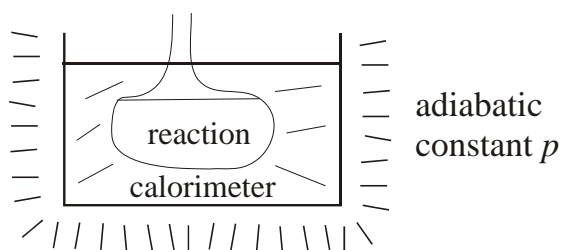


Calorimetry

The objective is to measure

$$\Delta H_{rx}(T_1) \quad \text{Reactants } (T_1) \quad \underset{\text{constant } p}{\overset{\text{isothermal}}{=}} \quad \text{Products } (T_1)$$

- Constant pressure (for solutions)



$$\text{I) } \Delta H_I \quad \text{React. } (T_1) + \text{Cal. } (T_1) \quad \underset{\text{constant } p}{\overset{\text{adiabatic}}{=}} \quad \text{Prod. } (T_2) + \text{Cal. } (T_2)$$

$$\text{II) } \Delta H_{II} \quad \text{Prod. } (T_2) + \text{Cal. } (T_2) \quad \underset{\text{constant } p}{=} \quad \text{Prod. } (T_1) + \text{Cal. } (T_1)$$

$$\Delta H_{rx}(T_1) \quad \text{React. } (T_1) + \text{Cal. } (T_1) \quad \underset{\text{constant } p}{=} \quad \text{Prod. } (T_1) + \text{Cal. } (T_1)$$

$$\Delta H_{rx}(T_1) = \Delta H_I + \Delta H_{II}$$

(I) Purpose is to measure $(T_2 - T_1)$

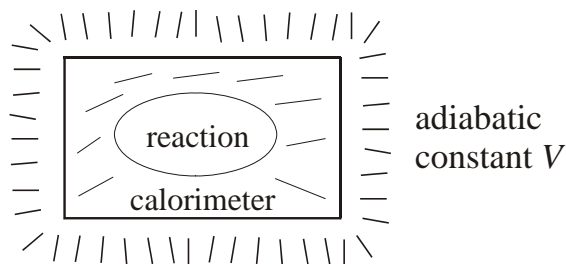
$$\text{Adiabatic, const. } p \Rightarrow q_p = 0 \Rightarrow \Delta H_I = 0$$

(II) Purpose is to measure heat q_p needed to take prod. + cal. from T_2 back to T_1 .

$$q_p = \int_{T_1}^{T_2} C_p (\text{Prod.} + \text{Cal.}) dT = \Delta H_{II}$$

$$\therefore \boxed{\Delta H_{rx}(T_1) = -\int_{T_1}^{T_2} C_p (\text{Prod.} + \text{Cal.}) dT}$$

- Constant volume (when gases involved)



$$\text{I) } \Delta U_I \quad \text{React. (} T_1 \text{) + Cal. (} T_1 \text{)} \stackrel{\text{adiabatic}}{\underset{\text{constant } V}{=}} \text{Prod. (} T_2 \text{) + Cal. (} T_2 \text{)}$$

$$\text{II) } \Delta U_{II} \quad \text{Prod. (} T_2 \text{) + Cal. (} T_2 \text{)} \stackrel{\text{adiabatic}}{\underset{\text{constant } V}{=}} \text{Prod. (} T_1 \text{) + Cal. (} T_1 \text{)}$$

$$\Delta U_{rx}(T_1) \quad \text{React. (} T_1 \text{) + Cal. (} T_1 \text{)} \stackrel{\text{adiabatic}}{\underset{\text{constant } V}{=}} \text{Prod. (} T_1 \text{) + Cal. (} T_1 \text{)}$$

$$\Delta U_{rx}(T_1) = \Delta U_I + \Delta U_{II}$$

(I) Purpose is to measure $(T_2 - T_1)$

$$\text{Adiabatic, const. } V \Rightarrow q_V = 0 \Rightarrow \Delta U_I = 0$$

(II) Purpose is to measure heat q_V needed to take prod. + cal. from T_2 back to T_1 .

$$q_V = \int_{T_1}^{T_2} C_V (\text{Prod.} + \text{Cal.}) dT = \Delta U_{II}$$

$$\therefore \boxed{\Delta U_{rx}(T_1) = -\int_{T_1}^{T_2} C_V (\text{Prod.} + \text{Cal.}) dT}$$

Now use $H = U + pV$ or $\Delta H = \Delta U + \Delta(pV)$

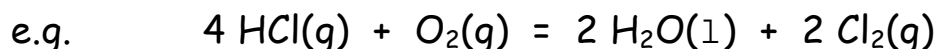
Assume only significant contribution to $\Delta(pV)$ is from gases.

$$\text{Ideal gas} \quad \Rightarrow \quad \Delta(pV) = R\Delta(nT)$$

Isothermal $T = T_1 \Rightarrow \Delta(pV) = RT_1\Delta n_{gas}$

$$\therefore \Delta H_{rx}(T_1) = \Delta U_{rx}(T_1) + RT_1\Delta n_{gas}$$

$$\Delta H_{rx}(T_1) = -\int_{T_1}^{T_2} C_V(\text{Prod.} + \text{Cal.}) dT + RT_1\Delta n_{gas}$$



$$T_1 = 298.15 \text{ K}$$

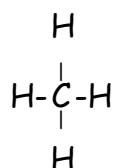
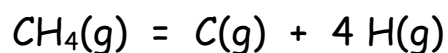
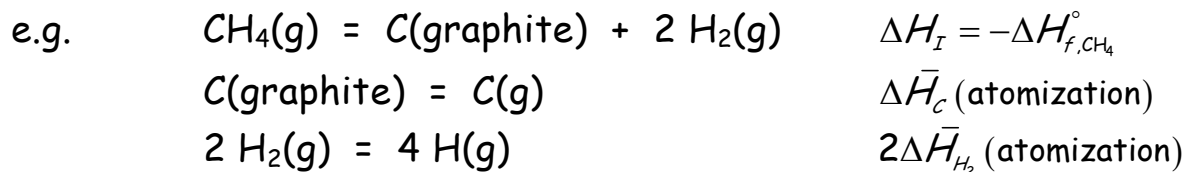
$$\Delta U_{rx}(T_1) = -195.0 \text{ kJ} \quad \Delta n_{gas} = -3 \text{ moles}$$

$$\begin{aligned} \Delta H_{rx}(T_1) &= -195.0 \text{ kJ} + (-3 \text{ mol})(298.15 \text{ K})(8.314 \times 10^{-3} \text{ kJ/K-mol}) \\ &= -202.43 \text{ kJ} \end{aligned}$$

Bond energies: An approximate method for estimating ΔH_f°

Really bond enthalpies, but usually $\Delta(pV) \ll$ difference

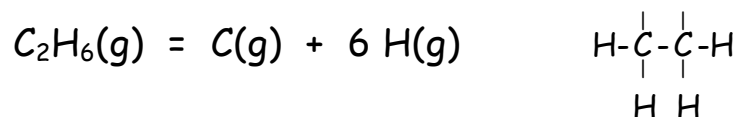
- 1) Measure bond energies for known compounds
- 2) Use them to estimate ΔH_f° for unknown compounds



$$\Delta H = 4B_{\text{C-H}} \quad \Delta H$$

$$B_{\text{C-H}} = 416.2 \text{ kJ}$$

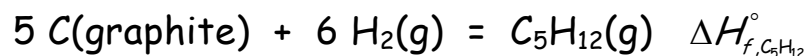
$$4 B_{C-H} = -\Delta H_{f,CH_4}^\circ + \Delta \bar{H}_{C(atom.)} + 2\Delta \bar{H}_{H_2(atom.)} \Rightarrow B_{C-H} = 416.2 \text{ kJ}$$



$$\begin{aligned} \Delta H &= B_{C-C} + 6B_{C-H} \\ &= -\Delta H_{f,C_2H_6}^\circ + 2\Delta \bar{H}_{C(atom.)} + 3\Delta \bar{H}_{H_2(atom.)} \Rightarrow B_{C-C} = 342 \text{ kJ} \end{aligned}$$

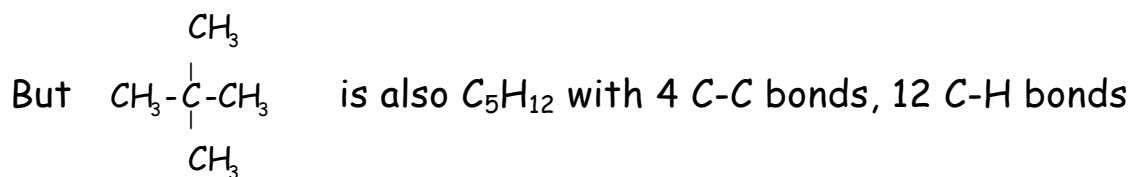
Now estimate ΔH_f° for n-pentane, C_5H_{12} $CH_3-CH_2-CH_2-CH_2-CH_3$

$$\begin{array}{ll} 5 C(\text{graphite}) = 5 C(g) & 5\Delta \bar{H}_{C(atom.)} \\ 6 H_2(g) = 12 H(g) & 6\Delta \bar{H}_{H_2(atom.)} \\ 5 C(g) + 12 H(g) = C_5H_{12}(g) & \Delta H \approx -(4B_{C-C} + 12B_{C-H}) \end{array}$$



$$\begin{aligned} \Delta H_{f,C_5H_{12}}^\circ &\approx -(4B_{C-C} + 12B_{C-H}) + 5\Delta \bar{H}_{C(atom.)} + 6\Delta \bar{H}_{H_2(atom.)} \\ &\sim \underline{-152.6 \text{ kJ}} \text{ (estimated)} \end{aligned}$$

$$\text{Actual } \Delta H_{f,C_5H_{12}}^\circ \text{ (n-pentane)} = \underline{-146.4 \text{ kJ}}$$



$$\Rightarrow \Delta H_{f,C_5H_{12}}^\circ \sim \underline{-152.6 \text{ kJ}} \text{ (estimated using bond energies)}$$

$$\text{Actual } \Delta H_{f,C_5H_{12}}^\circ \text{ (neopentane)} = \underline{-166.1 \text{ kJ}}$$