Thermogravimetric Analysis and Calorimetry (Mexico)

Unidad de Calorimetría Avanzada

Adiabatic Calorimetry – Related terms: heat flow, thermal insulation.
A technique where the sample is thermally isolated so that no heat is exchanged with the surroundings. The measured temperature rise directly reflects the heat released or absorbed by the reaction. In the Unidad de Calorimetría Avanzada, adiabatic calorimetry is used to determine reaction enthalpies of polymer degradation without the influence of external cooling. Example: measuring the exothermic cure of an epoxy resin in a sealed calorimetric cell. Practical application includes safety assessment of energetic materials. A key challenge is achieving true adiabatic conditions; any residual heat leak can lead to systematic under-estimation of the enthalpy.

Baseline Drift – Related terms: instrumental noise, signal correction.
A slow change in the detector output that is unrelated to the sample's thermal events. It can arise from temperature gradients in the reference arm, sensor aging, or ambient fluctuations. In advanced calorimetry, baseline drift is corrected by recording a blank run under identical conditions and subtracting the resulting curve. Example: a gradual upward shift observed during a 2 h isothermal hold. Proper correction improves the accuracy of peak integration. The main difficulty lies in distinguishing genuine low-intensity reactions from drift, especially when the drift pattern is non-linear.

Calibration Curve – Related terms: standard material, heat of fusion.
A plot that relates the measured calorimetric signal to a known quantity of heat, typically obtained using reference substances with well-documented enthalpies (e.g., indium, zinc). The curve is essential for converting raw voltage or current data into absolute energy units (J). In the Unidad, students generate calibration curves before each batch of experiments to account for sensor sensitivity changes. Example: plotting peak area versus enthalpy of melting for indium at 156 °C. Calibration accuracy directly influences quantitative heat flow results; errors in the curve propagate to all subsequent measurements.

Differential Scanning Calorimetry (DSC) – Related terms: heat flow, thermal transition.
A widely used technique that measures the difference in heat flow between a sample and an inert reference as both are subjected to a programmed temperature program. DSC provides information on melting points, glass transitions, crystallization, and curing reactions. Within the advanced calorimetry unit, DSC is coupled with thermogravimetric analysis to correlate mass loss with thermal events. Example: detecting the glass transition of poly(methyl methacrylate) at 105 °C while simultaneously measuring its weight change. Challenges include baseline stability at high heating rates and ensuring the reference remains truly inert.

Enthalpy of Reaction – Related terms: ΔH, exothermic, endothermic.
The total heat released or absorbed when a chemical reaction proceeds from reactants to products at constant pressure. Calorimetric measurements provide a direct experimental determination of ΔH. In the Unidad, students calculate the enthalpy of polymer degradation by integrating the heat flow signal over the temperature range where mass loss occurs. Example: a $150\,\mathrm{J\,g^{-1}}$ exotherm observed during the oxidative

breakdown of polyethylene. Accurate determination requires proper baseline correction, calibration, and accounting for heat of vaporization of evolved gases.

Furnace Temperature – Related terms: set point, temperature uniformity.
The nominal temperature programmed into the calorimetric furnace. It dictates the thermal environment experienced by the sample. Precise control of furnace temperature is critical for reproducible kinetic studies. In the advanced unit, a dual-zone furnace provides independent regulation of the sample and reference compartments, minimizing temperature lag. Example: setting a linear heating rate of 10 °C min^{-1} from 30 °C to 600 °C. Temperature gradients across the sample can cause non-uniform heating, leading to broadened peaks and erroneous kinetic parameters.

Heat Capacity (Cp) – Related terms: specific heat, thermal inertia.
The amount of heat required to raise the temperature of a unit mass of a material by one degree at constant pressure. Calorimetry can determine Cp by measuring the heat flow required to produce a known temperature ramp. In the Unidad, Cp values are obtained for both the sample and reference to correct for differences in thermal inertia. Example: measuring Cp of a glassy polymer near its Tg to assess the change in molecular mobility. Determining Cp at high temperatures is challenging due to radiative heat losses and instrument drift.

Isothermal Titration Calorimetry (ITC) – Related terms: binding constant, enthalpy of binding.
A technique that measures the heat released or absorbed during successive injections of a titrant into a sample solution held at constant temperature. ITC yields thermodynamic parameters of molecular interactions (ΔG, ΔH, ΔS, Kd). Although not the primary focus of the thermogravimetric module, the Unidad introduces ITC to illustrate complementary calorimetric methods. Example: determining the binding enthalpy of a small-molecule inhibitor to a protein. Limitations include the need for high-purity reagents and the difficulty of measuring very weak or very strong interactions due to signal-to-noise constraints.

Kinetic Analysis – Related terms: reaction order, activation energy.
The quantitative evaluation of the rate at which a thermal event proceeds, often expressed through Arrhenius parameters. In advanced calorimetry, kinetic analysis combines DSC/TGA data with model-free methods (e.g., Flynn-Wall–Ozawa, Kissinger) to extract activation energies without assuming a reaction mechanism. Example: applying the Kissinger method to the exothermic peak of a polyester cure to obtain an activation energy of 85 kJ mol^{-1}. Challenges include overlapping reactions, heat transfer limitations, and the need for multiple heating rates to achieve reliable parameter estimation.

Linear Heating Rate – Related terms: ramp rate, temperature program.
The constant rate at which temperature is increased during a DSC or TGA experiment, expressed in °C min^{-1}. A linear heating rate simplifies kinetic analysis and allows direct comparison between experiments. In the Unidad, students explore heating rates from 1 °C min^{-1} to 40 °C min^{-1} to study their impact on peak temperature and shape. Example: a 10 °C min^{-1} ramp shifts the decomposition peak of a cellulose sample from 320 °C to 340 °C. High heating rates can induce thermal lag, leading to apparent kinetic parameters that deviate from intrinsic values.

Mass Loss Curve – Related terms: thermogravimetric trace, derivative TG (DTG).

The plot of sample weight versus temperature or time obtained from TGA. The curve reveals the temperatures at which volatiles evolve, decomposition occurs, or residual ash remains. In the advanced unit, the mass loss curve is synchronized with DSC heat flow to assign enthalpic events to specific mass changes. Example: a two-step loss for a polymer blend, first at 250 °C (solvent evaporation) and second at 420 °C (polymer backbone degradation). Accurate baseline subtraction and buoyancy correction are essential for quantitative mass loss determination.

Non-Isothermal Conditions – Related terms: dynamic heating, temperature ramp.
Experimental situations where temperature changes continuously, as opposed to isothermal holds. Most DSC/TGA experiments are non-isothermal, enabling rapid screening of thermal stability. The Unidad emphasizes non-isothermal kinetic methods to extract activation energies from a single heating rate series. Example: analyzing the shift of a degradation peak with increasing heating rates to construct an Ozawa plot. The main difficulty is separating kinetic effects from heat transfer artifacts, especially at high rates.

Oxidative Degradation – Related terms: combustion, air atmosphere.
The breakdown of a material in the presence of oxygen, typically leading to exothermic heat release and mass loss. Oxidative degradation is investigated by performing DSC/TGA under flowing air or oxygen. In the Unidad, students compare inert-nitrogen and oxidative runs for a polymer to assess its fire-retardant performance. Example: a sharp exotherm at 380 °C in air, accompanied by a rapid mass loss due to CO_2 evolution. Controlling oxygen partial pressure and flow rate is critical; excessive flow can cause convective cooling, altering the observed kinetics.

Peak Integration – Related terms: area under curve, enthalpy calculation.
The quantitative process of measuring the area encompassed by a thermal event on a DSC trace, which corresponds to the heat exchanged. Accurate integration requires a well-defined baseline and correction for overlapping peaks. In the advanced unit, software tools perform numerical integration, but students are taught manual methods for verification. Example: integrating the melting peak of a metal alloy to obtain a latent heat of $210\,\mathrm{J\,g^{-1}}$. Integration errors may arise from baseline drift, peak asymmetry, or insufficient data points at high heating rates.

Quantitative Heat Flow – Related terms: heat rate, calorimetric sensitivity.
The calibrated measurement of heat entering or leaving the sample, expressed in watts (W) or milliwatts (mW). Quantitative heat flow enables determination of reaction rates, heat capacities, and enthalpies. The Unidad employs high-resolution heat flow sensors capable of detecting micro-joule changes. Example: a 0.5 mW heat flow signal during the glass transition of a polymer indicates a subtle change in molecular mobility. Achieving quantitative heat flow requires meticulous calibration, stable baseline, and correction for instrument response time.

Reference Sample – Related terms: inert pan, baseline.
A material placed in the reference cell of a DSC, typically an empty crucible or a non-reactive standard, used to generate the baseline against which the sample's heat flow is compared. The choice of reference influences baseline stability; a mismatched mass or thermal mass can introduce systematic errors. In the Unidad, identical crucibles are used for both sample and reference, and the reference is often loaded with an inert filler (e.g., alumina) to match the sample's heat capacity. Example: using a blank alumina pan when

measuring the heat flow of a ceramic powder. Ensuring identical thermal contact and geometry between sample and reference is a frequent source of experimental difficulty.

Specific Heat – Related terms: heat capacity per mass, Cp.
The amount of heat required to raise the temperature of one gram of a substance by one degree Celsius at constant pressure. Specific heat is derived from calorimetric measurements by dividing the measured heat flow by the mass and temperature change rate. In the advanced unit, specific heat data are collected for polymers, composites, and inorganic fillers to support composite design calculations. Example: a specific heat of $1.2\,\mathrm{J\,g^{-1}\,K^{-1}}$ for a silica-filled epoxy resin. Determination at elevated temperatures can be confounded by simultaneous decomposition, requiring careful selection of the temperature window.

Thermal Lag – Related terms: temperature gradient, response time.
The delay between the programmed furnace temperature and the actual temperature experienced by the sample. Thermal lag becomes significant at high heating rates or when the sample has low thermal conductivity. It leads to apparent shifts in peak temperatures and can distort kinetic parameters. In the Unidad, a dual-sensor configuration (thermocouple embedded near the sample) is used to monitor the true sample temperature and correct for lag. Example: a 5 °C lag observed at a $20\,\mathrm{°C\,min^{-1}}$ heating rate for a dense ceramic pellet. Mitigating lag involves optimizing sample size, improving thermal contact, and using appropriate heating rates.

Thermogravimetric Analysis (TGA) – Related terms: mass loss, derivative TG (DTG).
A technique that measures the change in weight of a sample as it is heated, cooled, or held isothermally under a controlled atmosphere. TGA provides information on decomposition temperatures, moisture content, and residue composition. In the Unidad, TGA is often coupled with DSC (simultaneous TGA–DSC) to correlate mass loss with enthalpic events. Example: a single-step mass loss of 85 % between 300 °C and 500 °C for a polyester, accompanied by an exothermic peak in the DSC trace. Challenges include buoyancy corrections for gaseous atmospheres and ensuring uniform heating of the sample.

Universal Calorimeter – Related terms: multifunctional, modular design.
A calorimetric instrument capable of performing a range of thermal analyses, including DSC, TGA, and modulated DSC, within a single platform. The Unidad employs a universal calorimeter with interchangeable sample holders, allowing rapid switching between mass-loss and heat-flow measurements. Example: using the same instrument to assess the curing exotherm of a resin and then its residual mass after complete degradation. The versatility simplifies laboratory logistics but requires careful validation of each mode to avoid cross-contamination of calibration factors.

Vaporization Enthalpy – Related terms: heat of vaporization, latent heat.
The heat required to convert a liquid or solid into vapor at a given temperature and pressure. In calorimetry, vaporization enthalpy appears as an endothermic event that may overlap with decomposition peaks. The Unidad teaches students to separate vaporization from chemical reactions by performing experiments under inert atmosphere and by employing modulated DSC techniques. Example: measuring the enthalpy of water loss from a hydrated mineral at 150 °C ($\approx 44\,\mathrm{kJ\,mol^{-1}}$). Accurate determination demands precise baseline subtraction and consideration of the mass loss associated with vapor release.

Zero-Order Kinetics – Related terms: constant rate, reaction mechanism.
A kinetic model where the reaction rate is independent of the concentration of reactants, leading to a linear mass loss or heat flow with time. In thermal analysis, zero-order behavior is identified when the derivative TG (DTG) curve shows a constant plateau. In the Unidad, students encounter zero-order degradation for certain polymer additives that decompose at a fixed rate due to surface-limited processes. Example: a constant mass loss of 0.02 % s^{-1} observed for a plasticizer over a 30 min isothermal hold. Distinguishing true zero-order kinetics from instrument-limited artifacts requires multiple experiments at varying temperatures.

Activation Energy (Ea) – Related terms: Arrhenius plot, temperature dependence.
The minimum energy barrier that must be overcome for a reaction to proceed. It is extracted from the temperature dependence of reaction rates using the Arrhenius equation. In advanced calorimetry, Ea is obtained from DSC peak shift data across several heating rates or from isoconversion methods. Example: an Ea of 120 kJ mol^{-1} calculated for the oxidative degradation of a polyolefin using the Kissinger method. Accurate Ea determination requires high-quality data, proper baseline correction, and awareness of possible multiple overlapping reactions that can bias the slope of the Arrhenius plot.

Baseline Correction – Related terms: signal offset, reference subtraction.
The process of adjusting raw calorimetric data to remove systematic deviations unrelated to the sample's thermal events. Baseline correction may involve fitting a polynomial to sections of the curve that are free of transitions and subtracting it from the entire dataset. In the Unidad, students practice both manual and automated baseline correction to improve reproducibility. Example: applying a linear baseline between 30 °C and 100 °C to isolate a low-temperature glass transition. Over-correction can erase genuine small-scale events, while under-correction leaves residual drift that inflates integrated enthalpy values.

Conductivity Sensor – Related terms: thermal conductivity, heat flux.
A component of some DSC instruments that measures the rate of heat transfer through the sample, providing a direct heat-flux signal rather than a temperature difference. Conductivity sensors enable faster response times and are advantageous for high-rate experiments. In the Unidad, a heat-flux sensor is used for modulated DSC to separate reversible (heat capacity) and non-reversible (kinetic) contributions. Example: detecting a subtle exotherm superimposed on a large endothermic melting peak. Sensor calibration against known standards is essential; otherwise, absolute heat flow values may be inaccurate.

Decomposition Temperature (Td) – Related terms: onset temperature, thermal stability.
The temperature at which a material begins to chemically break down, often identified as the point where the mass loss curve deviates from the baseline. Td is a key indicator of material performance under thermal stress. In the advanced unit, Td is determined from both TGA (mass loss) and DSC (exothermic peak) to provide complementary perspectives. Example: a Td of 380 °C for a polycarbonate, corresponding to the onset of a sharp exothermic reaction in the DSC trace. Accurate Td measurement requires consistent heating rates and well-controlled atmosphere, as oxygen presence can lower the apparent Td.

Enthalpy Calibration – Related terms: reference material, heat of fusion.
The procedure of establishing the relationship between the calorimeter's output signal and the known enthalpy of a calibration standard. This calibration enables conversion of peak areas into absolute energy values. In the Unidad, indium ($\Delta H = 28.45\,J\,g^{-1}$) and zinc ($\Delta H = 7.23\,J\,g^{-1}$) are frequently used because of their

sharp, well-characterized melting peaks. Example: a calibration factor of 0.015 mW s J^{-1} derived from the indium peak. Calibration must be repeated after any change in sensor or sample holder, as even minor alterations can affect sensitivity.

Fourier Transform Infrared (FT-IR) Coupled Calorimetry – Related terms: spectroscopic monitoring, simultaneous analysis.
An advanced technique that combines calorimetric measurement with FT-IR spectroscopy to monitor the chemical evolution of a sample in real time. In the Unidad, FT-IR is used to identify gaseous products released during TGA runs, while the calorimeter records the associated heat flow. Example: detecting CO_2 bands at 2350 cm^{-1} during the oxidative degradation of a polymer, coinciding with an exothermic peak. This dual approach provides mechanistic insight but introduces complexities such as aligning time scales, managing spectral baseline, and ensuring that the IR cell does not alter the thermal environment.

Glass Transition Temperature (Tg) – Related terms: viscous flow, amorphous polymers.
The temperature range over which an amorphous material transitions from a rigid, glassy state to a more flexible, rubbery state. In DSC, Tg appears as a step change in heat capacity rather than a peak. The Unidad teaches students to locate Tg by extrapolating the baseline before and after the step. Example: a Tg of 115 °C for a poly(vinyl acetate) sample, identified by a 0.025 J g^{-1} K^{-1} increase in Cp. Accurate Tg determination can be hindered by overlapping relaxation processes, low signal-to-noise ratios, or insufficient temperature resolution.

Heat Flow Sensor – Related terms: thermopile, Seebeck effect.
A device that converts temperature differences into an electrical voltage, often based on a series of thermocouples (thermopile). The sensor output is proportional to the heat flow between the sample and reference. In the advanced calorimeter, a high-sensitivity heat-flow sensor enables detection of micro-joule events. Example: a 0.2 mW heat flow signal associated with the crystallization of a low-density polyethylene sample. Calibration and temperature compensation are critical; sensor drift can introduce systematic errors in quantitative heat flow measurements.

Isoconversion Method – Related terms: fractional conversion, model-free analysis.
A kinetic approach that evaluates the temperature at which a fixed degree of conversion (α) occurs across different heating rates, allowing extraction of activation energy without assuming a reaction model. In the Unidad, students plot ln(β) versus 1/Tα for several α values to construct an isoconversion diagram. Example: obtaining an Ea of 95 kJ mol^{-1} at $\alpha = 0.5$ for the degradation of a cellulose derivative. The method requires high-quality data and precise determination of α, which can be compromised by baseline noise or overlapping reactions.

Modulated DSC (MDSC) – Related terms: temperature modulation, reversibility.
A DSC variant where a small sinusoidal temperature oscillation is superimposed on a linear heating ramp. This modulation separates the reversible heat capacity component from the non-reversible kinetic component. In the advanced unit, MDSC is used to resolve overlapping transitions such as a weak melting endotherm masked by a strong exothermic cure. Example: obtaining a reversing Cp signal for the glass transition of a polymer while the non-reversing signal captures the cure exotherm. Proper selection of modulation amplitude and period is essential; inappropriate settings can cause phase lag and

misinterpretation of the reversible component.

Oxidation Onset Temperature (To) – Related terms: thermal oxidative stability, air atmosphere.
The temperature at which a material first exhibits an exothermic oxidation reaction under an oxidative atmosphere, typically identified by the intersection of the baseline and the rising portion of the DSC curve. In the Unidad, To is compared between nitrogen and air runs to assess the protective effect of additives. Example: To = 310 °C for a polypropylene sample in air, versus no exotherm up to 400 °C in nitrogen. Accurate determination requires a stable baseline and careful control of oxygen flow, as variations can shift the apparent To.

Peak Temperature (Tp) – Related terms: maximum heat flow, reaction completion.
The temperature at which the heat flow signal reaches its maximum during a thermal event. Tp is commonly used as a kinetic indicator; higher Tp values at faster heating rates often imply kinetic hindrance. In the advanced unit, Tp is extracted from both DSC and TGA data to construct kinetic plots. Example: a Tp of 375 °C for the main degradation of a polyamide at a heating rate of 10 °C min^{-1}. Tp may be influenced by thermal lag, instrument response time, and sample size; thus, correction factors are sometimes applied.

Sample Preparation – Related terms: crushing, pelletizing.
The procedures used to condition a material before calorimetric analysis, including grinding, sieving, and loading into crucibles. Proper preparation ensures reproducible thermal contact and minimizes artifacts such as uneven heating or sample movement. In the Unidad, students are instructed to grind samples to a particle size below 200 µm, press them into a thin disc, and seal the crucible to prevent loss of volatiles. Example: preparing a 5 mg polymer sample for DSC by compressing it between two polished aluminum plates. Inadequate preparation can lead to peak broadening, baseline drift, or spurious mass loss signals.

Thermal Conductivity – Related terms: heat transfer coefficient, material property.
A measure of a material’s ability to conduct heat. In calorimetry, low thermal conductivity of the sample can cause temperature gradients, contributing to thermal lag and peak distortion. The advanced unit discusses methods to improve thermal conductivity, such as mixing the sample with a high-conductivity filler (e.g., graphite) or using a thin film geometry. Example: adding 5 % carbon black to a polymer to reduce the temperature difference between the furnace and the sample core. Accurate kinetic analysis requires accounting for the influence of thermal conductivity on the observed reaction rates.

Temperature Calibration – Related terms: thermocouple accuracy, reference point.
The process of verifying and adjusting the temperature reading of the instrument against known fixed points (e.g., melting of indium at 156.6 °C). Temperature calibration ensures that the programmed temperature profile matches the actual sample temperature. In the Unidad, calibration is performed before each series of experiments using a set of standard melting points spanning the operating range. Example: correcting a 2 °C offset observed at 400 °C by adjusting the instrument’s temperature coefficient. Errors in temperature calibration directly affect kinetic parameters and the reliability of Tg or Td values.

Thermal Decomposition – Related terms: pyrolysis, mass loss.
The breakdown of a material into smaller fragments or gases upon heating, often accompanied by heat flow signals. Thermal decomposition can be endothermic (bond breaking) or exothermic (oxidative reactions). In

the advanced calorimetry unit, decomposition pathways are investigated by coupling DSC/TGA with mass spectrometry to identify evolved species. Example: observing a two-stage decomposition of a polyester, the first stage being endothermic (loss of ester groups) and the second exothermic (cross-linking of residues). Challenges include overlapping events, rapid gas evolution causing pressure spikes, and the need for protective atmospheres to isolate purely thermal effects.

Zero-Shift Method – Related terms: baseline alignment, peak deconvolution.
A data-processing technique where the baseline of a DSC curve is shifted vertically until the pre- and post-transition baselines intersect at a common point, facilitating accurate peak integration. The method is useful for weak transitions where the baseline slope is non-linear. In the Unidad, students apply the zero-shift method to isolate a subtle crystallization exotherm superimposed on a broad glass transition. Example: adjusting the baseline by –0.03 mW to achieve a symmetric peak shape for integration. Improper shifting can either truncate the true signal or introduce artificial area, so the method requires careful visual inspection.

Atmospheric Control – Related terms: gas flow, purge gas.
The regulation of the composition, pressure, and flow rate of gases surrounding the sample during calorimetric experiments. Precise atmospheric control is essential for distinguishing oxidative from inert behavior, preventing moisture ingress, and maintaining consistent thermal conditions. In the advanced unit, a mass-flow controller supplies nitrogen or air at 50 mL min^{-1}, while a moisture trap removes water vapor. Example: switching from nitrogen to 20 % oxygen to study the effect on polymer oxidation. Inadequate control can lead to variable oxidation rates, baseline drift due to gas density changes, and safety hazards when analyzing energetic materials.

Dynamic Heat Capacity – Related terms: frequency-dependent Cp, modulated DSC.
The effective heat capacity measured under a temperature modulation, reflecting both the reversible (elastic) and irreversible (viscous) contributions of the material. Dynamic Cp provides insight into relaxation processes and glass-transition dynamics. In the Unidad, dynamic Cp is obtained by deconvoluting the reversing and non-reversing signals of an MDSC experiment. Example: a peak in the dynamic Cp centered at 120 °C indicating a secondary relaxation in a polymer blend. Interpretation can be complicated by instrument phase lag, requiring correction algorithms to recover true material properties.

Exothermic Reaction – Related terms: heat release, negative ΔH.
A process that releases heat to the surroundings, appearing as a downward peak in DSC (negative heat flow). Exotherms are common in polymer curing, oxidation, and crystallization. In the advanced calorimetry unit, exothermic peaks are quantified to determine cure kinetics and total heat released. Example: a sharp exotherm at 180 °C corresponding to the cross-linking of an epoxy system. Challenges include overlapping with endothermic events, baseline drift during large exotherms, and ensuring that the instrument's heat-flux sensor can handle the rapid heat release without saturation.

Fourier Number (Fo) – Related terms: heat diffusion, thermal penetration depth.
A dimensionless number that characterizes the ratio of heat conduction rate to heat storage rate in a material, defined as $\text{Fo} = \alpha t/L^2$ (where α is thermal diffusivity, t is time, and L is characteristic length). In calorimetry, the Fourier number helps assess whether a sample reaches thermal equilibrium during a

heating program. In the Unidad, students calculate Fo to justify the choice of sample size relative to heating rate. Example: Fo = 0.1 for a 2 mm thick polymer at a heating rate of 5 °C min^{-1}, indicating sufficient diffusion. Low Fo values can cause temperature gradients, leading to inaccurate kinetic parameters.

Heat of Fusion – Related terms: melting enthalpy, latent heat.
The enthalpy change associated with the transition from solid to liquid at the melting point. It appears as an endothermic peak in DSC. In the advanced unit, the heat of fusion is measured for crystalline polymers to assess degree of crystallinity. Example: a measured heat of fusion of 150 J g^{-1} for a semi-crystalline polyethylene sample, compared to the theoretical value of 293 J g^{-1} to calculate a crystallinity of ~51 %. Accurate measurement requires baseline correction, proper sample mass, and accounting for any overlapping transitions.

Isothermal Hold – Related terms: steady-state, reaction monitoring.
A period during which the sample temperature is held constant to observe reactions that proceed without temperature change, such as cure or degradation at a fixed temperature. In the Unidad, isothermal holds are used to study the kinetics of polymer cross-linking at temperatures below the cure peak. Example: holding a epoxy sample at 150 °C for 30 min and recording the decreasing exothermic heat flow as the reaction proceeds. Challenges include maintaining uniform temperature throughout the sample, avoiding thermal drift, and ensuring that the calorimeter's sensitivity remains adequate over the extended hold time.

Mass Balance – Related terms: material accounting, residue analysis.
The principle that the sum of mass losses and residues must equal the initial sample mass. In TGA, mass balance checks validate the completeness of the measurement and help identify missing volatile components. In the advanced unit, students perform a mass balance after a full degradation cycle to confirm that the measured mass loss matches the integrated evolved gas volume from a coupled FT-IR detector. Example: an initial mass of 10 mg reduced to 2 mg residue, with 8 mg accounted for by CO_2 and H_2O detection. Incomplete mass balance may indicate leaks, sensor errors, or undetected solid residues.

Non-Linear Baseline – Related terms: curve fitting, polynomial adjustment.
A baseline that does not follow a simple linear trend, often observed when the reference and sample have differing heat capacities or when the instrument experiences temperature-dependent drift. In the Unidad, a non-linear baseline is fitted using a third-order polynomial to improve integration accuracy for broad transitions. Example: a curved baseline required for a high-temperature melting event of a metal alloy. Over-fitting the baseline can remove genuine signal components, while under-fitting leaves residual drift that distorts enthalpy calculations.

Oxidative Exotherm – Related terms: combustion peak, heat release rate.
An exothermic event resulting from the reaction of a material with oxygen, typically accompanied by rapid mass loss and gas evolution. In DSC/TGA, the oxidative exotherm provides insight into fire-propagation behavior. In the advanced unit, the oxidative exotherm of a polymer is measured under a controlled air flow to determine the peak heat release rate (PHRR). Example: a sharp exotherm at 380 °C with a PHRR of 250 W g^{-1} for a polyurethane foam. Accurate measurement demands proper gas flow control and a calorimeter capable of handling high heat release without saturation.

Peak Deconvolution – Related terms: Gaussian fitting, overlapping events.
A mathematical technique used to separate overlapping thermal events into individual components, often by fitting Gaussian or Lorentzian functions to the composite peak. In the Unidad, deconvolution is applied to complex curing curves where multiple reactions occur in close temperature proximity. Example: resolving two overlapping exotherms at 150 °C and 170 °C in a mixed epoxy system. Successful deconvolution provides separate enthalpies and kinetic parameters for each reaction. The process is sensitive to initial guesses and noise; poor fitting can generate non-physical results.

Phase Transition – Related terms: first-order, second-order.
A change in the physical state of a material, such as melting, crystallization, or glass transition. First-order transitions involve latent heat and appear as peaks, while second-order transitions involve changes in heat capacity and appear as steps. In the advanced calorimetry unit, both types are studied to understand material behavior. Example: a first-order melting peak at 210 °C for a metallic alloy and a second-order glass transition at 85 °C for an amorphous polymer. Accurate identification requires appropriate heating rates and baseline correction.

Pressure Effects – Related terms: high-pressure DSC, volumetric change.
The influence of external pressure on the temperature and enthalpy of thermal events. Elevated pressure can shift Tg, melting points, and reaction kinetics. In the Unidad,