Bomb Calorimetry

A. Thermodynamics

1. **First Law**: \( \Delta E = q + w \) (\( E \) = internal energy; \( q \) & \( w \) are heat added to and work done on system)

2. **PV work**: \( w_{PV} = - \int PdV \) Thus, if \( w_{PV} \) is the only work, \( w = 0 \) when \( V \) is constant, yielding

3. \( \Delta E = q \) (= \( q_V \)), process at constant \( V \), \( PV \) work only.

4. **Enthalpy defined**: \( H \equiv E + PV \). With this definition, \( \Delta H = q \) (= \( q_P \)) for process at constant \( P \).

B. Chemical Reaction

1. \( \Delta E_{rx} = \sum \nu_i E_i \quad \nu_i = \text{stoichiometry number} (+ \text{ for products, } - \text{ for reactants}) \)

2. \( \Delta H_{rx} = \sum \nu_i H_i = \sum \nu_i \Delta H_{f,i} \quad \text{(formation enthalpy)} \)
3. **Standard States**: ° designates substances in standard state, which includes \( P = P^\circ = 1 \text{ bar} \ (\approx 750 \text{ Torr}) \). (see CP)

4. \[ \Delta H^\circ = \sum v_i \Delta H^\circ_{f,i} = \Delta E^\circ + \Delta (PV)^\circ = \Delta E^\circ + P^\circ \Delta V^\circ \]

5. For gases: \( \Delta H^\circ = \Delta E^\circ + \Delta v_g RT \) \( (\Delta v_g = \text{mol gaseous products} - \text{mol gaseous reactants}; \Delta V^\circ \text{ negligible for solids and liquids.}) \)

C. **Bomb Calorimetry**

1. \( V \) is constant \( \Rightarrow \) measure \( q_V = \Delta E \).

2. Determine by precisely measuring \( T \) change.

3. **Calibration**: Measure \( \Delta T \) for known standard (benzoic acid) and determine calorimeter constant, \( C_K = q/\Delta T \).

4. **Sample heat**: \( q_s = C_K \Delta T_s \) (from combustion of sample)
D. Estimation of $\Delta T$