Unit 8 · Chemical Equilibrium

HARDER PRACTICE QUESTIONS

Full marks 34

Write your answers on separate paper. Show your working. All concentrations are in mol/L. Take R = 0.0821 L atm/(mol K).

1 Which way will a mixture go? [8]

At 425 °C, $K_c = 54$ for $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$. Five sealed flasks of the same size are filled with different mixtures and kept at 425 °C until nothing more changes. The table gives what each flask started with and, for three of them, what was measured at the end.

Flask	Start: $[H_2]$	Start: $[I_2]$	Start: [HI]	End: $[H_2]$	End: $[I_2]$	End: [HI]
A	0.0200	0.0200	0	0.00428	0.00428	0.0314
B	0.0100	0.0100	0.100	0.0128	0.0128	0.0943
C	0.0400	0.0100	0.147			
D	0	0	0.0400	0.00428	0.00428	0.0314
E	0.0300	0.0100	0			

a. Without looking at the end columns, say whether the amount of HI in flask B and in flask C will rise, fall or stay the same, and show how you decided.

b. Show that the end mixtures of A and B are equilibrium mixtures, and that the changes in flask B are in the ratio the equation requires.

c. Kushal says: "K = 54 is much bigger than 1, so the forward reaction wins in every flask and HI is made." Which flask shows that he is wrong, and what is wrong with his reasoning?

d. Flasks A and D start very differently but end with the same mixture. Explain why they must.

e. Kushal now predicts that flask E will also end with 0.0314 mol/L of HI, "because K is the same". Without solving for E's end mixture, show that he can't be right.

2 Squeezing a brown gas [8]

A gas syringe holds a mixture of colorless dinitrogen tetroxide and brown nitrogen dioxide at equilibrium,

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

at a fixed temperature at which you may take $K_c = 4.0 \times 10^{-3}$ mol/L. The plunger is pushed in quickly, halving the volume from 1.00 L to 0.500 L, and the syringe is held at the same temperature. The concentrations were:

	$[N_2O_4]$	$[NO_2]$
before the push	0.100	0.0200
just after the push	0.200	0.0400
once it has settled	0.206	0.0287

a. Show that the mixture just after the push is not at equilibrium, and say from your numbers which way it must then react.

b. Show that the settled mixture is at equilibrium again.

c. Shristi says: "Le Chatelier's principle says that more pressure turns NO_2 into N_2O_4, so once it has settled the gas will be paler than it was before I pushed." Is she right? Use the table to say what really happened to the color, and what Le Chatelier's principle got right.

d. By what factor did the total pressure in the syringe rise from before the push to the settled state? What does this show about how far an equilibrium can "undo" a change?

e. Instead of pushing the plunger, some argon is added to the original mixture. Say what happens to the position of equilibrium and to the color i. if the syringe is clamped so its volume can't change; ii. if the plunger is drawn out as the argon goes in, so that the total pressure stays what it was and the volume grows.

3 Limestone in a closed vessel [5]

At 1073 K take $K_p = 0.22$ atm for $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. Three empty, sealed steel vessels are each heated to 1073 K with some calcium carbonate ($M = 100$ g/mol) inside, and the pressure of CO_2 is read once it stops changing:

Vessel	Volume	$CaCO_3$ put in	CO_2 pressure at the end
X	5.0 L	10.0 g	0.22 atm
Y	5.0 L	20.0 g	0.22 atm
Z	100 L	1.00 g	0.0088 atm

a. Y has twice as much limestone as X. Why is its CO_2 pressure the same?
b. What mass of calcium carbonate has decomposed in X?
c. Show that the pressure in Z is what you would expect if all its calcium carbonate decomposed. Is Z at equilibrium? Explain.
d. What is the least mass of calcium carbonate that would have let Z reach equilibrium? What does this tell you about the amount of solid an equilibrium like this needs?

4 Making ammonia: how far against how fast [8]

The table is for a 1 : 3 mixture of nitrogen and hydrogen at 200 atm passing over the iron catalyst of an ammonia converter ($N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, $\Delta H = -92$ kJ). The middle column is the percentage of ammonia in the gas **at equilibrium**, from the measured equilibrium constant. The last column is the percentage of ammonia in the gas **leaving** the converter, after its few seconds on the catalyst, from a simple made-up model of one converter (the one in the unit's ammonia widget), not a real plant's figures. Real plants, as the unit says, run at about 400–450 °C; the questions are about this model's numbers.

Temperature (°C)	Ammonia at equilibrium (%)	Ammonia in the gas leaving (%)
350	51.9	0.7
400	38.7	4.5
450	27.5	15.0
475	22.9	19.2
500	19.0	18.6
550	13.0	13.0

a. The percentage in the gas leaving rises and then falls. Explain both halves of this pattern, including why the percentage at equilibrium falls as the temperature rises.
b. Why is the percentage in the gas leaving never more than the percentage at equilibrium?
c. Dipesh, the plant's new engineer, says: "At 550 °C the gas leaving has reached equilibrium, so the plant works best there." Do you agree? Explain.
d. Suppose the gas spent twice as long on the catalyst. Without calculating, say whether the gas leaving at 450 °C could then pass 27.5% ammonia, and whether the longer time would raise the gas leaving more at 400 °C or at 500 °C. Explain.
e. A new catalyst is found that makes the reaction as fast at 400 °C as the old one does at 450 °C. Predict how the best temperature, and the best percentage in the gas leaving, would change, and say whether the middle column changes.

5 One equilibrium, written in different ways [5]

At 500 °C, $K_c = 6.0 \times 10^{-2}\ \text{L}^2\ \text{mol}^{-2}$ for $\text{N}_2(\text{g}) + 3\,\text{H}_2(\text{g}) \rightleftharpoons 2\,\text{NH}_3(\text{g})$, and from it (the unit's worked example) $K_p = 1.5 \times 10^{-5}\ \text{atm}^{-2}$.

a. Bibek needs K_c' for the splitting of ammonia, written per mole of ammonia: $\text{NH}_3(\text{g}) \rightleftharpoons ½\text{N}_2(\text{g}) + 3/2\ \text{H}_2(\text{g})$. He writes: "It is the reverse reaction, so $K_c' = 1/K_c = 17\ \text{L}^2\ \text{mol}^{-2}$." Find his two mistakes, and give the correct K_c' with its unit.

b. Find K_p' for Bibek's equation in two ways: from your K_c', and from the K_p above. Do they agree?

c. For two steps in the making of nitrogen dioxide, $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\,\text{NO}(\text{g})$ has equilibrium constant K_1, and $2\,\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\,\text{NO}_2(\text{g})$ has K_2, at the same temperature. Show that for the overall reaction $\text{N}_2(\text{g}) + 2\,\text{O}_2(\text{g}) \rightleftharpoons 2\,\text{NO}_2(\text{g})$, $K = K_1\,K_2$.

d. Write the equilibrium constant of $\text{NO}_2(\text{g}) \rightleftharpoons ½\text{N}_2(\text{g}) + \text{O}_2(\text{g})$ in terms of K_1 and K_2.