



DET 05970 Termodinâmica e Transmissão de Calor

Calorimetria

Aula 15-16

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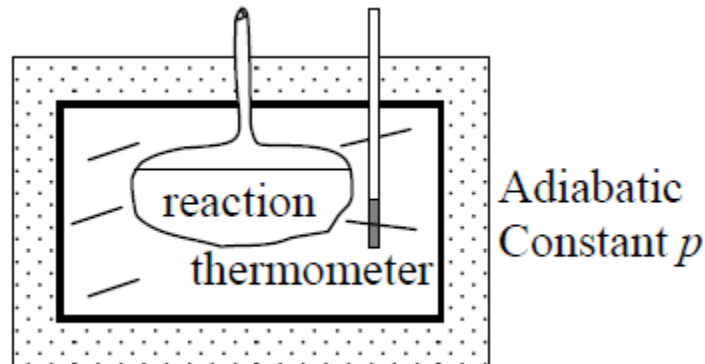
Objetivo

Medir:

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

- **Pressão constante** (para soluções)

Calorímetro



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

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

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

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

(I) O objetivo é medir $(T_2 - T_1)$

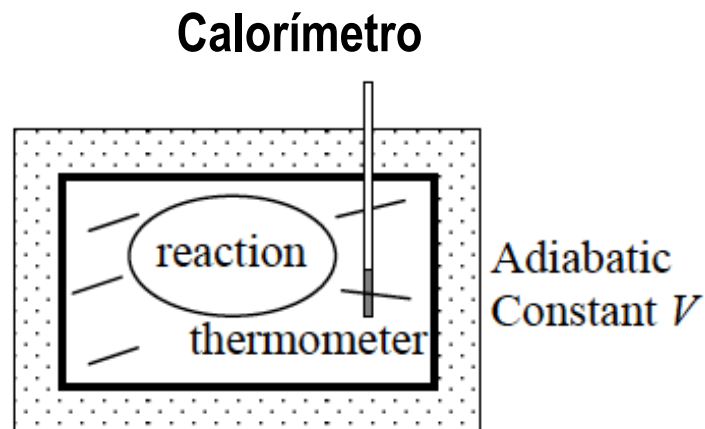
$$\text{Adiabático, } p \text{ constante} \quad \Rightarrow \quad q_p = 0 \quad \Rightarrow \quad \Delta H_I = 0$$

(II) O objetivo é medir q_p requerido para levar prod. + cal. de T_2 para T_1

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

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

- **Volume constante** (quando envolve gases)



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

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

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

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

(I) O objetivo é medir $(T_2 - T_1)$

$$\text{Adiabático, } V \text{ constante} \quad \Rightarrow \quad q_V = 0 \quad \Rightarrow \quad \Delta U_I = 0$$

(II) O objetivo é medir q_V requerido para levar prod. + cal. de T_2 para T_1

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

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

Use $H = U + pV$ ou $\Delta H = \Delta U + \Delta(pV)$

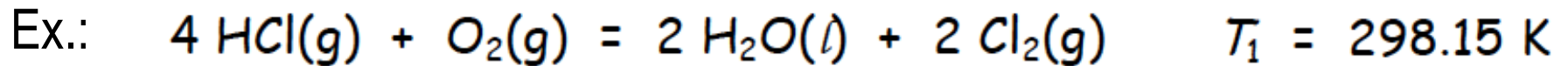
Assuma que contribuição significativa para $\Delta(pV)$ vem somente de gases

Gás ideal $\Rightarrow \Delta(pV) = R\Delta(nT)$

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

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

Diferença entre ΔU e ΔH é pequena, mas mensurável



$$\Delta U_{rx}(T_1) = -195.0 \text{ kJ}$$

$$\Delta n_{gas} = -3 \text{ moles}$$

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

Imagine essa reação ocorrendo em um calorímetro com V constante e $C_v = 10 \text{ kJ/K}$

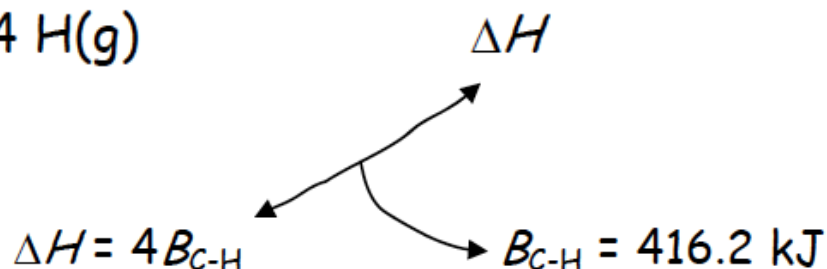
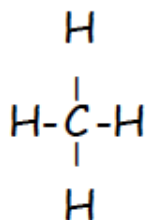
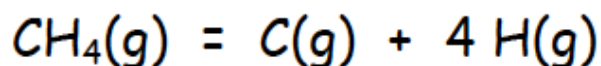
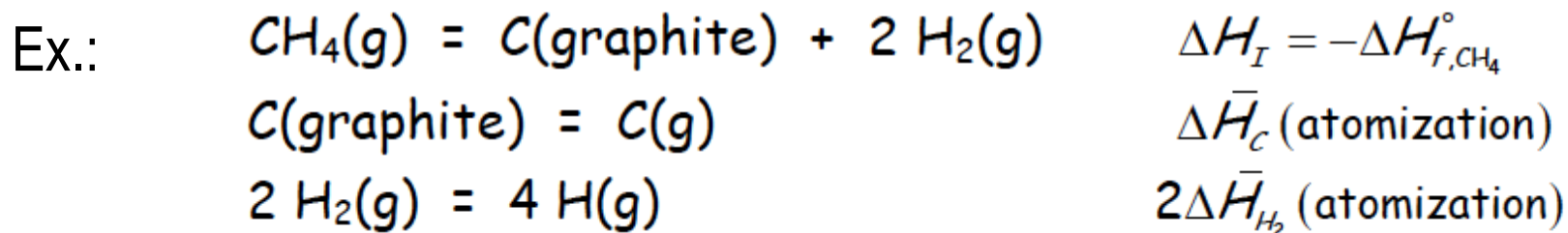
massa térmica do calorímetro \gg massa térmica do produto

calor trocado altera a T do calorímetro

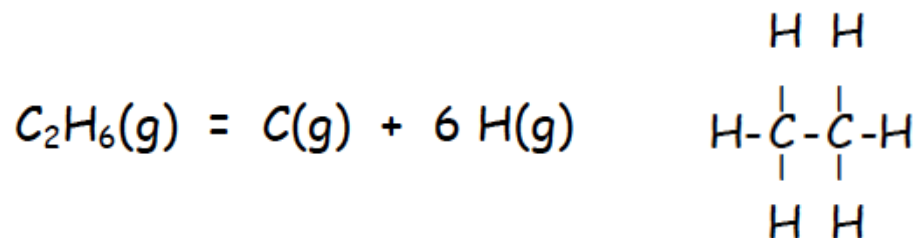
geralmente, não se precisa conhecer C_p ou C_v do produto

Energias de ligação: um método *aproximado* para estimar Δh_f°

- 1) Medir as energias de ligação para compostos conhecidos
- 2) Usar elas para estimar ΔH_f° para compostos desconhecidos



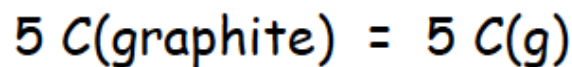
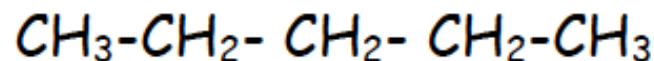
$$4 B_{\text{C-H}} = -\Delta H_{f,\text{CH}_4}^\circ + \Delta \bar{H}_{\text{C}(\text{atom.})} + 2\Delta \bar{H}_{\text{H}_2(\text{atom.})} \Rightarrow \boxed{B_{\text{C-H}} = 416.2 \text{ kJ}}$$



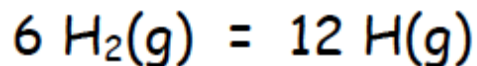
$$\Delta H = B_{\text{C-C}} + 6 B_{\text{C-H}}$$

$$= -\Delta H_{f, \text{C}_2\text{H}_6}^{\circ} + 2\Delta \bar{H}_{\text{C}(\text{atom.})} + 3\Delta \bar{H}_{\text{H}_2(\text{atom.})} \Rightarrow B_{\text{C-C}} = 342 \text{ kJ}$$

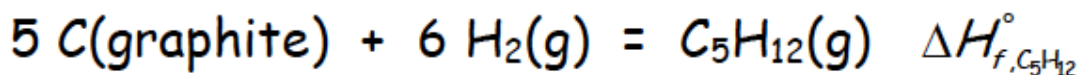
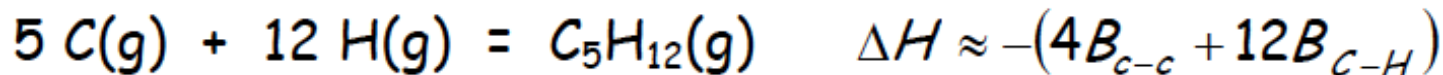
Estime Δh_f° para o n-pentano, C_5H_{12}



$$5\Delta \bar{H}_{\text{C}(\text{atom.})}$$



$$6\Delta \bar{H}_{\text{H}_2(\text{atom.})}$$



$$\Delta H_{f,C_5H_{12}}^{\circ} \approx -(4B_{C-C} + 12B_{C-H}) + 5\Delta \bar{H}_{C(atom.)} + 6\Delta \bar{H}_{H_2(atom.)}$$

$$\sim \underline{-152.6 \text{ kJ}} \text{ (estimated)}$$

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

Mas $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$ é também conhecido como C_5H_{12} com 4 C-C e 12 C-H ligações.

$\Rightarrow \Delta H_{f,C_5H_{12}}^{\circ} \sim \underline{-152.6 \text{ kJ}}$ (estimativa usando energias de ligação)

Na verdade, $\Delta H_{f,C_5H_{12}}^{\circ}$ (neopentane) = -166.1 kJ

