**Reflecting on Acids and bases HL**

**18.1 Lewis acids and bases (HL)**

**NATURE OF SCIENCE**

Lewis acid–base theory is compatible with Brønsted–Lowry theory, it does not falsify it. By changing the perspective of acid–base reactions from the proton to the lone pair of electrons, it opens up a wider field of application. The proton no longer has a central role, it is just one example of a lone pair acceptor. Lewis acids include a wide range of both organic and inorganic species that are not recognized as acids in Brønsted–Lowry theory. Yet, in many cases, as we will see in the following sections, Brønsted–Lowry theory is sufficient and could be considered a more useful theory for the description of acid–base reactions, especially those occurring in aqueous solution.

**Comparing the Lewis and Brønsted–Lowry definitions**

Gilbert Lewis, whose name famously belongs to electron dot structures reasoned that the entire reaction between acids and bases could be viewed in terms of the electron pair rather than in terms of proton transfer.

For example, the reaction between ammonia and H ions to form ammonium ions,

+

H

H

**H**+

+

 N H

**H** N H

H

H

Discuss this example and define the Lewis acid and base

How are the definitions similar and different from the Brønsted–Lowry definition?

Lewis bases:

Lewis Acids:

Describe the type of bond that forms between Lewis’s acid and a Lewis base.

**Question**

1. **Describe the reaction between BF3 and NH3 to illustrate the Lewis acid-base reactions**
2. **What other elements in the periodic table demonstrate Lewis’s acid-base reactions? Use Cu 2+ and water ligands to show this and identify the Lewis acid and base in this example.**

**Nucleophiles and electrophiles: alternate language to electron donor and acceptor**

At about the same time as Lewis developed his acid-base theory, alternate language was being introduced to describe the behavior of reactants with respect to electron pairs.

**Define these terms and relate them to Lewis acids and bases.**

**Question3**

**Give some examples of nucleophiles and electrophiles completing the table below**

|  |  |
| --- | --- |
| **Nucleophiles (Electron rich)** | **Electrophiles (electron deficient)** |
| OH- | BF3 |
|  |  |
|  |  |

In conclusion, many reactions cannot be described as Brønsted–Lowry acid–base reactions, but do qualify as Lewis acid–base reactions. These are reactions where no transfer of H+ occurs.

**18.2 Calculations involving acids and bases**

**Learning objectives**

• Understand what is meant by an acid dissociation constant and a base ionisation constant

• Arrange acids and bases in order of strength based on *K*a, p*K*a, *K*b or p*K*b values

• Carry out calculations involving *K*a, *K*b, p*K*a, p*K*b, pH and pOH

• Use the relationships *K*w = *K*a × *K*b and p*K*a + p*K*b = p*K*w

**Understandings:**

* The expression for the dissociation constant of a weak acid (Ka) and a weak base (Kb).
* For a conjugate acid–base pair, Ka × Kb = Kw.

**Guidance**

* The value Kw depends on the temperature.
* Only examples involving the transfer of one proton will be assessed.
* Calculations of pH at temperatures other than 298 K can be assessed.
* The relationship between Ka and pKa is pKa = –log10Ka and between Kb and pKb is

 pKb = –log10Kb.

***K*w is temperature dependent, and temperature should always be stated alongside pH measurements.**

Give the expression for the ionic product of water at 298K

Dissociation of water is **endothermic, and** the pH of pure water is 7.00 only when the temperature is 298 K**. How does an increase in temperature affect the PH of water? Does the water become acidic or neutral? Explain.**

pH and pOH scales are inter-related

pH = –log10[H+]; and was introduced in order to simplify the expression of the H+ concentration in a solution.

The same rationale can be applied to the OH– ions to simplify the expression of OH- concentration in solution.

Thus; the parallel scale, known as the **pOH scale**, is therefore used to describe the OH– content of solutions.

 **•** pOH = –log10[OH–]; and [OH–] = 10–pOH

 **•** pH = –log10[H+]; and [H+] = 10–pH

What is the relationship between the POH and PH scales at 298K?

Derive the relationship between **p***K***w**, POH and PH.

**Converting H+ and OH– into pH and pOH examples**

**Example: Lemon juice has a pH of 2.90 at 25°C. Calculate its [H+], [OH–], and pOH**.

**Strong acids and bases: pH and pOH can be deduced from their concentrations**

We assume full dissociation for strong acids and bases. Because of this we can deduce the ion concentrations and so calculate the pH or pOH directly from the initial concentration of the solution.

**Example: Worked example**

**Calculate the pH of the following at 298 K:**

**(a) 0.10 mol dm–3 NaOH(aq)**

**(b) 0.15 mol dm–3 H2SO4(aq)**

**Dissociation constants express the strength of weak acids and bases.**

Weak acids and bases, unlike solid acids and bases, do not dissociate fully. This means we *cannot* deduce the concentrations of ions in their solutions from the initial concentrations, as the ion concentrations will depend on the extent of dissociation that has occurred. So, we need some means of quantifying the degree of dissociation – and the process takes us back to equilibrium considerations.

Consider the generic weak acid HA dissociating in water to derive the expression for ***K*a** is known as the **acid dissociation constant**.

 HA(aq) + H2O(l)  H3O+(aq) + A–(aq)

*K*a depends on the position of the equilibrium of acid dissociation and gives a direct measure of the strength of an acid.

*How does the value of Ka relate to the strength of the acid.*

**Similarly, we can consider the ionization of a base using the generic weak base B.**

**Questions**

1. **Derive the base constant Kb for the generic base B as above.**
2. Write the expressions for *K*a and *K*b for the following acid and base.

 **(a)** CH3COOH(aq)

 **(b)** NH3(aq)

**Calculations involving *K*a and *K*b**

The following points are to remind you of some key issues and guide you in all the calculations that follow:

**•** The given concentration of an acid or base is its *initial* concentration – before dissociation occurs.

**•** The pH (or pOH) of a solution refers to the concentration of H+ ions (or OH– ions) at *equilibrium*.

**•** The concentration values substituted into the expressions for *K*a and *K*b must be the *equilibrium* values for all reactants and products.

**•** When the extent of dissociation is very small (very low value for *K*a or *K*b) it is appropriate to use the approximations:

 [acid]initial ≈ [acid]equilibrium

 [base]initial ≈[base]equilibrium

1 Calculation of *K*a and *K*b from pH and initial concentration

1. **Calculate *K*a at 298 K for a 0.01mol dm–3 solution of ethanoic acid (CH3COOH). It has a pH of 3.4 at this temperature.**

Write the equation for the dissociation of the acid. Insert the data in three rows: initial, change, and equilibrium. Apply ICE to demonstrate how to solve these problems.

1. **Calculate the *K*b for a 0.100 mol dm–3 solution of methylamine, CH3NH2 at 25°C . Its pH is 11.80 at this temperature.**

**2 Calculation of [H+] and pH, [OH–] and pOH from *K*a and *K*b**

1. **A 0.75 mol dm–3 solution of ethanoic acid has a value for *K*a = 1.8 × 10–5 at a specified temperature. What is its pH at this temperature?**

To calculate pH we need to know [H+] at equilibrium, and therefore the amount of dissociation of the acid that has occurred: this is the ‘change’ amount in the reaction.

So let the change in concentration of CH3COOH = –*x*

Therefore, change in concentration of CH3COO– and H+ = +*x*

1. **A 0.20 mol dm–3 aqueous solution of ammonia has *K*b of 1.8 × 10–5 at 298 K . What is its pH?**

Let the change in concentration of NH3 = –*x*

 Therefore, change in concentration of NH4+ and OH– = +*x*

**p*K*a and p*K*b**

Like pH and POH, due to very small values, it is convenient to use p*K*a and pKb as follows:

**•** p*K*a = –log10*K*a;and *K*a = 10– p*K*a

**•** pKb = –log10*K*b; and*K*b = 10 – p*K*b

Some examples of *K*a and p*K*a, *K*b and p*K*b values are given below, all at 298 K.

Table 1Weak acids

|  |  |  |  |
| --- | --- | --- | --- |
| **Acid**methanoic | **Formula**HCOOH | ***K*a**1.8 × 10–4 | **pKa**3.75 |
| ethanoic | CH3COOH | 1.8 × 10–5 | 4.76 |
| propanoic | C2H5COOH | 1.4 × 10–5 | 4.87 |
| Table 2 Weak Bases  |  |  |  |
| **Table 2 Weak bases**  |  **Formula**  |  **Kb p** |  **pKb** |
| ammonia | NH3 | 1.8 × 10–5 | 4.75 |  |
| methylamine | CH3NH2 | 4.6 × 10–4 | 3.34 |  |
| ethylamine | C2H5NH2 | 4.5 × 10–4 | 3.35 |  |

**The following points follow from the table.**

1. p*K*a and p*K*b numbers are usually positive and have no units.
2. The relationship between *K*a and p*K*a and between *K*b and p*K*b is inverse.
3. A change of one unit in p*K*a or p*K*b represents a 10 fold change in the value of *K*a or *K*b.
4. pKa and pKb must be quoted at a speci­fied temperature.
5. The lower the value of p*K*a, the stronger the acid.
6. The lower the value of p*K*b, the stronger the base.

**Relationship between *K*a and *K*b, p*K*a and p*K*b for a conjugate pair**

Show the relationship between , p*K*a and p*K*b for the conjugate acid-base pair HA and A-

