HL Answers to Equilibrium law questions

1. i. Initial concentration of $PCl_5(g) = a/V$

Equilibrium concentration of $PCl_5(g) = (a-x)/V$

Equilibrium concentration of $PCl_3(g)$ = equilibrium concentration of $Cl_2(g) = x/V$

$K_c = [PCl_3(g)][Cl_2(g)] / [PCl_5(g)]$

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

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) $2H_2O(g) + CH_4(g) \rightleftharpoons CO_2(g) + 4H_2(g)$

(b) Initial concentration of H_2O = 54.06 / 18.02 = 3.0 mol dm^{-3}

Initial concentration of CH_4 = 16.04 / 16.04 = 1.0 mol dm^{-3}

Equilibrium concentration of H_2 = 4.04 / 2.02 = 2.0 mol dm^{-3}

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

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

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

$K_c = [CO_2(g)][H_2(g)]^4 / [CH_4(g)][H_2O]^2 = 0.5 \times 2.0^4 / 0.5 \times 2.0^2 = 2.0^2 = 4.0$

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

(ii) the value of the equilibrium constant increases

3. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Let the volume of the container be V dm^3

$K_c = [HI(g)]^2 / [H_2(g)][I_2(g)] = (2.4/V)^2 / (0.45/V) \times (0.55/V) = 2.4^2/0.45 \times 0.55 = 23$ (to 2 sig figs).

4. $C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

Let the volume of the container be V dm^3

$K_c = [CH_3COOC_2H_5(l)][H_2O(l)] / [C_2H_5OH(l)][CH_3COOH(l)]$

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

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

	$CH_3COOH(l)$ +	$C_2H_5OH(l)$ $\rightleftharpoons$	$CH_3COOC_2H_5(l)$ +	$H_2O(l)$
$\Delta H^\ominus_f$ / kJ mol^{-1}	– 484	– 278	– 480	– 286
$S^\ominus$ / J mol^{-1} K^{-1}	+ 160	+ 161	+ 259	+ 70

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

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

$\Delta G^\ominus_{\text{reaction}} = \Delta H^\ominus_{\text{reaction}} - T\,\Delta S^\ominus_{\text{reaction}} = -4 - (298 \times 8/1000) = -6.38$ kJ mol^{-1} $= -6380$ J mol^{-1}

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

$K_c = e^{2.576} = 13.1$

(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 $\Delta H^\ominus_f$ 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 $\Delta G^\ominus_{\text{reaction}}$ 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.