

## CHEM1612 Worksheet 4 – Answers to Critical Thinking Questions

The worksheets are available in the tutorials and form an integral part of the learning outcomes and experience for this unit.

### Model 1: The Equilibrium Constant

- $$K_c(\text{A}) = \frac{[\text{N}_2\text{O}_4(\text{g})]}{[\text{NO}_2(\text{g})]^2} \quad K_c(\text{B}) = \frac{[\text{N}_2\text{O}_4(\text{g})]^{1/2}}{[\text{NO}_2(\text{g})]}$$
$$K_c(\text{C}) = \frac{[\text{NO}_2(\text{g})]^2}{[\text{N}_2\text{O}_4(\text{g})]} \quad K_c(\text{D}) = \frac{[\text{NO}_2(\text{g})]}{[\text{N}_2\text{O}_4(\text{g})]^{1/2}}$$
- (a)  $K_c(\text{B}) = \sqrt{K_c(\text{A})}$  (b)  $K_c(\text{A}) = 1 / K_c(\text{C})$
- $K_c(\text{A}) = 0.078, K_c(\text{B}) = 0.280, K_c(\text{C}) = 12.8.$

### Model 2: The Reaction Quotient

- The reaction will shift to the right to decrease  $[\text{NO}_2(\text{g})]$ .
- The reaction will shift to the left to increase  $[\text{NO}_2(\text{g})]$ .
- (a)  $Q_c = 0.0500$   
(b)  $Q_c = 0.200.$
- (a) If  $Q_c < K_c$ , the reaction will shift to the right.  
(b) If  $Q_c > K_c$ , the reaction will shift to the left.

### Model 3: Equilibrium calculations

Model 2 gives you the tools to predict the direction in which a reaction will move if it is not at equilibrium. The concentrations that will be obtained when equilibrium is finally reached can be calculated using an ICE table: initial-change-equilibrium.

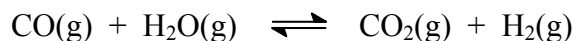
Consider the starting mixture in Q1 of Model 2:  $[\text{NO}_2(\text{g})] = 2.00 \text{ M}$  and  $[\text{N}_2\text{O}_4(\text{g})] = 0.20 \text{ M}$ . These are the initial concentrations and are written in the first row of the *reaction table* below. You know from Model 2 that this reaction will shift so that some  $\text{NO}_2(\text{g})$  reacts to make  $\text{N}_2\text{O}_4(\text{g})$ . We do not know *how much* will react but we *can* calculate it:

	$2\text{NO}_2(\text{g})$	$\rightleftharpoons$	$\text{N}_2\text{O}_4(\text{g})$
initial	2.00		0.20
change	-2x		+x
equilibrium	$2.00 - 2x$		$0.20 + x$

### Critical thinking questions

- See above.
- Complete the third row of the table.
- $$K_c(\text{A}) = \frac{[\text{N}_2\text{O}_4(\text{g})]}{[\text{NO}_2(\text{g})]^2} = \frac{(0.20+x)}{(2.00-2x)^2}$$
- $x = 0.070 \text{ M}$  so  $[\text{NO}_2(\text{g})] = 1.86 \text{ M}$  and  $[\text{N}_2\text{O}_4(\text{g})] = 0.27 \text{ M}$   
(The second root is non-physical as it leads to a negative concentration for  $\text{NO}_2$ .)

The CO(g) in water gas can be reacted further with H<sub>2</sub>O(g) in the so-called “water-gas shift” reaction:



At 900 K,  $K_c = 1.56$  for this reaction. A sample of water gas flowing over coal at 900 K contains a 1:1 mole ratio of CO(g) and H<sub>2</sub>(g), as well as 0.250 mol L<sup>-1</sup> H<sub>2</sub>O(g). This sample is placed in a sealed container at 900 K and allowed to come to equilibrium, at which point it contains 0.070 mol L<sup>-1</sup> CO<sub>2</sub>(g). What was the initial concentration of CO(g) and H<sub>2</sub>(g) in the sample?

**Marks**  
**4**

The reaction table is

	CO(g)	H <sub>2</sub> O(g)	$\rightleftharpoons$	CO <sub>2</sub> (g)	H <sub>2</sub> (g)
<b>initial</b>	<b>x</b>	<b>0.250</b>		<b>0</b>	<b>x</b>
<b>change</b>	<b>-0.070</b>	<b>-0.070</b>		<b>+0.070</b>	<b>+0.070</b>
<b>equilibrium</b>	<b>x - 0.070</b>	<b>0.250 - 0.070</b>		<b>0.070</b>	<b>x + 0.070</b>

The equilibrium constant in terms of concentrations,  $K_c$ , is:

$$K_c = \frac{[\text{CO}_2\text{(g)}][\text{H}_2\text{(g)}]}{[\text{H}_2\text{O(g)}][\text{CO(g)}]} = \frac{(0.070)(x + 0.070)}{(0.180)(x - 0.070)} = 1.56$$

$$x = [\text{CO(g)}]_{\text{initial}} = [\text{H}_2\text{(g)}]_{\text{initial}} = 0.12 \text{ mol L}^{-1}$$

$$[\text{CO}] = [\text{H}_2] = 0.12 \text{ mol L}^{-1}$$

If the walls of the container are chilled to below 100 °C, what will be the effect on the concentration of CO<sub>2</sub>(g)?

At temperatures below 100 °C, the water vapour will condense to form H<sub>2</sub>O(l). Following Le Chatelier's principle, the equilibrium will shift to the left as [H<sub>2</sub>O(g)] is reduced by this process and so [CO<sub>2</sub>(g)] will decrease.

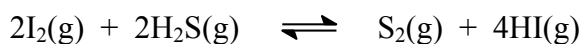
- At 700 °C, hydrogen and iodine react according to the following equation.



Hydrogen also reacts with sulfur at 700 °C:



Determine  $K_c$  for the following overall equilibrium reaction at 700 °C.



**The overall reaction corresponds to the twice the first reaction combined with the reverse of the second reaction:**



The 1<sup>st</sup> reaction is doubled so the original equilibrium constant is squared.

The 2<sup>nd</sup> reaction is reversed so the reciprocal of the equilibrium constant is used.

The two reactions are then combined and the overall equilibrium constant is then the product:

$$K_c(3) = K_c(1) \times K_c(2) = (49.0)^2 \times (1/(1.075 \times 10^8)) = 2.23 \times 10^{-5}$$

$$K_c = 2.23 \times 10^{-5}$$

If 0.250 mol of HI(g) is introduced into a 2.00 L flask at 700 °C, what will be the concentration of I<sub>2</sub>(g) at equilibrium?

**The initial concentration of HI(g) is 0.250 / 2.00 mol L<sup>-1</sup> = 0.125 mol L<sup>-1</sup>.**

	H <sub>2</sub> (g)	I <sub>2</sub> (g)	⇌	2HI(g)
<b>Initial</b>	0	0		0.125
<b>Change</b>	+x	+x		-2x
<b>Equilibrium</b>	x	x		0.125 - 2x

Thus,

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.125 - 2x)^2}{(x)(x)} = \frac{(0.125 - 2x)^2}{x^2} = 49.0 \quad (\text{from 2008-N-5})$$

$$(49.0)^{1/2} = \frac{(0.125 - 2x)}{x}$$

Rearranging gives  $x = [\text{I}_2(\text{g})] = 0.0139 \text{ M}$ .

$$\text{Answer: } 0.0139 \text{ M}$$

If 0.274 g of H<sub>2</sub>S were now introduced into the same flask, what would be the concentration of S<sub>2</sub>(g) at equilibrium?

The molar mass of H<sub>2</sub>S is (2 × 1.008 (H) + 32.06 (S)) = 34.08 g mol<sup>-1</sup>. Hence, 0.274 g of H<sub>2</sub>S corresponds to:

$$\begin{aligned} \text{number of moles} &= \text{mass} / \text{molar mass} \\ &= (0.274 \text{ g}) / (34.08 \text{ g mol}^{-1}) = 8.04 \times 10^{-3} \text{ mol} \end{aligned}$$

The initial concentration of H<sub>2</sub>S is thus  $8.04 \times 10^{-3} \text{ mol} / 2.00 \text{ M} = 4.02 \times 10^{-3} \text{ M}$ .

From above, [I<sub>2</sub>(g)] = 0.0139 M and [HI(g)] = (0.125 – 2 × 0.0139) M = 0.0972 M.

Using the overall equilibrium reaction derived in 2008-N-5:

	2I <sub>2</sub> (g)	2H <sub>2</sub> S(g)	⇌	S <sub>2</sub> (g)	4HI(g)
<b>Initial</b>	0.0139	0.00402		0	0.0972
<b>Change</b>	-2x	-2x		+x	+2x
<b>Equilibrium</b>	0.0139 - 2x	0.00402 - 2x		x	0.0972 + 4x

Thus,

$$\begin{aligned} K_c &= \frac{[S_2][HI]^4}{[I_2]^2[I_2]^2} = \frac{(x)(0.0972+4x)^4}{(0.0139-2x)^2(0.00402-2x)^2} \\ &\sim \frac{(x)(0.0972)^4}{(0.0139)^2(0.00402)^2} = 2.23 \times 10^{-5} \text{ (from 2008-N-5)} \end{aligned}$$

where the small x approximation has been used as K<sub>c</sub> is so small. This gives:

$$x = [S_2(g)] = 7.82 \times 10^{-10} \text{ M}$$

Answer:  $7.82 \times 10^{-10} \text{ M}$

**Key to success: practice further by completing this week's tutorial homework**

**Key to even greater success: practice even further by completing this week's suggested exam questions**