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Topic 6.1: Endothermic and Exothermic Processes

Revision Notes · AP Chemistry

UNIT 6 · THERMOCHEMISTRY

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The System, the Surroundings and the Boundary

Every energy question in this unit starts by drawing an imaginary boundary. The system is the part under study: usually the reactants and products of one reaction, or the substance melting, dissolving or evaporating.

The surroundings are everything else that can exchange energy with the system: the solvent, the container, the thermometer, the air, and your hand on the beaker.

In a coffee-cup calorimetry experiment the system is the reacting chemicals only. The water, the cup and lid, the thermometer and the stirrer all belong to the surroundings, because they are what absorb or supply the heat the reaction exchanges.

The labels matter because every sign and every temperature reading in this unit is reported from one side of that boundary or the other.

Heat Flows One Way or the Other

Heat is energy transferred between the system and the surroundings because of a temperature difference. It is not something a substance contains; it exists only while energy is crossing the boundary.

An endothermic process absorbs heat from the surroundings. Energy flows into the system, the system gains energy, and the surroundings lose energy and cool down.

An exothermic process releases heat to the surroundings. Energy flows out of the system, the system loses energy, and the surroundings gain energy and warm up.

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What your hand feels always reports the surroundings. A beaker that feels cold is losing heat to the process inside it, so the process is endothermic. A flask that feels hot has received heat from the process inside it, so the process is exothermic.

Dissolving ammonium nitrate in water is endothermic: the solution draws heat from the beaker and from your hand, which is exactly how a cold pack works.

The Sign of ΔH Belongs to the System

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

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

Every sign in this unit follows from that one choice of viewpoint.

Endothermic: the system gains enthalpy, products sit higher than reactants, and ΔH is positive. A process with ΔH = +45 kJ/mol absorbs 45 kJ for every mole that reacts.

Exothermic: the system loses enthalpy, products sit lower than reactants, and ΔH is negative. A reaction that gives off 120 kJ of heat per mole has ΔH = −120 kJ/mol, because the system's enthalpy fell by that amount.

On an enthalpy diagram the same story is drawn: the product level below the reactant level means exothermic, the product level above means endothermic, and the vertical gap between the levels is ΔH.

Energy is still conserved in both cases. Conservation applies to system and surroundings together: whatever enthalpy the system loses, the surroundings gain, and the two changes cancel. ΔH is not zero, because ΔH describes the system alone.

Where the Energy Goes: Attractions and Particle Motion

At particle level, an exothermic process converts stored chemical potential energy into kinetic energy of the surroundings' particles, which is why their temperature rises.

Forming attractions releases energy; separating particles against their attractions costs energy. Combustion is exothermic because the strong new bonds formed in CO_2 and H_2O release more energy than breaking the reactant bonds cost.

Phase changes involve intermolecular attractions, not chemical bonds. Melting, evaporating and subliming all pull particles apart against their attractions, so all three are endothermic.

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Freezing, condensing and depositing bring particles together and form attractions, so all three are exothermic. Water vapour condensing on a mirror releases heat for exactly this reason.

Photosynthesis is endothermic: plants store energy from sunlight in glucose. Respiration, the reverse process, is exothermic and releases that stored energy.

Heat Is Not Temperature

Heat is an amount of energy, measured in joules or kilojoules. Temperature is not an amount of energy at all: it measures the average kinetic energy of the particles.

The same quantity of heat therefore produces different temperature changes in different amounts of material. Heat released into a small volume of water raises its temperature far more than the same heat released into a large volume, because the energy is shared among fewer particles.

A temperature reading also belongs to whatever the thermometer touches. In calorimetry the thermometer sits in the surroundings, so a rising temperature shows heat arriving in the surroundings, which means the system released it: the reaction is exothermic.

Worked Examples

Example 1: Reading an enthalpy diagram. A reaction has reactants at 180 kJ/mol and products at 60 kJ/mol. From the system's point of view, $\Delta H = 60 - 180 = -120$ kJ/mol. The negative sign classifies the reaction as exothermic: the system loses 120 kJ per mole and the surroundings gain 120 kJ per mole. The reverse reaction has $\Delta H = +120$ kJ/mol and is endothermic.

Example 2: The cold pack, with numbers. Dissolving 8.0 g of ammonium nitrate (0.100 mol) in water absorbs 2.6 kJ of heat. Per mole, $\Delta H = 2.6 \div 0.100 = +26$ kJ/mol, positive because the system gained the energy. The ledger balances: the system gains 2.6 kJ, the surroundings (solution, beaker, hand) lose 2.6 kJ, and the total change is zero. The surroundings lost kinetic energy, so the solution's temperature falls and the pack feels cold.

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Example 3: Melting against freezing. Melting 1 mol of ice absorbs 6.01 kJ, so ΔH = +6.01 kJ/mol from the system's point of view, and melting 3 mol absorbs 3 × 6.01 = 18.03 kJ. Freezing is the exact reverse: freezing 5.0 mol of water releases 5.0 × 6.01 = 30.05 kJ, so ΔH = −6.01 kJ/mol. Reverse processes always carry opposite signs and equal sizes.

Example 4: Neutralisation warming the solution. Mixing HCl and NaOH solutions reacts with ΔH = −57 kJ/mol, from the system's point of view. If 0.20 mol reacts, the system loses 0.20 × 57 = 11.4 kJ. That 11.4 kJ arrives in the solution, the surroundings, whose particles gain kinetic energy, so the measured temperature rises. A temperature rise in the surroundings is the signature of an exothermic system.

Traps That Cost Marks in Topic 6.1

"The products feel hot, so the reaction is endothermic." Hot surroundings mean heat flowed out of the system into them. That is the definition of exothermic; the student's conclusion reverses the evidence.

"ΔH is positive because heat was released." The sign is read from the system's side of the boundary. Released heat means the system lost enthalpy, so ΔH is negative.

"Energy is conserved, so ΔH must be zero." Conservation covers system plus surroundings. Each side can gain or lose a large amount, provided the two changes cancel.

"A cold pack makes cold." Nothing is cooled by adding "cold". The dissolving process absorbs heat from the skin, and the skin feels cold because it lost energy.

"Melting breaks attractions, so it releases energy." Breaking and separating always costs energy. Forming attractions is the direction that releases energy, which is why freezing and condensing are exothermic.

"The system in calorimetry is the cup and the water." The system is the reaction being studied. The cup, water and thermometer are the surroundings that measure the heat the system exchanged.

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Key Relationships to Remember

- System: the reactants and products under study; surroundings: everything else, including solvent, container and thermometer
- Heat: energy transferred across the boundary because of a temperature difference; temperature: average kinetic energy of the particles
- Endothermic: system absorbs heat, surroundings cool, ΔH positive, products higher in enthalpy than reactants
- Exothermic: system releases heat, surroundings warm, ΔH negative, products lower in enthalpy than reactants
- ΔH is always reported from the system's point of view; the surroundings show the opposite change of the same size
- Separating particles against attractions (melting, evaporating, subliming) is endothermic; forming attractions (freezing, condensing, depositing) is exothermic
- Reverse processes have ΔH values of equal size and opposite sign
- A cold container signals an endothermic process inside it; a hot container signals an exothermic process inside it

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