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. $\Delta E_{\text{rx}} = \Sigma\ \nu_i E_i$ ν_i = *stoichiometry number* (+ for products, – for reactants)

2. $\Delta H_{\text{rx}} = \Sigma\ \nu_i H_i = \Sigma\ \nu_i \Delta H_{f,i}$ (*formation enthalpy*)

3. *Standard States*: ° designates substances in standard state, which includes $P = P° = 1$ bar (≈ 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

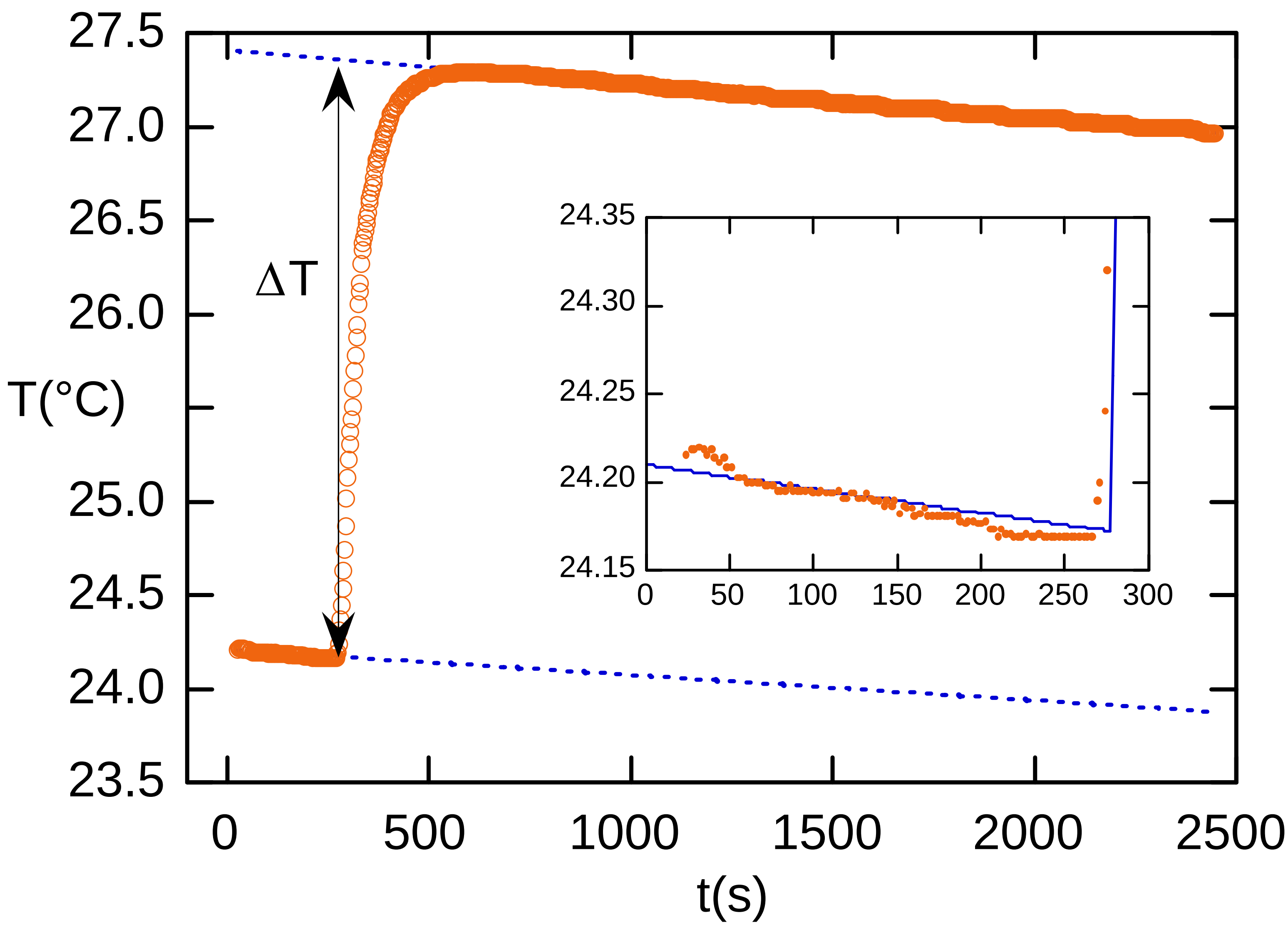
1. V is constant $\Rightarrow$ measure $q_V = \Delta E$.

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 Δ*T*



Today's Practice Quiz

1. A solution is prepared by dissolving 13.71 g of smactose in water and bringing the volume to 0.100 L in a volumetric flask. The optical rotation observed at λ_D for this solution in a 0.500-m polarimetry cell is –34.7°. Calculate the specific rotation of smactose (units deg mL g^{-1} dm^{-1}) at this wavelength and *T*.
   a. –0.95 b. –23.8 c. –50.6 d. –126.5 e. none of these

2. 70.0 mL of 3.0 m Na_2SO_4 is mixed with 30.0 mL of 1.0 m NaCl. Assuming the volumes are additive, the resulting concentration of sodium ion is:
   a. 2.0 m b. 2.4 m c. 4.0 m d. 4.5 m e. none of these

3. The reaction, $2A + 2B \rightarrow C + D$, has a rate constant of 6.0×10^{-3} L^2 mol^{-2} s^{-1} at 0°C. The order of this reaction is
   a. 1 b. 2 c. 3
   d. indeterminate without additional information. e. none of these

4. For a certain reaction, a plot of ln [A] versus *t* gives a straight line with a slope of –1.46 s^{-1} and a *y*–intercept of 4.30. The rate constant is
   a. 0.68 s b. –1.46 s^{-1} c. 1.46 s^{-1} d. 4.30 s^{-1}
   e. This cannot be determined without additional information.

5. An acid-calalyzed reaction has a rate constant of 0.0434 L mol^{-1} min^{-1}. A reaction is initiated by mixing HCl with the other reactant to give an acid molarity of 1.3. What is the half-life of the reaction?

a. 0.056 min
b. 12.3 min
c. 17.7 min
d. Need additional information.
e. none of these

6. As a good rule of thumb, many reactions double in speed for a 10°C increase in *T* at room temperature. Taking the two temperatures to be 20°C and 30°C, the activation energy for such reactions would be

a. 0.35 kJ mol^{-1}
b. 6.2 kJ mol^{-1}
c. 22 kJ mol^{-1}
d. 51 kJ mol^{-1}
e. 148 kJ mol^{-1}

7. In a reaction the reactant A is observed to drop to ½ its starting concentration after 10.0 min. How much longer will it take to drop to ¼ $[A]_0$?

a. 5.0 min
b. 10.0 min
c. 20.0 min
d. Need additional information.
e. none of these