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Topic 6.10: Enthalpy of Solution

Revision Notes · AP Chemistry

UNIT 6 · THERMOCHEMISTRY

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What Enthalpy of Solution Means

When a solid dissolves in water, energy is exchanged with the surroundings. The enthalpy of solution, ΔHsol, is the enthalpy change when one mole of a solute dissolves in enough solvent to form a dilute solution. The system is the dissolving solute; the surroundings are the water and the beaker. If the solution warms up, heat flowed from the system into the surroundings. If it cools down, heat flowed the other way.

For sodium chloride:

$NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$

The value of ΔHsol for this change is +3.9 kJ/mol, so the solution cools very slightly.

Measuring ΔHsol

ΔHsol is measured in a calorimeter. A known mass of solute is dissolved in a known mass of water, and the temperature change is recorded. The heat exchanged is found from the calorimetry equation:

$q = mc\Delta T$

with $c = 4.18\ J\ g^{-1}\ °C^{-1}$ for water. Dividing by moles gives ΔHsol per mole.

The Sign of ΔHsol Belongs to the System

Enthalpy change is defined from the system's point of view.

$\Delta H_{sol} = H(products) - H(reactants)$

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Endothermic dissolving: the system absorbs heat, the aqueous ions sit higher in enthalpy than the solid, and ΔHsol is positive. A salt with ΔHsol = +34.9 kJ/mol absorbs 34.9 kJ for every mole that dissolves. Exothermic dissolving: the system releases heat, the aqueous ions sit lower in enthalpy than the solid, and ΔHsol is negative. A salt with ΔHsol = −44.5 kJ/mol releases 44.5 kJ for every mole that dissolves.

Exothermic Dissolving: Hot Packs and Warm Beakers

Some salts release heat when they dissolve. Sodium hydroxide is the classic example, with ΔHsol = −44.5 kJ/mol. Dissolving it in water warms the solution sharply, and the beaker feels hot.

Anhydrous calcium chloride has ΔHsol = −81.3 kJ/mol, so it warms strongly, which is why it is used in hot packs and de-icing products. Magnesium sulfate is warmer still, with ΔHsol = −91.2 kJ/mol. For these salts, the energy released when water molecules surround the ions is larger than the energy needed to break the lattice apart, so the surplus leaves the system as heat.

Endothermic Dissolving: Cold Packs and Falling Temperatures

Other salts absorb heat when they dissolve. Potassium nitrate has ΔHsol = +34.9 kJ/mol, and ammonium nitrate has ΔHsol = +25.7 kJ/mol. Dissolving ammonium nitrate cools the solution, which is exactly how a cold pack works: squeezing the pack mixes the salt with water, the dissolving absorbs heat from the surroundings, and the pack turns cold against the skin.

Why the Solution Cools

For these salts, breaking the lattice apart costs more energy than hydration releases. The shortfall is taken from the surroundings, so the measured temperature falls. The solution feels cold because it holds less energy than before.

Lattice Enthalpy and Hydration Enthalpy

Dissolving an ionic solid happens in two conceptual steps. First, the crystal lattice is broken apart into separate gaseous ions. This step is called the lattice enthalpy, and it always costs energy, so it is always positive. Second, the gaseous ions are surrounded by water molecules. This step is called the hydration enthalpy, and it always releases energy, so it is always negative. Forming attractions releases energy.

Adding the Two Steps

Because enthalpy is a state function, the enthalpy of solution is the sum of the two steps:

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$\Delta H_{sol} = \Delta H_{lattice} + \Delta H_{hydration}$

This is Hess's law applied to dissolving, so the sum gives the measured ΔH_{sol}.

Which Step Wins

Whether dissolving is exothermic or endothermic depends on which step wins. For sodium hydroxide, the lattice enthalpy is +900 kJ/mol and the hydration enthalpy is −944 kJ/mol, so the sum is −44 kJ/mol and the solution warms. For potassium chloride, the lattice enthalpy is +717 kJ/mol and the hydration enthalpy is −700 kJ/mol, so the sum is +17 kJ/mol and the solution cools.

Temperature and Solubility

The solubility of a solid is the maximum mass that dissolves in a given mass of solvent at a given temperature. For most solids, solubility increases as the temperature rises. Potassium nitrate is the dramatic example: 13.3 g dissolve in 100 g of water at 0 °C, 31.6 g at 20 °C, 63.9 g at 40 °C, and 110 g at 60 °C. Dissolving potassium nitrate is endothermic, so heat acts like a reactant: raising the temperature pushes the dissolving forward, and more solid dissolves. This is Le Chatelier's principle applied to a dissolving equilibrium.

When Solubility Falls with Temperature

A few solids become less soluble as the temperature rises. Calcium hydroxide is the standard example: 0.173 g dissolve in 100 g of water at 20 °C, but only 0.077 g at 60 °C. Its dissolving is exothermic, with $\Delta H_{sol} = -16.7$ kJ/mol, so heat acts like a product, and raising the temperature pushes the dissolving backwards.

The Qualitative Rule

If dissolving is endothermic, solubility increases with temperature. If dissolving is exothermic, solubility decreases with temperature. If ΔH_{sol} is close to zero, solubility barely changes with temperature.

Worked Examples

> **Example 1: Sodium hydroxide warms the water. Dissolving 4.00 g of sodium hydroxide (0.100 mol) in water releases 4.45 kJ of heat. Per mole, $\Delta H_{sol} = 4.45 \div 0.100 = 44.5$ kJ/mol, and the sign is negative because the system released the heat, so $\Delta H_{sol} = -44.5$ kJ/mol. The surroundings gain 4.45 kJ and the temperature rises.**

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Example 2: Potassium nitrate cools the water. Dissolving 10.11 g of potassium nitrate (0.100 mol) in 100 g of water absorbs 3.49 kJ of heat. Per mole, ΔHsol = 3.49 ÷ 0.100 = +34.9 kJ/mol, positive because the system gained the energy. The water loses 3,490 J, so its temperature falls by 3,490 ÷ (100 × 4.18) = 3,490 ÷ 418 = 8.35 °C.

Example 3: Adding lattice and hydration enthalpies. For sodium chloride, the lattice enthalpy is +787 kJ/mol and the hydration enthalpy is −783 kJ/mol. Adding the two steps gives ΔHsol = +787 + (−783) = +4 kJ/mol. This matches the measured ΔHsol of +3.9 kJ/mol within rounding.

Example 4: Predicting a temperature rise. Dissolving 11.10 g of anhydrous calcium chloride (0.100 mol) in 100 g of water releases 0.100 × 81.3 = 8.13 kJ of heat, which is 8,130 J. The water gains that heat, so its temperature rises by 8,130 ÷ (100 × 4.18) = 8,130 ÷ 418 = 19.45 °C.

Traps That Cost Marks in Topic 6.10

"ΔHsol is positive, so the solution warms up." A positive ΔHsol means the system absorbs heat, so the surroundings lose heat and cool down. The sign is read from the system's side, and the temperature change you feel is the surroundings' side.

"The lattice enthalpy is negative because the lattice breaks apart." Breaking a lattice costs energy, so the lattice enthalpy is always positive. It is the hydration step, forming attractions between water and ions, that is always negative.

"ΔHsol is the lattice enthalpy." ΔHsol is the sum of the lattice enthalpy and the hydration enthalpy. Using the lattice value alone gives a large positive number and the wrong sign for salts like sodium hydroxide.

"All salts become more soluble when heated." Most do, but exothermic dissolvers do the opposite. Calcium hydroxide becomes less soluble as the temperature rises. Always check the sign of ΔHsol before predicting the temperature effect.

"Doubling the mass dissolved doubles ΔHsol." Doubling the mass doubles the heat exchanged, but ΔHsol in kJ/mol stays the same, because it is defined per mole.

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Key Relationships to Remember

- ΔHsol is the enthalpy change when one mole of solute dissolves to form a dilute solution, reported from the system's point of view
- Endothermic dissolving: ΔHsol positive, system absorbs heat, surroundings cool, solubility increases with temperature
- Exothermic dissolving: ΔHsol negative, system releases heat, surroundings warm, solubility decreases with temperature
- ΔHsol = ΔHlattice + ΔHhydration, a Hess's law cycle for dissolving
- Lattice enthalpy is always positive, because separating ions against their attractions costs energy
- Hydration enthalpy is always negative, because water molecules form attractions with the ions
- Small, highly charged ions are hydrated most strongly, so their salts often have strongly negative ΔHsol values
- A ΔHsol close to zero means temperature has almost no effect on solubility, as with sodium chloride
- Doubling the amount dissolved doubles the heat exchanged, but ΔHsol in kJ/mol is unchanged

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