

HL Answers to Equilibrium law questions

1. i. Initial concentration of $\text{PCl}_5(\text{g}) = a/V$

Equilibrium concentration of $\text{PCl}_5(\text{g}) = (a-x)/V$

Equilibrium concentration of $\text{PCl}_3(\text{g}) =$ equilibrium concentration of $\text{Cl}_2(\text{g}) = x/V$

$K_c = [\text{PCl}_3(\text{g})][\text{Cl}_2(\text{g})] / [\text{PCl}_5(\text{g})]$

$$= (x/V)^2 / (a-x)/V = x^2/V^2 / (a-x)/V = x^2 / (a-x)V$$

ii. From the gas laws increasing the pressure at the same temperature can be achieved by reducing the volume. From the equation when V decreases x must also decrease to keep K_c constant hence increasing the pressure causes the position of equilibrium to shift back to the phosphorus(V) chloride side.

2. (a) $2\text{H}_2\text{O}(\text{g}) + \text{CH}_4(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + 4\text{H}_2(\text{g})$

(b) Initial concentration of $\text{H}_2\text{O} = 54.06 / 18.02 = 3.0 \text{ mol dm}^{-3}$

Initial concentration of $\text{CH}_4 = 16.04 / 16.04 = 1.0 \text{ mol dm}^{-3}$

Equilibrium concentration of $\text{H}_2 = 4.04 / 2.02 = 2.0 \text{ mol dm}^{-3}$

1 mol of CO_2 is formed for every 4 mol of H_2 so equilibrium concentration of $\text{CO}_2 = 0.5 \text{ mol dm}^{-3}$

1 mol of H_2O gives 2 mol of hydrogen so equilibrium concentration of steam

$$= (3.0 - 1.0) = 2.0 \text{ mol dm}^{-3}$$

0.5 mol of CH_4 gives 2 mol of hydrogen so equilibrium concentration of methane

$$= (1.0 - 0.5) = 0.5 \text{ mol dm}^{-3}$$

$$K_c = [\text{CO}_2(\text{g})][\text{H}_2(\text{g})]^4 / [\text{CH}_4(\text{g})][\text{H}_2\text{O}]^2 = 0.5 \times 2.0^4 / 0.5 \times 2.0^2 = 2.0^2 = 4.0$$

(c) (i) the amount of hydrogen in the equilibrium increases

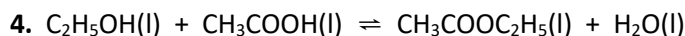
(ii) the value of the equilibrium constant increases

3. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

Let the volume of the container be $V \text{ dm}^3$

$$K_c = [\text{HI}(\text{g})]^2 / [\text{H}_2(\text{g})][\text{I}_2(\text{g})] = (2.4/V)^2 / (0.45/V) \times (0.55/V) = 2.4^2 / 0.45 \times 0.55 = 23 \text{ (to 2 sig figs).}$$





Let the volume of the container be $V \text{ dm}^3$

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})][\text{H}_2\text{O}(\text{l})]}{[\text{C}_2\text{H}_5\text{OH}(\text{l})][\text{CH}_3\text{COOH}(\text{l})]}$$

$$= \frac{(0.42/V \times 0.42/V)}{(1-0.42)/V \times (0.5-0.42)/V} = 0.42^2 / 0.58 \times 0.08 = 3.8$$

5. (a) From the information given and from Section 12 of the data booklet

	$\text{CH}_3\text{COOH}(\text{l})$	+	$\text{C}_2\text{H}_5\text{OH}(\text{l})$	\rightleftharpoons	$\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})$	+	$\text{H}_2\text{O}(\text{l})$
$\Delta H_{\text{f}}^{\ominus} / \text{kJ mol}^{-1}$	- 484		- 278		- 480		- 286
$S^{\ominus} / \text{J mol}^{-1} \text{ K}^{-1}$	+ 160		+ 161		+ 259		+ 70

$$\Delta H_{\text{reaction}}^{\ominus} = [- 480 + (- 286)] - [- 484 + (- 278)] = - 4 \text{ kJ mol}^{-1}$$

$$\Delta S_{\text{reaction}}^{\ominus} = (+ 259 + 70) - (+ 160 + 161) = 8 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G_{\text{reaction}}^{\ominus} = \Delta H_{\text{reaction}}^{\ominus} - T \Delta S_{\text{reaction}}^{\ominus} = - 4 - (298 \times 8/1000) = - 6.38 \text{ kJ mol}^{-1} = - 6380 \text{ J mol}^{-1}$$

$$\ln K_c = - \Delta G_{\text{reaction}}^{\ominus} / RT = 6380 / (8.31 \times 298) = 2.576$$

$$K_c = e^{2.576} = 13.1$$

(b) This is considerably different to the literature value of 4. It is a consequence of the logarithmic part of the expression. Data book values for $\Delta H_{\text{f}}^{\ominus}$ and S^{\ominus} can vary slightly from source to source. There only needs to be a difference of 3 kJ mol^{-1} for the calculated value of $\Delta G_{\text{reaction}}^{\ominus}$ to make it 3380 instead of 6380 J mol^{-1} which would make $\ln K_c$ have the value 1.36 which then gives the literature value of 4 for K_c .

