far more at **400 °C**, where the gas is far from equilibrium (4.5% of a possible 38.7%) and the slow rate is what limits it (the model: 8.5%). At 500 °C the gas is already almost at equilibrium (18.6 of 19.0%), so extra time adds almost nothing (19.0%). (The tempting answer: "more time, more ammonia, wherever".)

e. The middle column **doesn't change**: a catalyst speeds up the forward and backward reactions alike, so K and the equilibrium percentages stay the same. But the gas now gets close to equilibrium at lower temperatures, where equilibrium has more ammonia in it. So the best temperature moves **lower**, and the best percentage in the gas leaving goes **up** (towards the higher equilibrium values of the cooler rows).

MARKING SCHEME

- ✓ a. Rising part: low temperature, slow reaction, far from equilibrium in the time.

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✓ a. Falling part: exothermic, so K and the equilibrium percentage fall as it gets hotter; the fast reaction reaches that lower equilibrium. HA · 8

✓ b. The gas moves towards equilibrium and can't pass it.

✓ c. Disagree: 13.0% at 550 °C is less than 19.2% at 475 °C; the most ammonia per pass, not reaching equilibrium, is the aim.

✓ d. Not past 27.5%: more time only gets closer to equilibrium.

✓ d. More gain at 400 °C, where the rate limits; little at 500 °C, already near equilibrium.

✓ e. Equilibrium column unchanged: a catalyst doesn't change K.

✓ e. Best temperature lower and best outlet percentage higher.

5 One equilibrium, written in different ways

ANSWER A · 5

Tests: K belongs to the equation as written: reversing gives the reciprocal, halving the square root, adding equations the product; the unit and Kp/Kc follow the equation too.

a. Write the expression for his equation:

$$K_c' = \frac{[N_2]^{1/2}[H_2]^{3/2}}{[NH_3]} = \left(\frac{[N_2][H_2]^3}{[NH_3]^2}\right)^{1/2} = \frac{1}{\sqrt{K_c}}$$

His first mistake: the reversed equation is also **halved**, so K is not only reciprocated but square-rooted. His second: the unit is not $L^2\ mol^{-2}$ any more; with $\Delta n = 2 - 1 = +1$ it is $(mol/L)^{+1}$. $K_c' = 1/\sqrt{6.0 \times 10^{-2}} =$ **4.1 mol/L**. (The tempting 17 is right only for $2\,NH_3 \rightleftharpoons N_2 + 3\,H_2$, and then its unit is $mol^2\ L^{-2}$.)

b. From K_c': $RT = 0.0821 \times 773 = 63.5$ and $\Delta n = +1$, so $K_p' = K_c'RT = 4.08 \times 63.5 =$ **259 atm**. From K_p: the same two changes, $K_p' = 1/\sqrt{1.5 \times 10^{-5}} =$ **258 atm**. They agree (the small difference is the rounding of 1.5×10^{-5}).

c. $K_1 = \frac{[NO]^2}{[N_2][O_2]}$ and $K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]}$. In one mixture at equilibrium both hold together, so

$$K_1K_2 = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2}$$

which is the expression for $N_2 + 2\,O_2 \rightleftharpoons 2\,NO_2$: $K = K_1K_2$. (The NO, made in one step and used in the next, cancels, just as it cancels when the equations are added.)

d. It is the overall reaction reversed and halved: $K = \frac{1}{\sqrt{K_1K_2}}$.

MARKING SCHEME

✓ The equation is reversed **and** halved, so $K_c' = 1/\sqrt{K_c}$, not $1/K_c$.

✓ $K_c' = 4.1$ mol/L (unit mol/L, $\Delta n = +1$).

✓ $K_p' = 259$ atm from $K_c'RT$, and 258 atm from $1/\sqrt{K_p}$: they agree.

✓ K_1K_2 multiplied out gives the overall expression (NO cancels).

✓ $K = 1/\sqrt{K_1K_2}$.

Marks by level	Knowledge	Understanding	Application	Higher ability	Total
Marks	0	0	10	24	**34**

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