Extension 9: Gas Concentrations, pH and Molality

1. Prerequisites

The key ideas required to understand this section are:

Topic	Book page
Concentration expressed as a mole fraction	151
pH scale	152
Molar concentration	137

2. Mole fractions in gas mixtures

In a gas mixture, the number of moles of each gas component is directly proportional to its partial pressure (the pressure exerted by that component and its contribution to the total pressure of the mixture); so if we have data describing the partial pressures of each gas in the mixture, we can calculate the mole fractions of the gases

For example, for air, which is roughly a gas mixture of O_2, N_2, and CO_2:

$$n_{O2} = Cp_{O2}$$

where nO_2 = number of moles of O_2, p_{O2} = partial pressure of O_2 and C = a constant. So the mole fraction of O_2 in the mixture is given by:

$$X_{O2} = \frac{n_{O2}}{n_{O2} + n_{N2} + n_{CO2}}$$

$$= \frac{CpO_2}{Cp_{O2} + Cp_{N2} + Cp_{CO2}}$$

$$= \frac{p_{O2}}{p_{O2} + P_{N2} + p_{CO2}}$$

EXERCISE 9A

Gas mixtures

(i)   If the total air pressure is 101 325 Pa, and the partial pressure of oxygen in the air is 20 800 Pa, what is the mole fraction of oxygen in the air?

(ii) What mole percentage does the answer to (i) represent?

(iii) If the mole percentage of nitrogen in the air sample in (i) is 78%, what is the partial pressure of nitrogen?

3. The pH of very dilute solutions

What is the pH of a very dilute solution of a strong acid such as HCl(aq)? Consider the question 'What is the pH of an aqueous solution of hydrochloric acid of concentration 1.0×10^{-8} mol dm^{-3} at 25°C?'

Often students will reason as follows:

$[H_3O^+(aq)]$ from acid $= 1.0 \times 10^{-8}$ mol dm^{-3}

pH $= -\log_{10}[H_3O^+(aq)] = -\log_{10}[1.0 \times 10^{-8}] = 8.00$ – a basic solution

Can this be right? Well no, it isn't. The student has forgotten that, in a solution of an acid, there are two sources of $[H_3O^+(aq)]$ – one from the ionization of the acid and another from the autoionization of water.

So total $[H_3O^+(aq)]$total $= [H_3O^+(aq)]$from water $+ [H_3O^+(aq)]$from acid

At stronger concentrations of acid (say 0.1 mol dm^{-3} HCl), $[H_3O^+(aq)]$from acid swamps the contribution from the water which we would tend to ignore, but at very weak concentrations, ($<1 \times 10^{-6}$ mol dm^{-3} HCl), $[H_3O^+(aq)]$ from water becomes important.

> ## EXERCISE 9B
>
> What is the pH of an aqueous solution of hydrochloric acid of concentration 1.0×10^{-8} mol dm^{-3} at 25°C?

4. The pH of very concentrated solutions

Most pH measurements fall between the 0–14 pH scale, but is it valid to quote a pH outside this range? What, for example, is the pH of a concentrated solution of hydrochloric acid (12 mol dm^{-3})?

According to previous theory pH $= -\log_{10}[H_3O^+(aq)] = -\log_{10}[12] = -1.08$.

Can we have a negative pH? Is this possible? Well yes, but there are complications in dealing with concentrated acid solutions that make simple pH calculations inaccurate (for example, strong acids do not dissociate completely at high concentrations) and it is very difficult to measure the pH of such solutions experimentally, using pH meters (glass pH meters tend to give misleading readings under these conditions). However, with carefully calibrated pH meters, scientists have managed to measure extremely acidic mine waters from Iron Mountain, California, with pH values as low as –3.6.

5. Small changes in pH make a difference

Because it is a logarithmic scale, small changes in pH make big differences. For example, suppose that the pH of sample decreases from 4.60 to 4.30 – a decrease of only 0.30 units.

$[H^+(aq)]$ at lower pH $= 10^{-4.30} = 5.0 \times 10^{-5}$ mol dm^{-3}
$[H^+(aq)]$ at higher pH $= 10^{-4.60} = 2.5 \times 10^{-5}$ mol dm^{-3}

The ratio of hydrogen ion concentrations is $(5.0 \times 10^{-5})/(2.5 \times 10^{-5}) = 2.0$ In other words, decreasing the pH by 0.30 requires that the hydrogen ion concentration be *doubled*.

We can put this in context. Suppose that an environmental group wished to set the lowest pH of a waste stream from a factory at 4.60. Any waste with a pH below this would need to be treated (neutralised) before it was emitted into the river. The factory however, might want a different definition of maximum acidity, one with a pH of 4.30. To non-scientists this might appear too small a

difference to argue about but in practice this might save the factory a lot of money in treatment because the allowable hydrogen ion concentration would be double that of the environmentalists.

The nature of logarithms means that the same differences in pH represent the same relative changes in [H+(aq)]. A decreasae in pH of 0.30 always involves a doubling of [H+(aq)] and an increase of pH of 0.30 always involves a halving of [H+(aq)]. These rules apply whatever the initial and final pH values – as long as difference in pH is 0.30.

Similarly, a decrease in pH of:

0.5 increases the hydrogen ion concentration by approximately three times.
0.6 increases the hydrogen ion concentration by approximately four times.
1.0 increases the hydrogen ion concentration by approximately ten times.

6. Molality – not quite the same as Molarity!

Remember that molar concentration, or molarity, can be expressed by:

$$\text{Molarity} = \frac{\text{amount of solute in mol}}{\text{volume of solution in dm}^3}$$

Molarity is the most commonly used measure of concentration, particularly for dilute aqueous solutions, but it has some drawbacks. Masses can be determined with great precision because balances can be very precise, volume measurements are often not so precise. Also the molarity of a solution changes with temperature, owing to the thermal expansion of the solution.

Molality

$$\text{Molality of a solute} = \frac{\text{amount of solute in mol}}{\text{mass of solvent in kg}}$$

Molality is the number of moles of solute per kilogram of solvent and not solution. It is independent of temperature, unlike molarity.

For example, if 0.5 mole of solute is added to 1.0 kilograms of solvent the solution has a molality of 0.50 mol kg^{-1} and can also be described as 0.50 molal.

In a dilute aqueous solution, under normal conditions of temperature and pressure, the values of molarity and molality are very similar. Under these conditions, 1 kg of water roughly corresponds to a volume of 1 dm^3 and addition of solute makes a very small change to the volume of the solution.

When do you use the terms mole fraction, molality and molarity?

* Mole fractions tend to be used for liquid mixtures
* Molalities for precise work with solid solutes
* Molarities for less precise work with solid solutes

Revision questions

1. What volume of dilute hydrochloric acid (concentration 0.050 mol dm^{-3}) is needed to react with a tablet containing 400 mg of calcium carbonate?

2. Calculate the mass, in grams, of sodium chloride present in 230 g of a 12.5% solution of sodium chloride by mass.

3. What is the pH of a solution of sodium hydroxide at 25°C and of concentration 1.0×10^{-7} mol dm^{-3}?

4. Why is it not valid to refer to the pH of 100% pure sulfuric acid?

5. If 5.3 g of Na_2CO_3 are dissolved in 520 g of H_2O, what is the molality of the solution?

6. Convert the answer to question 1 into molarity (mol dm^{-3}). Assume 1 kg of water has a volume of 1 dm^3 and the volume of the solution is the same as the volume of water.

7. What is the molality of a solution of urea ($CO(NH_2)_2$) that contains 0.50 g of the solute in 250 cm^3 of water?

Answers

Exercises
Exercise 9A
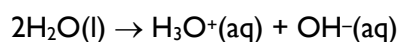   **(i)** 0.21   **(ii)** 21   **(iii)** 79034 Pa

Exercise 9B
$[H_3O^+(aq)]$total $= [H_3O^+(aq)]$from water $+ [H_3O^+(aq)]$from acid
Let $[H_3O^+(aq)]$from water $= y$
So $[H_3O^+(aq)]$total $= y + (1.0 \times 10^{-8})$
When water autoionizes there is an OH^- produced for every $H_3O^+(aq)$ produced:
      $2H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq)$
So $[OH^-(aq)] = y$ At 25°C, $[H_3O^+(aq)]$ $[OH^-(aq)] = 1.0 \times 10^{-14}$ mol^2 dm^{-6}
Substituting: $\{y + (1.0 \times 10^{-8})\}y = 1.0 \times 10^{-14}$
Rearranging: $y^2 + (1.0 \times 10^{-8})y - (1.0 \times 10^{-14}) = 0$
This is a quadratic equation of the type $ax^2 + bx + c = 0$, and can be solved by the formula:
$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$
Where $a = 1$, $b = 1.0 \times 10^{-8}$ and $c = 1.0 \times 10^{-14}$
Solving and ignoring the negative answer, $x = 9.5 \times 10^{-8}$ mol dm^{-3}
$[H_3O^+(aq)]$total $= [H_3O^+(aq)]$from water $+ [H_3O^+(aq)]$from acid
$[H_3O+(aq)]$total $= 9.5 \times 10^{-8} + 1.0 \times 10^{-8}$ mol dm^{-3}
$[H_3O+(aq)]$total $= 10.5 \times 10^{-8}$ mol dm^{-3}
pH $= -\log_{10}[H_3O+(aq)] = 6.98$.

Revision questions
1. $CaCO_3(s) + 2HCl(aq)$ $CaCl_2(aq) + H_2O(l) + CO_2(g)$
1 mol $CaCO_3$ reacts with 2 mol HCl
$$\frac{\text{amount in mol } CaCO_3}{\text{amount in mol HCl}} = \frac{1}{2}$$
amount in mol $CaCO_3 = 400 \times 10^{-3}/100 = 4 \times 10^{-3}$ mol
amount in mol HCl = volume 0.050
Therefore:
$$\frac{4 \times 10^{-3}}{\text{volume } 0.050} = \frac{1}{2}$$

volume HCl = $\frac{24 \times 10^{-3}}{0.050}$ = 0.16 dm³

2. Percentage composition by mass = $\frac{mass\ of\ solute}{mass\ of\ solution} \times 100$

Substituting: $12.5 = \frac{mass\ of\ sodium\ chloride}{230} \times 100$

Mass of sodium chloride = $\frac{12.5 \times 230}{100}$ = 28.8 g

3. [OH⁻(aq)] total = [OH⁻(aq)]from water + [OH⁻(aq)]from NaOH
Let [OH– (aq)] from water = p
Then [H_3O + (aq)]from water = p
So at 25°C, p{p + (1.0 × 10⁻⁷)}= 1.0 × 10⁻¹⁴ mol² dm⁻⁶
Solving the quadratic p = 6.2 × 10⁻⁸ mol dm⁻³
pH = –log₁₀[H_3O+(aq)] = –log10[6.2 × 10⁻⁸] = 7.21

4. The most important point here is that sulfuric acid is a covalent liquid; the pH scale refers to aqueous solutions only (water must be present) and is generally used to describe relatively dilute solutions.

5. Molality of a solute = $\frac{amount\ of\ solute\ in\ mol}{mass\ of\ solvent\ in\ kg}$

m(Na_2CO_3) = 106
amount Na_2CO_3 = 5.3/106 = 0.05 mol
Molality = 0.050/0.520= 0.096 mol kg⁻¹

6. Molarity = $\frac{amount\ of\ solute\ in\ mol}{volume\ of\ solution\ in\ dm^3}$
i.e. 0.05 mol in 520 cm³ solution is equivalent to a concentration of 0.05 x 1000/520 mol dm⁻³ or 0.096 mol dm⁻³. The answer is the same as for (1) because of the assumptions made in the question, valid because the solution is dilute.

7. Molality of a solute = $\frac{amount\ of\ solute\ in\ mol}{mass\ of\ solvent\ in\ kg}$

m($CO(NH_2)_2$) = 60
amount $CO(NH_2)_2$ = 0.50/60 = 0.0083 mol
Molality = 0.0083/0.250 = 0.03 mol kg⁻¹