

Lecture 28 CH101 A1 (MWF 9 am) Fall 2016

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[TP] Atom X that has an orange emission line (650 nm) with photon energy $E_{\text{orange}} = hc/\lambda$ and a green emission line (510 nm) with photon energy $E_{\text{green}} = hc/\lambda$. Which of the following statements are true about a single emission process of atom X?

- 20% 1. An atom of X can emit light with any amount of energy.
 20% 2. An atom of X can emit light with energy between E_{orange} and E_{green} .
 20% 3. An atom of X can emit light in multiples of E_{orange} or E_{green} .
 20% 4. An atom of X can emit light only of E_{orange} or E_{green} .
 20% 5. None of the above.



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Monday, November 14, 2016

- Complete: Using $\Delta_b H$'s to **estimate** $\Delta_r H$
- If some substances are not gases, using $\Delta_b H$'s works poorly

Begin ch 8: Modeling atoms and their electrons

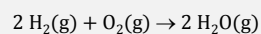
- Review: What light is and how it interacts with matter
- Natural frequencies of atoms

Next lecture: Light and matter exchange energy smoothly and slowly; Light energy is exchanged in tiny amounts called photons



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Using $\Delta_b H$'s to **estimate** $\Delta_r H$ 

How much enthalpy change to break reactants apart into atoms?

How much enthalpy change to combine reactant atoms into products?

What is the total enthalpy change?



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Using $\Delta_b H$'s to **estimate** $\Delta_r H$

The **key feature** of standard **bond dissociation energies** is that, the enthalpy change of **any reaction**, $\Delta_r H$, can be **estimated** using them, as ...

$$\begin{aligned} \Delta_r H &= \text{Sum}[\text{energy spent breaking bonds}] - \\ &\quad \text{Sum}[\text{energy evolved forming bonds}] \\ &= \text{Sum}[\Delta_b H(\text{reactants})] - \text{Sum}[\Delta_b H(\text{products})] \end{aligned}$$



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If some substances are not gases, using $\Delta_b H$'s works poorly

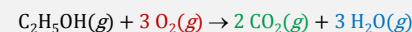


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$\Delta_f H$'s versus $\Delta_b H$'s to compute $\Delta_r H$



Using standard enthalpies of formation:

$$\begin{aligned} \Delta_r H &= + 2 \Delta_f H(\text{CO}_2, g) + 3 \Delta_f H(\text{H}_2\text{O}, g) \\ &\quad - \Delta_f H(\text{C}_2\text{H}_5\text{OH}, g) = -1,277.38 \text{ kJ} \end{aligned}$$

Using bond enthalpies:

$$\begin{aligned} \Delta_r H &= + \Delta H_{\text{break}}(\text{C}_2\text{H}_5\text{OH}) + 3 \Delta H_{\text{break}}(\text{O}_2) \\ &\quad - 2 \Delta H_{\text{make}}(\text{CO}_2) - 3 \Delta H_{\text{make}}(\text{H}_2\text{O}) = -1,232 \text{ kJ} \end{aligned}$$

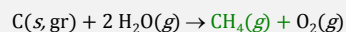


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$\Delta_f H$'s versus $\Delta_b H$'s to compute $\Delta_r H$



Using standard enthalpies of formation:

$$\begin{aligned} \Delta_r H &= + \Delta_f H(\text{CH}_4, g) - 2 \Delta_f H(\text{H}_2\text{O}, g) \\ &= -74.81 - 2(-241.82) = +408.83 \text{ kJ (actual)} \end{aligned}$$

Using bond enthalpies:

$$\begin{aligned} \Delta_r H &= + 2 \Delta H_{\text{break}}(\text{H}_2\text{O}) - \Delta H_{\text{make}}(\text{CH}_4) - \Delta H_{\text{make}}(\text{O}_2) \\ &= + 4 (\text{O-H}) - 4 (\text{C-H}) - (\text{O=O}) \\ &= 4(460) - 4(414) - 498.7 = -315 \text{ kJ (approximate)} \end{aligned}$$

Big error!

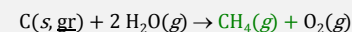


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$\Delta_f H$'s versus $\Delta_b H$'s to compute $\Delta_r H$



Using standard enthalpies of formation:

$$\begin{aligned} \Delta_r H &= + \Delta_f H(\text{CH}_4, g) - 2 \Delta_f H(\text{H}_2\text{O}, g) \\ &= -74.81 - 2(-241.82) = +408.83 \text{ kJ (actual)} \end{aligned}$$

Using bond enthalpies:

$$\begin{aligned} \text{C}(s, \text{gr}) &\rightarrow \text{C}(g), \Delta_f H(\text{C}, g) \\ \Delta_r H &= \Delta_f H(\text{C}, g) + 2 \Delta H_{\text{break}}(\text{H}_2\text{O}) - \Delta H_{\text{make}}(\text{CH}_4) - \Delta H_{\text{make}}(\text{O}_2) \\ &= \Delta_f H(\text{C}, g) + 4 (\text{O-H}) - 4 (\text{C-H}) - (\text{O=O}) \\ &= 716.7 + 4(460) - 4(414) - 498.7 = +402 \text{ kJ (approximate)} \end{aligned}$$

Much better!



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[Quiz] “In my lecture I was told that change in enthalpy is **products minus reactants**, but my discussion leader told me that it is **reactants minus products**. I’ve also looked in another chemistry book and it say products minus reactants. Which is right?”

- 25% 1. products minus reactants
 25% 2. reactants minus products
 25% 3. both
 25% 4. neither



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Review: What light is and how it interacts with matter

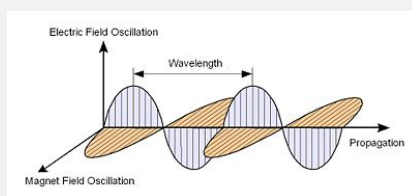


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Matter experiences light as an oscillating electric field



The electric field strength changes direction at frequency ν_{light} .
 (The effect of the magnetic field is **relatively negligible**.)



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The changing electric field of light tugs on matter ...

Matter can respond to tugs only at “natural” frequencies of “motion” in matter

$$\nu_{\text{light}} = \nu_{\text{matter}}$$



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Matter responds only at its “natural” frequencies

C-O stretch $\sim 1000 \text{ cm}^{-1} = 3 \times 10^{13} / \text{s}$ ν_{stretch} = relative motion of atoms $\nu_{\text{light}} = \nu_{\text{stretch}}$ 

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What are natural frequencies of atoms?

H atom emission spectrum



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What are natural frequencies of atoms?

H atom emission spectrum



What could account for natural frequencies of atoms?

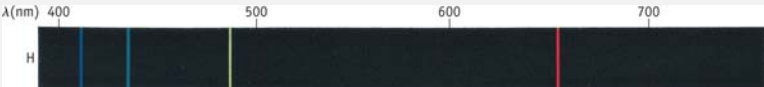


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What are natural frequencies of atoms?

H atom emission spectrum



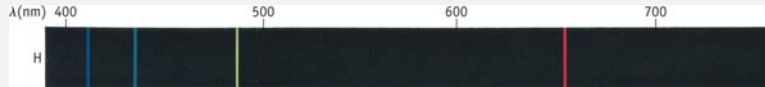
What is the frequency (in Hz) of the lowest-energy line in the H atom emission spectrum?

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What are natural frequencies of atoms?

H atom emission spectrum



The red light emitted has frequency 4×10^{14} Hz. IR light, due to the oscillation of protons and neutrons (nuclei), has a frequency of $\sim 1 \times 10^{13}$ Hz.

Estimate the ratio of the mass of the object oscillating in H atom that leads to the emission of visible light, relative to the mass of a proton.

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