

Marks
8

- Calcium chloride (3.42 g) is completely dissolved in 200 mL of water at 25.00 °C in a 'coffee cup' calorimeter. The temperature of the water after dissolution is 27.95 °C. Calculate the standard enthalpy of solution of CaCl₂ (in kJ mol⁻¹). The heat capacity of water is 4.184 J K⁻¹ g⁻¹. Ignore the heat capacity of the CaCl₂.

As water has a density of 0.997 g mL⁻¹, 200 mL of water corresponds to a mass of:

$$m = \text{density} \times \text{volume} = (0.997 \text{ g mL}^{-1}) \times (200 \text{ mL}) = 199 \text{ g}$$

The temperature change, ΔT , is (27.95 – 25.00) °C = 2.95 °C (or 2.95 K)

The heat change accompanying a change in temperature is given by:

$$q = m \times C \times \Delta T = (199 \text{ g}) \times (4.184 \text{ J K}^{-1} \text{ g}^{-1}) \times (2.95 \text{ K}) = 2460 \text{ J} = 2.46 \text{ kJ.}$$

As the temperature of the water increases, the dissolution is exothermic and hence, $\Delta H = -2.46 \text{ kJ}$.

The formula mass of CaCl₂ is 40.08 (Ca) + (2 × 35.45 (Cl)) g mol⁻¹ = 110.98 g mol⁻¹. Hence, 3.42 g corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{3.42 \text{ g}}{110.98 \text{ g mol}^{-1}} = 0.0308 \text{ mol}$$

If this amount gives rise to an heat change of 2.46 kJ, the molar enthalpy change is given by $\frac{-2.46 \text{ kJ}}{0.0308 \text{ mol}} = -79.9 \text{ kJ mol}^{-1}$

Answer: -79.9 kJ mol⁻¹

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What would be the vapour pressure of water above this solution?
($P^0(\text{H}_2\text{O}) = 3.17 \text{ kPa}$)

According to Raoult's Law, the vapour pressure of pure solvent, P_{solvent}^0 is lowered by the presence of solute by an amount ΔP :

$$\Delta P = i \times X_{\text{solute}} \times P_{\text{solvent}}^0$$

where X_{solute} is the mole fraction of the solute and i is the amount (mol) of particles in solution divided by the amount (mol) of dissolved solute.

The molar mass of H_2O is $(2 \times 1.008 \text{ (H)}) + 16.00 \text{ (O)} \text{ g mol}^{-1} = 18.016 \text{ g mol}^{-1}$ so the number of moles of water in 199 g is:

$$\text{moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{199 \text{ g}}{18.016 \text{ g mol}^{-1}} = 36.0 \text{ mol}$$

As the solution contains 0.0308 mol of CaCl_2 , the mole fraction of the solute is:

$$X_{\text{solute}} = \frac{\text{moles of solute}}{\text{moles of solute} + \text{moles of solvent}} = \frac{0.0308}{(0.0308 + 36.0)} = 8.55 \times 10^{-4}$$

CaCl_2 dissolves to give three particles, $\text{Ca}^{2+} + 2\text{Cl}^-$, so $i = 3$. Thus,

$$\Delta P = i \times X_{\text{solute}} \times P_{\text{solvent}}^0 = 3 \times (8.55 \times 10^{-4}) \times 3.17 \text{ kPa} = 8.14 \times 10^{-3} \text{ kPa}$$

The vapour pressure is lowered to $(3.17 - 8.14 \times 10^{-3}) \text{ kPa} = 3.16 \text{ kPa}$.

Answer: 3.16 kPa

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What would be the freezing point of this solution? The molal freezing point depression constant (K_f) for water is $1.86\text{ }^\circ\text{C kg mol}^{-1}$.

From above, **0.0308 mol of CaCl_2 are dissolved in 199 g of water. The molality is:**

$$\text{molality} = \frac{\text{number of moles of solute (mol)}}{\text{mass of solvent (kg)}} = \frac{0.0308 \text{ mol}}{(199 \times 10^{-3} \text{ kg})} = 0.155 \text{ mol kg}^{-1}$$

The freezing point depression, ΔT_f , is given by:

$$\Delta T_f = i \times K_f m$$

where K_f is the molal freezing point depression constant and m is the molality. As $i = 3$,

$$\Delta T_f = i \times K_f m = 3 \times (1.86\text{ }^\circ\text{C kg mol}^{-1}) \times (0.155 \text{ mol kg}^{-1}) = 0.865\text{ }^\circ\text{C}$$

At atmospheric pressure, the water freezes at $0\text{ }^\circ\text{C}$. The solution will freeze at **$-0.865\text{ }^\circ\text{C}$** .

Answer: **$-0.865\text{ }^\circ\text{C}$**

Which would you expect to cause the greater freezing point depression of water, 3.42 g of CaCl_2 or 3.42 g of NaCl ? Explain your answer.

The formula mass of NaCl is $22.99\text{ (Na)} + 35.43\text{ (Cl)}\text{ g mol}^{-1} = 58.42\text{ g mol}^{-1}$. The number of moles of NaCl is therefore:

$$\text{number of moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{3.42 \text{ g}}{58.42 \text{ g mol}^{-1}} = 0.0585 \text{ mol}$$

NaCl dissolves to give two particles, $\text{Na}^+ + \text{Cl}^-$ so $i = 2$.

As $\Delta T_f = i \times K_f m$, the freezing point depression of x kg of water is given by:

$$\Delta T_f = i \times K_f m = i \times K_f \times \frac{\text{moles of solute}}{x}$$

$$\text{For NaCl, } \Delta T_f = 2 \times K_f \times \frac{0.0585}{x}. \text{ For CaCl}_2, \Delta T_f = 3 \times K_f \times \frac{0.0308}{x}.$$

Hence, $\Delta T_f \propto 0.117$ for NaCl and $\Delta T_f \propto 0.0924$ for CaCl_2 . The freezing point depression is larger for NaCl .