**The Equilibrium Constant**

Consider the hypothetical reversible reaction below.

a A + b B ⇌ c C + d D

As we have established, at equilibrium, the rates of the forward and reverse reactions are the same. This means although both forward and reverse reactions are occurring, the concentrations of all of the substances are constant. The **equilibrium constant (Keq)** is the ratio of the concentrations of the reagents in a reaction that is at equilibrium. The generalised form of the Keq expression is:

Each concentration is raised to the power of its coefficient (in the balanced chemical equation). Thus the equilibrium constant expression is:

Where the concentrations represent the equilibrium concentrations, not the initial or starting concentrations of the reagents. The equilibrium constant is a “constant” value for each equilibrium system – it does not change when stress or changes are applied to an equilibrium. This seems a little counterintuitive given the previous section where we discussed equilibrium shifting to respond to changes. However, although the concentrations of individual reactants or products may change when a stress is applied to an equilibrium, the concentrations will change in such a way that the equilibrium constant will equal the same value. This means that changes to any equilibrium can be precisely predicted as the new concentrations created by a shift in equilibrium must “fit” the equilibrium constant (this is a huge area for maths calculations… get ready!)

There is one exception to this - when the stress applied to an equilibrium is a change in temperature. A change in temperature will change the rates of both the forward and reverse reactions, but not to the same extent. As a result, a change in temperature changes the equilibrium constant. The general shift in equilibrium can still be predicted using Le Chatelier’s principle, but the precise changes in concentration cannot be calculated unless you know the new value of the Keq at the new equilibrium temperature. One practical (but minor) implication of this is that for any reaction in which a Keq is stated, the temperature should be specified, or it should at least be stated that a constant temperature is maintained as other equilibrium conditions (concentration and pressure) are changed.

The value of the equilibrium constant for any reaction can only be determined by experiment. The general value of the equilibrium constant gives us information about whether the reactants or the products are favoured at equilibrium. A Keq >> 1 means that the products are favoured over the reactants. A Keq << 1 means that the reactants are favoured over the products. A Keq of approximately 1 suggests the equilibrium favours neither reactants or products.

The general rule when quoting or calculating a Keq is that all units are dropped, and Keq values are written without units.

**Calculating an Equilibrium Constant**

**Example one (simple):**

Equilibrium occurs when nitrogen monoxide gas reacts with oxygen gas to form nitrogen dioxide gas.

2NO(g) +O2(g) ⇌ 2NO2(g)

At 230°C, the equilibrium concentrations for this reaction are measured to be [NO] = 0.0542 M, [O2] = 0.127 M, and [NO2] = 15.5 M. Calculate the equilibrium constant at this temperature.

**Step 1**- Complete **ICE** table (not actually necessary for this Q but a good habit to form)

2NO(g) + O2(g) ⇌ 2NO2(g)

|  |  |  |  |
| --- | --- | --- | --- |
| **I**nitial conc | - | - | - |
| **C**hange in conc | - | - | - |
| **E**quilibrium conc | 0.0542 | 0.127 | 15.5 |

**Step 2**- Write Keq expression and calculate unknown (in this case the value of Keq)

**Step 3**- Think about your answer

This Keq value is much larger than 1, meaning the products are favoured. This makes sense as the product, NO2 has a much higher conc at equilibrium than the reactants. This should create a high Keq which is our result.

**Example two:**

The Haber process for the production of ammonia results in the equilibrium represented by the reaction: N2(g)+3H2(g)⇌2NH3(g). Initially there were 5.5 moles of NH3 gas added to an otherwise empty 5.0 L flask. At equilibrium at a temperature, the 5.0 L flask contained 1.25 mol N2. Calculate Keq for the reaction at this temperature. ***HINT – use conc’s not moles in your ice table!***

N2(g) + 3H2(g) ⇌ 2NH3(g)

|  |  |  |  |
| --- | --- | --- | --- |
| **I**nitial conc | **0** (given) | **0** (given) | **1.1** (5.5/5) |
| **C**hange in conc | **+**0.435 (0.87/2) | **+**1.305 (0.87\*3/2) | * 0.87 (1.1-0.23) |
| **E**quilibrium conc | 0.435 | 1.305 | **0.23** (5.5/5) |

**Some things you should remember about the Equilibrium constant**

* The equilibrium expression only includes those substances whose concentrations are variable during the reaction. A pure solid or a pure liquid have constant, unchanging concentrations. Therefore, an equilibrium expression omits pure solids and liquids and only shows the concentrations of gases and aqueous solutions. The decomposition of mercury(II) oxide is an example:

2HgO(s) ⇌ 2Hg(l) + O2(g)    The equilibrium constant is  Keq = [O2]

* The stoichiometry of an equation is an important consideration in determining equilibrium changes. Anytime that an equilibrium is subject to change and then shifts to be re-established, the concentrations of the reagents can only change according to the stoichiometric ratios in the equation. This can sometimes limit and pre-define concentrations. For example at 40°C, a sample of solid ammonium carbonite was allowed to decompose to ammonia and carbon dioxide gases.

NH4CO2NH2(s) ⇌ 2NH3(g) + CO2(g)

At equilibrium, [CO2] is found to be 4.71 × 10−3 M. You can calculate the Keq value from just this information. Because the ammonium carbamate is a solid, it is not present in the equilibrium expression.

Keq=[NH3]2 [CO2]

* The value of an equilibrium constant tells you a great deal about the concentrations of the reagents at equilibrium. If a Keq is very high it means the reaction lies well to the right, favours the products, and practically speaking has gone to completion, with very small amounts of reactants remaining. If a Keq is very low it means a reaction lies well to the left, favours the reactants, and practically speaking may not appear to be occurring at all. For example, an insoluble solid would have a very low Keq for the dissolution equilibrium.
* The equilibrium position (and equilibrium constant) are not dependent on the starting concentrations of the reagents. No matter what the concentrations of a reversible reaction begin at, the final concentrations will be determined by the equilibrium constant and the stoichiometric ratios.
* Some questions involving equilibrium constants, the most difficult questions, can appear to involve solving one or more quadratic equations. When this occurs an assumption is usually made to simplify the question. This assumption depends on the Keq being very small (<0.001) or very large (>1000). If this condition is met, Keq expressions can be simplified by simply ignoring values associated with unknowns. You need to be able to solve these types of Qs.
* A question alluded to in the SC is the concept of a Reaction Quotient (Q) (this is often called a Trial Keq). You calculate Q using the Keq expression, but the calculation is done with concentrations which may not be at equilibrium. Calculating Q for non-equilibrium positions allows us to make decisions about what changes will occur to reach equilibrium concentrations. If Q is less than the given Keq value, then the system is not at equilibrium, and it will shift to the right to establish equilibrium. If Q is greater than Keq, then the system is not at equilibrium and the system will shift to the left to establish equilibrium.

**Questions**

1. How does the position of equilibrium depend upon the starting concentrations of all the reactants and products?
2. What types of substances are not included in equilibrium expressions and why?
3. In general, which reaction is favoured (forward, reverse, or neither) if the value of Keq at a specified temperature is
   1. equal to 1?
   2. very small?
   3. very large?
4. Write equilibrium expression for the following reactions.
   1. 3O2(g) ⇌ 2O3(g)
   2. H3PO4(aq) ⇌ 3H+(aq) + PO43−(aq)
   3. 2NO2(g) + 7H2(g) ⇌ 2NH3(g) + 4H2O(l)
   4. 2NaHCO3(s) ⇌ Na2CO3(s) + CO2(g) + H2O(g)
5. Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.
   * 1. H2(g) + I2(g) ⇌ 2HI(g)  K(700K) = 54
     2. 2CO2(g) ⇌ 2CO(g) + O2(g)  K(1200K) = 3.1×10−18
     3. PCl5(g) ⇌ PCl3(g) + Cl2(g)  K(613K) = 97
     4. 2O3(g) ⇌ 3O2(g)  K(298K) = 5.9×1055
6. Oxygen reacts with hydrogen chloride to form chlorine gas and water vapor:

4HCl(g) + O2(g) ⇌ 2Cl2(g) + 2H2O(g)

At a certain temperature, the equilibrium mixture consists of 0.0012 M HCl, 3.8 × 10−4 M O2, 0.058 M Cl2, and 0.058 M H2O. Calculate the value of the equilibrium constant at this temperature.

1. At equilibrium at 2500 K, [HCl] = 0.0625 M and [H2] = [Cl2] = 0.00450 M for the reaction: H2(g) + Cl2(g) ⇌ 2HCl(g).
   1. Calculate the equilibrium constant for the reaction as written above.
   2. Calculate the equilibrium constant for the reaction written instead as: 2HCl(g) ⇌ H2(g) + Cl2(g) What is the relationship of the Keq values in parts a and b?
2. Consider the following reaction: H2S(aq) ⇌ H+(aq) + HS−(aq), Keq=9.5 × 10-8 at 25°C. In a equilibrium mixture at 25°C, [H+] = [HS−] = 2.7 × 10−4 M. Determine the concentration of H2S in this mixture.
3. Phosphorus pentachloride gas decomposes to phosphorus trichloride and chlorine:  PCl5(g) ⇌ PCl3(g) + Cl2(g). In a certain reaction, 0.500 mol of PCl5 is introduced into a 5.00 L container at 250°C. When the reaction reaches equilibrium, the mixture is analyzed and found to contain 0.194 mol Cl2. Determine the value of Keq at 250°C for this reaction.
4. Nitrogen monoxide combines with chlorine at 400°C to form nitrosyl chloride by the following reaction: 2NO(g) + Cl2(g) ⇌ 2NOCl(g), Keq=28.1 at 400°C. In a certain reaction, a quantity of NOCl is allowed to decompose at 400°C until equilibrium is reached. The [NO] at equilibrium is 9.40 × 10−3 M. Find the concentrations of Cl2 and NOCl.