

Solution 2.

The following data has been given:

3000 km² = 3 x 10⁵ ha = 3 x 10⁹ m³ (this number will not be required),
rainfall 850 mm (= 0.850 m), pH = 4.27

66% as H₂SO₄ and 34% as HNO₃

Is there excessive SO₄²⁻ loading compared to a maximum 20 kg ha⁻¹ ?

Volume of rainfall per ha = 10 000 m² x 0.850 m = 8500 m³ = 8.5 x 10⁶ L

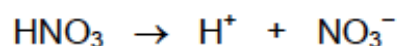
pH = 4.27, ∴ in 1L 5.37 x 10⁻⁵ mol of H⁺.

This H⁺ is derived from both H₂SO₄ and HNO₃



H₂SO₄ provides 2 moles of H⁺

while,



provides only 1 mole of H⁺.

The second proton on H₂SO₄ is not strong (K_a = 1.3 x 10⁻²), but deprotonation of HSO₄⁻ will still contribute a second H⁺ at the pH of 4.27, which is higher than the pK_a value.

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Amount of acid attributed to H₂SO₄: (assuming 1 L for the calculation)

$$0.66 \times 5.37 \times 10^{-5} \text{ mol} = 3.54 \times 10^{-5} \text{ mol of H}^+ \text{ from H}_2\text{SO}_4$$

divide by 2] gives 1.77 x 10⁻⁵ mol of SO₄²⁻ (in 1L)

total sulfate supplied to 1 ha in 1 year (8.5 x 10⁶ L) is then

$$1.77 \times 10^{-5} \text{ mol L}^{-1} \text{ (of SO}_4^{2-}) \times 8.5 \times 10^6 \text{ L} = 150 \text{ mol (of SO}_4^{2-})$$

$$150 \text{ mol (of SO}_4^{2-}) \times 96 \text{ g mol}^{-1} = 1.44 \times 10^4 \text{ g (of SO}_4^{2-})$$

or 14.4 kg (of SO₄²⁻)

The soil is not subject to excessive sulphate loading based on this calculation.

Solution 4.

Summary of data:	Anions:	SO ₄ ²⁻	207 mg m ⁻³	M.W. = 96 g mol ⁻¹
		NO ₃ ⁻	18	= 62
	Cations:	NH ₄ ⁺	385	= 18
		K ⁺	180	= 39
		Na ⁺	247	= 23
(pH = 5.22)		H ⁺	???	= 1

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Assuming volume of 1 m³, the amount in moles of each is calculated by:

$$\text{SO}_4^{2-} \quad 207 \text{ mg} \div 1 \times 10^3 \text{ mg g}^{-1} = 2.07 \times 10^{-1} \text{ g}$$

$$2.07 \times 10^{-1} \text{ g} \div 96 \text{ g mol}^{-1} = 2.156 \times 10^{-3} \text{ mol of SO}_4^{2-}$$

Amount of charge is two times the number of moles to give:

$$4.3 \times 10^{-3} \text{ equivalents of charge from SO}_4^{2-}$$

The others are similarly calculated;

SO ₄ ²⁻ ,	NO ₃ ⁻ ,	NH ₄ ⁺ ,	K ⁺ ,	Na ⁺ ,	H ⁺ (calc. from pH)
4.3 x 10 ⁻³	2.9 x 10 ⁻⁴	2.1 x 10 ⁻²	4.6 x 10 ⁻³	1.1 x 10 ⁻²	6.0 x 10 ⁻³

Total anion (negative charge) concentration is 4.6 x 10⁻³ mol m⁻³.

Total cation (positive charge) concentration is 4.3 x 10⁻³ mol m⁻³,

This type of charge balance is typical for experimental measurements of precipitation chemistry. A large number of other cations and anions could be present in small amounts. Most often other common ions would include Ca²⁺, Mg²⁺, Cl⁻ and OM.

6. The estimated atmospheric carbon dioxide concentration in the Northern Hemisphere in 1950 was 310 ppmv. It may be predicted with some certainty that the concentration in 2010 will be 390 ppmv. Calculate the pH of *pure* rain which would be in equilibrium with the carbon dioxide in each of the two years cited, and comment on the contribution which carbon dioxide makes towards precipitation acidity.

Solution 6.

Assume total pressure is $P^{\circ} = 101\,325\text{ Pa}$ and temperature is 298 K.

The mixing ratios given (in units of ppmv) are also a mole fraction ($\times 10^6$), and therefore, the partial pressure of carbon dioxide is given by:

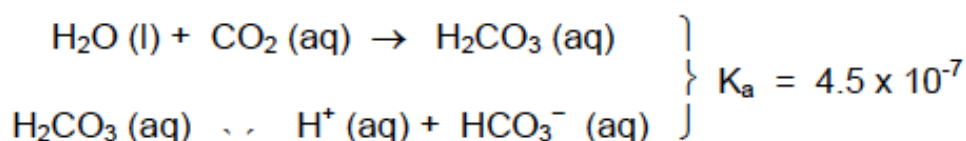
$$310\text{ ppmv CO}_2 = 310 \times 10^{-6} \times 101\,325\text{ Pa} = 31.4\text{ Pa}$$

Henry's Law constant for CO_2 is $3.3 \times 10^{-7}\text{ mol L}^{-1}\text{ Pa}^{-1}$ (Table 11.1, p. 237)

Using Henry's Law : (see p. 237, Chapter 11)

$$[G]_l = K_H P_g$$

$$[\text{CO}_2]_{\text{(aq)}} = 3.3 \times 10^{-7}\text{ mol L}^{-1}\text{ Pa}^{-1} \times 31.4\text{ Pa} = 1.04 \times 10^{-5}\text{ mol L}^{-1}$$



(see p. 241 for complete description of carbon dioxide in water)

$$K_a = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2]} = 4.5 \times 10^{-7}$$

Assume $[\text{CO}_2] = 1.04 \times 10^{-5}\text{ mol L}^{-1}$, and that $[\text{HCO}_3^-] = [\text{H}^+]$

Solve for $[\text{H}^+]$, $[\text{H}^+] = 2.16 \times 10^{-6}$ \therefore pH = 5.67

Repeat the calculation for 370 ppmv: result is pH = 5.63

The increase in CO_2 concentration in the atmosphere from 310 ppmv to 370 ppmv over the fifty year period will cause a very slight (< 0.05 pH units) increase in the pH of *pure* rainfall. This increase is negligible compared to the pH changes from nitrogen and sulphur oxides emitted from anthropogenic sources.

8. Assuming an atmospheric pressure of 83 kPa, an atmospheric mixing ratio of 1.5 ppbv for hydrogen peroxide, and a value of $K_H(\text{H}_2\text{O}_2) = 7.0 \times 10^{-1} \text{ mol L}^{-1} \text{ Pa}^{-1}$, calculate its solubility in the cloud water droplets. Will this concentration depend on pH over the range 5 to 8?

Solution 8.

Assume a temperature of 288 K, and a volume of 1 m^3 for this problem. The total number of moles is therefore approximated by $n_{(\text{total})} = PV / RT$

$$n_{(\text{total})} = 83\,000 \text{ Pa} \times 1 \text{ m}^3 / 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 288 \text{ K} = 34.66 \text{ mol}$$

1.5 ppbv (H_2O_2) needs to be converted to Pa;

$$\frac{x \text{ moles } (\text{H}_2\text{O}_2)}{34.66} \times 10^9 = 1.5 \text{ ppbv}$$

$$\text{moles } (\text{H}_2\text{O}_2) = 5.2 \times 10^{-8}$$

$$\begin{aligned} \text{using } P = nRT/V \quad P \text{ (Pa)} &= 5.2 \times 10^{-8} \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 288 \text{ K} / 1 \text{ m}^3 \\ &= 1.25 \times 10^{-4} \text{ Pa} \end{aligned}$$

$$\text{Using equation 11.2} \quad [\text{H}_2\text{O}_2] = 7.0 \times 10^{-1} \text{ mol L}^{-1} \text{ Pa}^{-1} \times 1.25 \times 10^{-4} \text{ Pa}$$

$$[\text{H}_2\text{O}_2] = 8.7 \times 10^{-5} \text{ mol L}^{-1}$$

The K_a of H_2O_2 is 2.2×10^{-12} ($\text{p}K_a = 11.7$), so it is not expected that the concentration of H_2O_2 will depend on the pH over the range of 5-8.