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 $NO_2(g)$ and $N_2O_4(g)$ whether you start with pure $NO_2(g)$ or pure $N_2O_4(g)$. 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.

$$w\text{W(g)} + x\text{X(g)} \rightleftharpoons y\text{Y(g)} + z\text{Z(g)}$$

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:

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

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 NO_2 and its dimer N_2O_4. Starting from NO_2, the formation of the dimer can be studied using one of the two equations below:

$2NO_2(g) \rightleftharpoons N_2O_4(g)$ (A)

$NO_2(g) \rightleftharpoons \frac{1}{2} N_2O_4(g)$ (B)

Starting from the dimer, the formation of NO_2 can be studied using one of the two equations below:

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ (C)

$\frac{1}{2} N_2O_4(g) \rightleftharpoons NO_2(g)$ (D)

Critical thinking questions

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

K_c (A) = ________ K_c (B) = ________ K_c (C) = ________ K_c (D) = ________

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

(a) K_c (A) and K_c (B) (b) K_c (A) and K_c (C)

3. At equilibrium at room temperature, $[NO_2(g)] = 1.60$ M and $[N_2O_4] = 0.20$ M. Calculate the values of K_c(A) and K_c(B) and K_c(C) and hence confirm your analysis in Q2.

Model 2: The Reaction Quotient

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

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

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 $2NO_2(g) \rightleftharpoons N_2O_4(g)$ to be at equilibrium with $[NO_2(g)] = 1.60$ M, $[N_2O_4] = 0.20$ M and $K_c = 0.078$.

1. Predict *qualitatively* what will happen to this reaction if more NO_2 is added so that $[NO_2(g)] = 2.00$ M?

2. Predict *qualitatively* what will happen to this reaction if instead NO_2 is removed so that $[NO_2(g)] = 1.00$ M?

3. Calculate the values for Q_c for these two experiments.

   (a) $[NO_2(g)] = 2.00$ M and $[N_2O_4] = 0.20$ M: $Q_c =$

   (b) $[NO_2(g)] = 1.00$ M and $[N_2O_4] = 0.20$ M: $Q_c =$

4. Using your answers to Q1 - 3, what in general happens to a reaction if

   (a) $Q_c < K_c$

   (b) $Q_c > K_c$

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: **i**nitial-**c**hange-**e**quilibrium.

Consider the starting mixture in Q1 of Model 2: $[NO_2(g)] = 2.00$ M and $[N_2O_4(g)] = 0.20$ M. These are the **i**nitial 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 $NO_2(g)$ reacts to make $N_2O_4(g)$. We do not know *how much* will react but we *can* calculate it:

	$2NO_2(g)$	$\rightleftharpoons$	$N_2O_4(g)$
initial	2.00		0.20
change			$+x$
equilibrium			$0.20 + x$

Critical thinking questions

1. From the chemical equation: every time *one* N_2O_4 molecule is formed, *two* NO_2 molecules are lost. If $[N_2O_4(g)]$ *increases* by x to reach equilibrium, what will the change in $[NO_2(g)]$ be? Add this change to the second row of the table. (*Hint*: is the change positive or negative.

2. Complete the third row of the table.

3. 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 $[NO_2(g)]$ and $[N_2O_4(g)]$.

Exercises

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Marks
4

The CO(g) in water gas can be reacted further with H_2O(g) in the so-called "water-gas shift" reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

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_2(g), as well as 0.250 mol L^{-1} H_2O(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} CO_2(g). What was the initial concentration of CO(g) and H_2(g) in the sample?

[CO] = $[H_2]$ =

If the walls of the container are chilled to below 100 ºC, what will be the effect on the concentration of CO_2(g)?

Marks
10

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

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K_c = 49.0$$

Hydrogen also reacts with sulfur at 700 °C:

$$2H_2(g) + S_2(g) \rightleftharpoons 2H_2S(g) \qquad K_c = 1.075 \times 10^8$$

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

$$2I_2(g) + 2H_2S(g) \rightleftharpoons S_2(g) + 4HI(g)$$

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 $I_2(g)$ at equilibrium?

Answer:

If 0.274 g of H_2S were now introduced into the same flask, what would be the concentration of $S_2(g)$ at equilibrium?

Answer: