

## CHEM1612: Worksheet 4: Equilibrium

### Model 1: The Equilibrium Constant

Many chemical reactions lead to a mixture of reactants and products. You will end up with a mixture of both  $\text{NO}_2(\text{g})$  and  $\text{N}_2\text{O}_4(\text{g})$  whether you start with pure  $\text{NO}_2(\text{g})$  or pure  $\text{N}_2\text{O}_4(\text{g})$ . Such reactions are said to reach an equilibrium in which the amount of each substance does not change.

Consider a reaction such as that below which has been left long enough to reach equilibrium.



The *equilibrium constant* in terms of concentrations,  $K_c$ , is a constant at a given temperature that defines how much of each substance there will be at equilibrium:

$$K_c = \frac{[\text{Y}(\text{g})]^y [\text{Z}(\text{g})]^z}{[\text{W}(\text{g})]^w [\text{X}(\text{g})]^x}$$

If  $K_c > 1$ , the mixture will contain more of the substances on the right hand side (Y and Z) of the equation.

If  $K_c < 1$ , the mixture will contain more of the substances on the left hand side (W and Z) of the equation.

In worksheets 2 and 3, you studied the thermodynamics of the equilibrium between  $\text{NO}_2$  and its dimer  $\text{N}_2\text{O}_4$ . Starting from  $\text{NO}_2$ , the formation of the dimer can be studied using one of the two equations below:



Starting from the dimer, the formation of  $\text{NO}_2$  can be studied using one of the two equations below:



### Critical thinking questions

1. Write down the expression for  $K_c$  for reactions A, B, C and D in Model 1.

$$K_c (\text{A}) = \text{—————} \quad K_c (\text{B}) = \text{—————} \quad K_c (\text{C}) = \text{—————} \quad K_c (\text{D}) = \text{—————}$$

2. Looking at the equations in Q1, what is the *mathematical* relationship between the different forms of  $K_c$ ?

(a)  $K_c (\text{A})$  and  $K_c (\text{B})$

(b)  $K_c (\text{A})$  and  $K_c (\text{C})$

3. At equilibrium at room temperature,  $[\text{NO}_2(\text{g})] = 1.60 \text{ M}$  and  $[\text{N}_2\text{O}_4] = 0.20 \text{ M}$ . Calculate the values of  $K_c(\text{A})$  and  $K_c(\text{B})$  and  $K_c(\text{C})$  and hence confirm your analysis in Q2.

### Model 2: The Reaction Quotient

The reaction quotient,  $Q_c$ , for a reaction  $w\text{W}(\text{g}) + x\text{X}(\text{g}) \rightleftharpoons y\text{Y}(\text{g}) + z\text{Z}(\text{g})$ , is defined as follows:

$$Q_c = \frac{[\text{Y}(\text{g})]^y [\text{Z}(\text{g})]^z}{[\text{W}(\text{g})]^w [\text{X}(\text{g})]^x}$$

It *looks* similar to the equilibrium constant expression. The difference is that  $Q_c$  can be calculated at any time during a reaction or if a reaction is disturbed. It is used to predict the direction in which a reaction will move.

### Critical thinking questions

Consider the reaction  $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$  to be at equilibrium with  $[\text{NO}_2(\text{g})] = 1.60 \text{ M}$ ,  $[\text{N}_2\text{O}_4] = 0.20 \text{ M}$  and  $K_c = 0.078$ .

- Predict *qualitatively* what will happen to this reaction if more  $\text{NO}_2$  is added so that  $[\text{NO}_2(\text{g})] = 2.00 \text{ M}$ ?
- Predict *qualitatively* what will happen to this reaction if instead  $\text{NO}_2$  is removed so that  $[\text{NO}_2(\text{g})] = 1.00 \text{ M}$ ?
- Calculate the values for  $Q_c$  for these two experiments.
  - $[\text{NO}_2(\text{g})] = 2.00 \text{ M}$  and  $[\text{N}_2\text{O}_4] = 0.20 \text{ M}$ :  $Q_c =$
  - $[\text{NO}_2(\text{g})] = 1.00 \text{ M}$  and  $[\text{N}_2\text{O}_4] = 0.20 \text{ M}$ :  $Q_c =$
- Using your answers to Q1 - 3, what in general happens to a reaction if
  - $Q_c < K_c$
  - $Q_c > K_c$

### 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			+x
equilibrium			$0.20 + x$

### Critical thinking questions

- From the chemical equation: every time *one*  $\text{N}_2\text{O}_4$  molecule is formed, *two*  $\text{NO}_2$  molecules are lost. If  $[\text{N}_2\text{O}_4(\text{g})]$  *increases* by  $x$  to reach equilibrium, what will the change in  $[\text{NO}_2(\text{g})]$  be? Add this change to the second row of the table. (*Hint*: is the change positive or negative.)
- Complete the third row of the table.
- Substitute the equilibrium concentrations from the third row into your expression for  $K_c(A)$  from Q1 in Model 1.

4. You now have a *mathematical* expression to solve for  $x$ . Using  $K_c = 0.078$ . solve for  $x$  and hence work out the equilibrium values of  $[\text{NO}_2(\text{g})]$  and  $[\text{N}_2\text{O}_4(\text{g})]$ .

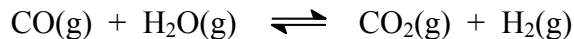
### Exercises

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The  $\text{CO}(\text{g})$  in water gas can be reacted further with  $\text{H}_2\text{O}(\text{g})$  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  $\text{CO}(\text{g})$  and  $\text{H}_2(\text{g})$ , as well as  $0.250 \text{ mol L}^{-1} \text{ H}_2\text{O}(\text{g})$ . This sample is placed in a sealed container at 900 K and allowed to come to equilibrium, at which point it contains  $0.070 \text{ mol L}^{-1} \text{ CO}_2(\text{g})$ . What was the initial concentration of  $\text{CO}(\text{g})$  and  $\text{H}_2(\text{g})$  in the sample?

**Marks**  
**4**

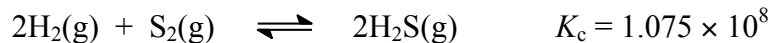
$$[\text{CO}] = [\text{H}_2] =$$

If the walls of the container are chilled to below  $100 \text{ }^\circ\text{C}$ , what will be the effect on the concentration of  $\text{CO}_2(\text{g})$ ?

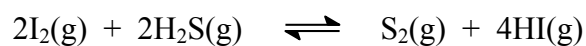
- At 700 °C, hydrogen and iodine react according to the following equation.



Hydrogen also reacts with sulfur at 700 °C:



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



$K_c$

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?

Answer:

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?

Answer:

