Using the concept of heat capacity, explain why the dilution of sulfuric acid is carried out by adding acid to water rather than water to acid.

Marks 6

$$H_2SO_4(1)$$
: $C = 1.42 \text{ J g}^{-1} \text{ K}^{-1}$,

$$H_2O(1)$$
: $C = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$

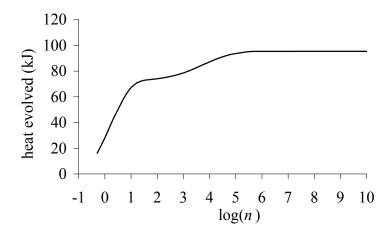
The dilution of sulfuric acid generates 95 kJ mol⁻¹ of heat.

As $q = Cm\Delta T$, the temperature change when a quantity of heat is generated is *inversely* proportional to the heat capacity of the substance.

If water is added to $H_2SO_4(l)$, the *same* quantity of heat generates a much *larger* temperature change than occurs if $H_2SO_4(l)$ is added to water as the heat capacity of $H_2SO_4(l)$ is much *smaller* than that of water.

If water is added to acid, the temperature change is so large so it produces localized boiling of the solution at the surface. This causes the acid to spit out causing potential safety issues.

The figure below shows the heat evolved when one mole of H_2SO_4 is mixed with n moles of H_2O . Explain the shape of curve.



H₂SO₄ is a diprotic acid as it has two acidic protons:

$$H_2SO_4(aq) + H_2O(l) \implies HSO_4^-(aq) + H_3O^+(aq)$$

$$HSO_4^-(aq) + H_2O(l) \iff SO_4^{2-}(aq) + H_3O^+(aq)$$

At normal dilutions levels, $H_2SO_4(aq)$ is completely ionized into SO_4^{2-} . A 1 M solution contains roughly a 1:55 molar ratio of acid: water.

However, in the dilution curve above, the amount of H_2O is initially very low – when $\log(n) = 0$, $n_{\text{water}} = 1$ mol so there is a 1 : 1 molar ratio of acid : water. Low amounts of water lead both equilibria to shift towards the left.

Hence, the curve shows an initial increase in temperature as the first ionization occurs. Increasing the amount of water causes a higher percentage to be ionized and more heat to be generated.

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When $\log(n) \sim 1$, $n_{\text{water}} = 10$ mol. At this point, the first ionization is essentially complete and further dilution up to $\log(n) \sim 3$ generates little extra heat as all the solution contains HSO_4 (aq).

As more water is added, the second ionization begins to occur. Again, addition of more water causes a higher percentage of the HSO₄⁻ to ionize, generating more heat.

When $\log(n) \sim 5$, the second ionization is essentially completely and the solution contains only $\mathrm{SO_4}^{2-}(\mathrm{aq})$. Further addition of water does not cause any additional ionization and no more heat is evolved.