

CHEM1109 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 $[\text{NO}_2(\text{g})] = 0.86 \text{ M}$ 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 NO_2 .)

The CO(g) in water gas can be reacted further with H₂O(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 H₂(g), as well as 0.250 mol L⁻¹ H₂O(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⁻¹ CO₂(g). What was the initial concentration of CO(g) and H₂(g) in the sample?

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The reaction table is

	CO(g)	H ₂ O(g)	\rightleftharpoons	CO ₂ (g)	H ₂ (g)
initial	x	0.250		0	x
change	-0.070	-0.070		+0.070	+0.070
equilibrium	x - 0.070	0.250 - 0.070		0.070	x + 0.070

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 CO₂(g)?

At temperatures below 100 °C, the water vapour will condense to form H₂O(l). Following Le Chatelier’s principle, the equilibrium will shift to the left as [H₂O(g)] is reduced by this process and so [CO₂(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 1st reaction is doubled so the original equilibrium constant is squared.

The 2nd 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 I₂(g) at equilibrium?

The initial concentration of HI(g) is 0.250 / 2.00 mol L⁻¹ = 0.125 mol L⁻¹.

	H ₂ (g)	I ₂ (g)	\rightleftharpoons	2HI(g)
Initial	0	0		0.125
Change	+x	+x		-2x
Equilibrium	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 H₂S were now introduced into the same flask, what would be the concentration of S₂(g) at equilibrium?

The molar mass of H₂S is (2 × 1.008 (H) + 32.06 (S)) = 34.08 g mol⁻¹. Hence, 0.274 g of H₂S 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 H₂S is thus $8.04 \times 10^{-3} \text{ mol} / 2.00 \text{ M} = 4.02 \times 10^{-3} \text{ M}$.

From above, [I₂(g)] = 0.0139 M and [HI(g)] = (0.125 – 2 × 0.0139) M = 0.00972 M.

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

	2I ₂ (g)	2H ₂ S(g)	⇌	S ₂ (g)	4HI(g)
Initial	0.0139	0.00402		0	0.00972
Change	-2x	-2x		+x	+2x
Equilibrium	0.0139 - 2x	0.00402 - 2x		x	0.00972 + 4x

Thus,

$$\begin{aligned} K_c &= \frac{[\text{S}_2][\text{HI}]^4}{[\text{I}_2]^2[\text{H}_2\text{S}]^2} = \frac{(x)(0.00972+4x)^4}{(0.0139-2x)^2(0.00402-2x)^2} \\ &\sim \frac{(x)(0.00972)^4}{(0.0139)^2(0.00402)^2} = 2.23 \times 10^{-5} \text{ (from 2008-N-5)} \end{aligned}$$

where the small x approximation has been used as K_c is so small. This gives:

$$x = [\text{S}_2(\text{g})] = 7.82 \times 10^{-10} \text{ M}$$

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