

Lecture #22 (Tuesday April 11th)

I. ΔE_{rxn} computed for excited states given the energy level.

II. Bond Energies

III. Bomb Calorimeter

IV. Enthalpy - Definition

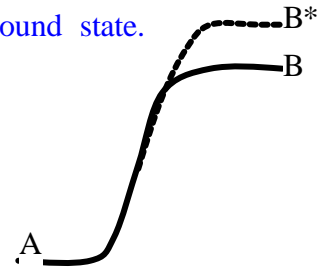
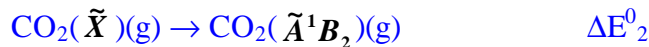
I. ΔE_{rxn} computed for excited states given the energy level.



CO_2 first electronic excited state, $\tilde{\text{A}}^1\text{B}_2$, lies 46000 cm^{-1} above the ground state.

Note: $83.6 \text{ cm}^{-1} = 1 \text{ KJ mol}^{-1}$ Compute ΔE_{rxn}^0

Use Hess law to deconvolute:

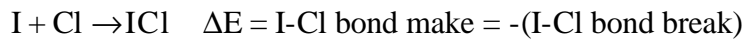


II. Bond Energies

The bond dissociation energy of a diatomic XY, designate D_{XY} is the ΔE for $\text{XY}(\text{g}) \rightarrow \text{X}(\text{g}) + \text{Y}(\text{g})$. We will avoid the temperature distinctions since bond energy varies only slightly with T.

Gas phase reactions = bond breaking then bond making, i.e.

$\text{I}_2 + \text{HCl} \rightarrow \text{ICl} + \text{HI}$ is actually (via Hess)



$\Delta E = \text{stoichiometric } D_{\text{reactants}} - D_{\text{prod}} = D_{\text{I}_2} + D_{\text{HCl}} - (D_{\text{ICl}} + D_{\text{HI}})$.

Can you predict how to express ΔE for $\text{I}_2 + \text{H}_2 \rightarrow 2\text{HI}$?

Mean Bond Energies

For polyatomics the leaving group affects the bond energy. The ΔE for breaking the O-H bond in the following rxns differ: $\text{H}_2\text{O} \rightarrow \text{OH} + \text{O}$, $\text{OH} \rightarrow \text{O} + \text{H}$, $\text{CH}_3\text{OH} \rightarrow \text{CH}_3 + \text{OH}$. Averaged over many such reactions to obtain mean bond energies.

Example: Calculate the ΔE for methane combustion: $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}$

Reactants: $\Delta E_{\text{I}} = \text{Break four CH bonds and 2 times one O=O} = 4D_{\text{CH}} + 2D_{\text{O=O}} = 4 \times 99 + 2 \times 119 = 634 \text{ Kcal mol}^{-1}$

Products: $\Delta E_{\text{II}} = \text{Form two C=O bonds and two moles of two O-H bonds} = -(2D_{\text{C=O}} + 2 \times 2D_{\text{O-H}}) = -(2 \times 192 + 4 \times 111) = -828 \text{ Kcal mol}^{-1}$

$\Delta E = \Delta E_{\text{I}} + \Delta E_{\text{II}} = \text{stoichiometric } D_{\text{react}} - D_{\text{prod}} = -194 \text{ kcal mol}^{-1}$

Above rxn is example of **combustion** (rxn with O_2) to produce $CO_2 + H_2O$, usually exothermic since the C=O bond in CO_2 is very strong.

Endo or Exothermicity easily explained: If the sum of the reactant bonds requires more energy (stronger bonds or larger # of bonds) than the products, then endothermic.

Strong & Weak Bonds: 1. Multiple bonds stronger than single ones 2. More polar are stronger. 3. Bonds involving Hydrogen tend to be strong since H is the most electropositive

III. Bomb Calorimeter

A bomb calorimeter measures the q at constant volume, thus one obtains a measure of $q_{rxn} = \Delta E_{rxn}$, for a combustion rxn.

Heat lost by exothermic chemical rxn = heat gained by the calorimeter (manifest as a temp change in the water)

Thus: $q_{rxn} = -C_{cal} * \Delta T$. C_{cal} = heat capacity of the calorimeter in energy per K (mass or moles of the calorimeter is accounted for). Usually determined by a standard.

Example: A bomb calorimeter initially at $25.1^\circ C$ with $C_{cal} = 3.75 \text{ KJ } ^\circ C^{-1}$ measures the combustion of 189 mg of acetylene leads and arrives at a final temperature of $27.3^\circ C$.

(a) Show that the absolute (extensive) ΔE for this rxn is -8.25 KJ ?

(b) Show that the relative (intensive) ΔE for this rxn is $-1130 \text{ KJ mol}^{-1}$?

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IV. Enthalpy

$$H = E + PV, \Delta H = \Delta E + \Delta(PV)$$

Heat change measured at constant pressure = $\Delta H = q_p$

This is justified by noting for constant pressure: $w = -P_{ext} \Delta V = -P \Delta V$ and substituting into $\Delta H = \Delta E + P\Delta V$

Many rxns occur under these conditions (open beaker, $P = \text{constant}$)

It's a state function since E, P, V are state functions.