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*: $w_{PV} = -\int P dV$ 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. $\Delta E_{rx} = \sum \nu_i E_i$ ν_i = *stoichiometry number* (+ for products, – for reactants)
2. $\Delta H_{rx} = \sum \nu_i H_i = \sum \nu_i \Delta H_{f,i}$ (*formation enthalpy*)

3. *Standard States*: ° designates substances in standard state, which includes $P = P° = 1$ bar ($\approx$ 750 Torr). (see CP)

4. $\Delta H° = \sum \nu_i \, \Delta H°_{f,i} = \Delta E° + \Delta (PV)° = \Delta E° + P°\Delta V°$

5. For *gases*: $\Delta H° = \Delta E° + \Delta\nu_g \, RT$ ($\Delta\nu_g$ = mol gaseous products – mol gaseous reactants; $\Delta V°$ 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 ΔT 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 combusion of sample)

D. Estimation of ΔT