ChemActivity **32**

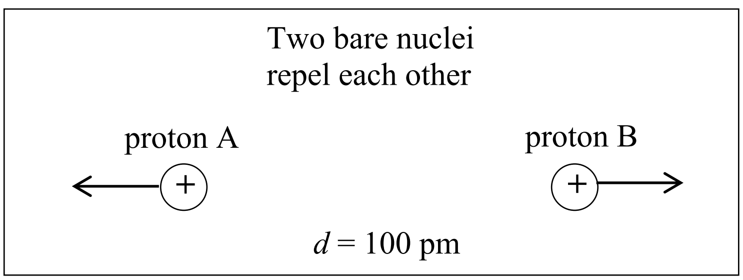
Is Energy Released or Used When a Bond Breaks?

WARM-UP

Model 1: Nuclei are Held Together by Coulombic Attraction to Electrons.

Consider two *bare* nuclei, in this case two protons, as shown in Figure 1. From Coulomb's Law we know that these protons will repel each other.

Figure 1. Coulombic interaction of two protons.



The (repulsive) Coulombic potential energy is (see CA 3):

$$V = \frac{k\, q_1\, q_2}{d} = \frac{2.31\times10^{-16}\,\text{J} \bullet \text{pm}}{100\ \text{pm}} = 2.31 \times 10^{-18}\ \text{J} \quad \text{(repulsive)} \qquad (1)$$

where $k = 2.31 \times 10^{-16}$ J • pm.

Critical Thinking Questions

1. a) Why is "100 pm" in the denominator of equation 1?

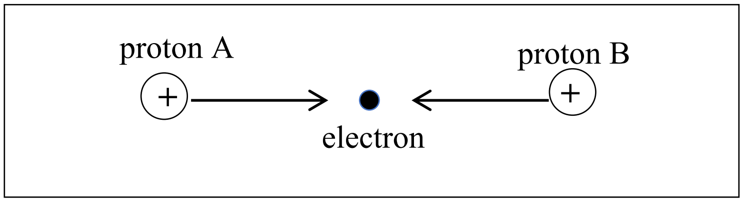
   b) Let q_1 = charge on nucleus A and q_2 = charge on nucleus B. What are the values of q_1 and q_2 for equation 1?

   c) Show explicitly how the value for the numerator in equation 1 was obtained from the Coulombic potential energy expression.

Model 2: An Electron Between Two Nuclei.

If an electron is placed halfway between the nuclei, then each nucleus is attracted toward the electron.

Figure 2. Nuclei are attracted to an electron.



The (attractive) Coulombic potential energy is given by the sum of the interactions of nucleus A with the electron and nucleus B with the electron.

$$V = \frac{-2.31\times10^{-16}\text{J}\bullet\text{pm}}{50\text{ pm}} + \frac{-2.31\times10^{-16}\text{J}\bullet\text{pm}}{50\text{ pm}} = -9.24 \times 10^{-18}\text{ J (attractive)} \qquad (2)$$

The net Coulombic potential energy is the sum of the energy of interaction of the two nuclei (given in equation 1) and the energy of interaction of the two nuclei with the electron (given in equation 2):

$$V = 2.31 \times 10^{-18}\text{ J} + (-9.24 \times 10^{-18}\text{ J}) = -6.93 \times 10^{-18}\text{ J} \qquad \text{(attractive)}$$

Critical Thinking Questions

2. a) Why is "50 pm" in the denominator of each term in equation 2?

   b) Show explicitly how the value for the numerator in both terms of equation 2 was obtained from the Coulombic potential energy expression.

3. Explain why the numerator in equation 1 is positive, but the numerator in equation 2 is negative.

4. The net attractive potential energy in Figure 2 is -6.93×10^{-18} J. Will energy be required to separate the nuclei or will energy be released upon separation? Explain.

Information

This model, of course, only approximates reality. One cannot simply place a stationary electron between two nuclei. Electrons move (have kinetic energy) and occupy certain regions of space (domains or orbitals). Nonetheless, the model above demonstrates that nuclei can be held together by electron sharing between nuclei.

As we have seen previously, typically there are two electrons (or multiples of two) being shared between atoms to form a bond in real molecules. Based on the concepts developed in Models 1 and 2, we expect that energy will be required to break a bond.

END OF WARM-UP

Model 3: Endothermic and Exothermic Processes.

When chemical processes occur, energy (typically as heat) is either released—an **exothermic** process, or absorbed—an **endothermic** process. The breaking of bonds requires energy to pull the atoms apart; bond-breaking is thus an endothermic process. When bonds are formed, energy is released—precisely the same amount of energy which would be required to break those bonds. Thus, the making of bonds is an exothermic process.

The quantity of energy released or absorbed in a chemical process can be designated by an enthalpy (energy) change, ΔH, for that process. If there is a release of energy when the reaction occurs, the value of ΔH is negative, and the reaction is exothermic. If the reaction results in a net consumption of energy, then ΔH is positive, and the reaction is endothermic.

Figure 3. A simple chemical process.

$$H_2 \longrightarrow H + H$$

Critical Thinking Questions

Answer CTQs 5 – 7 as a team.

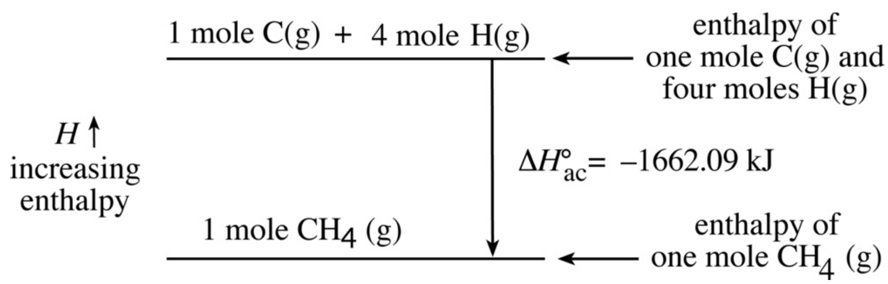
5. Is the chemical reaction represented in Figure 3 exothermic or endothermic?

6. Is ΔH for the chemical reaction represented in Figure 3 positive or negative?

1. Provide a chemical equation for a reaction with a value of ΔH that has the same magnitude of ΔH as the reaction in Figure 3, but has the opposite sign.

Model 4: Enthalpy of Atom Combination.

Figure 4. The enthalpy of atom combination of CH_4(g) at 25 °C.



When a mole of a compound is produced from its constituent atoms in the gas phase at 1 atmosphere pressure and 25 °C, energy is released as bonds are formed. The standard state heat (or enthalpy) of atom combination, ΔH°_{ac}, is the difference in enthalpy of product and reactants ($H^\circ_{product}$ - $H^\circ_{reactants}$) when this occurs. Equation 3 is the (hypothetical) chemical equation for this process for CH_4(g), and Figure 4 provides a visual representation of this process.

$$C(g) + 4H(g) \longrightarrow CH_4(g) \qquad (3)$$

Critical Thinking Questions

Answer CTQs 8 – 12 as a team.

8. Based on the information in Model 4, what is the value of ΔH° for reaction 3?

9. Is the enthalpy of atom combination for CH_4(g) exothermic or endothermic?

Table 1. Standard state enthalpies of atom combination, ΔH°_{ac}.

Substance	ΔH°_{ac} (kJ/mol)	Substance	ΔH°_{ac} (kJ/mol)
H(g)	0	CH_4(g)	–1662.09
C(g)	0		
N(g)	0	H_2O(g)	–926.29
O(g)	0	H_2O(ℓ)	–970.30
H_2(g)	–435.30	NH_3(g)	–1171.76
N_2(g)	–945.408	NO_2(g)	–937.86
O_2(g)	–498.340	N_2O_4(g)	–1932.93

10. Based on the data in Table 1, what is ΔH° for the reaction represented by

$$H(g) + H(g) \longrightarrow H_2(g)?$$

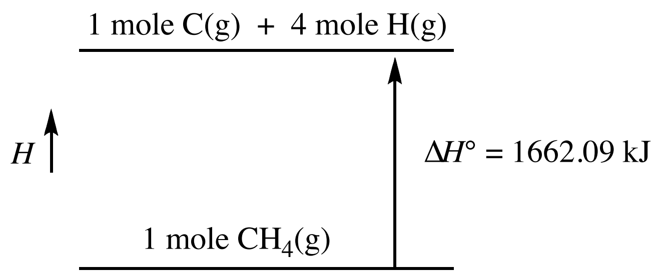
11. Why is ΔH°_{ac} of C(g) = 0? Why is ΔH°_{ac} of H(g) = 0?

12. For molecules, why are all of the values for enthalpies of atom combination negative?

13. a) Individually, draw the Lewis structures for N_2 and O_2. Once all team members are done, compare answers and make any needed changes.

b) Individually, explain how these Lewis structures are consistent with the relative enthalpies of atom combination for N_2(g) and O_2(g). Once all team members are done, compare your answers and reach consensus on a team best answer.

Model 5: Breaking One Mole of CH_4(g) into its Constituent Atoms.



One can also imagine the process in which a mole of a substance is broken apart into its constituent gas phase atoms. This is precisely the reverse of an "enthalpy of atom combination reaction," and, in this case, energy will be consumed. For example, the value of $\Delta H°$ for the reaction represented by

$$CH_4\,(g) \longrightarrow C(g) + 4H(g)$$

is 1662.09 kJ/mole, as shown in Model 4.

Critical Thinking Questions

Answer CTQs 14 and 15 as a team.

14. What is the value of $\Delta H°$ for the overall process of separating one mole of CH_4 into its constituent atoms, and then reforming one mole of CH_4?

15. a) Calculate the amount of energy released (always a positive number) when exactly 2 moles of CH_4 are formed from the appropriate constituent atoms (as opposed to forming *one* mole of CH_4).

    b) Calculate the change in enthalpy when 1.5 moles of C(g) combines with 6 moles of H(g) to form 1.5 moles of CH_4 (g).

Model 6: Bond Strength and Enthalpies of Atom Combination.

Recall that for bonds between pairs of atoms, "the stronger the bond, the shorter the bond length." That is, a C–O double bond is stronger than a C–O single bond, and the double bond is also shorter. For bonds between similar atoms, we also find that "the shorter the bond length, the stronger the bond."

Critical Thinking Questions

16. Consider H–F, H–Cl, and H–Br.
    a) Individually, rank the three molecules in order of increasing bond length and explain your reasoning. Check your answer with your teammates before continuing to part b.
    b) Based on the answer to part a, list the three molecules in order of increasing bond strength.
    c) Examine the ΔH°_{ac} data for these species [see Table A.3 in the Appendix]. As a team, discuss and explain how the answer to part b is (or is not) consistent with these values.

For CTQ 17, discuss and answer each part as a team.

17. a) Which bond is longer: C-H or C-Cl? Explain your reasoning.
    b) Based on your answer to part a, which do you expect to be the stronger bond, C–H or C–Cl?
    c) Examine the ΔH°_{ac} data for CH_4(g) and CH_3Cl(g) and explain how your answer to part b is (or is not) consistent with these values.
    d) Based on the ΔH°_{ac} values for CH_4(g) and CH_3Cl(g), predict ΔH°_{ac} for CH_3F(g) and CH_3Br(g). Explain your reasoning.

Exercises

1. When a bond breaks, is energy released or consumed? Provide an explanation that would convince someone who thinks that your answer is not correct.
2. Predict whether the reactions represented by each of the following equations is exothermic or endothermic:
   a) $CO(g) \longrightarrow C(g) + O(g)$
   b) $2\ H(g) + O(g) \longrightarrow H_2O(g)$
   c) $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$
3. What is the sign for ΔH in each of the reactions in Exercise 1?
4. Which of the following enthalpies of atom combination is obviously incorrect?
   i) $CHCl_3(g)$ ΔH°_{ac} = –1433.84 kJ/mole
   ii) $Cr(g)$ ΔH°_{ac} = 0
   iii) $I_2(s)$ ΔH°_{ac} = 213.68 kJ/mole
   iv) none of these is obviously incorrect
5. The ΔH°_{ac} of C(graphite) is –716.682 kJ/mole and the ΔH°_{ac} of C(diamond) is – 714.787 kJ/mole. Overall, are the bonds stronger in diamond or graphite? Explain your reasoning.
6. Based on their values of ΔH°_{ac} (see Table A.3 in Appendix), indicate whether the following statement is true or false and explain your reasoning.

   The bonds in $SiCl_4(g)$ are stronger than the bonds in $SnCl_4(g)$.
7. Potentially useful information:

Substance	ΔH°_{ac} (kJ/mole)
$H_2O(g)$	–926.29
$H_2S(g)$	–734.74

   a) Determine the O-H bond energy in H_2O and the S–H bond energy in H_2S.
   b) Based on your answer to part a, which is the stronger bond, O-H or S-H?
   c) Give a rationale based on the structures of the molecules for the relative bond strengths of O-H and S-H found above.
8. For each of the following groups of compounds, draw the Lewis structures, predict which molecule will have the most negative ΔH°_{ac}, and explain your reasoning.
   a) Cl_2, Br_2, I_2
   b) N_2, P_2, As_2
9. a) Which do you predict has the stronger bond, C–H or C–Cl?
   b) Calculate the average C–H bond energy in CH_4 from ΔH°_{ac}.
   c) Calculate the average C–Cl bond energy in CCl_4 from ΔH°_{ac}.
   d) Compare the two bond energies. Is this the result you predicted?

10. The O–H bond energy in H_2O is 464 kJ/mole.

    a) Do you expect the C–H bond energy in CH_4 to be less than or greater than the O–H bond energy? Explain.

    b) Is your prediction consistent with the ΔH°_{ac} data? Explain your reasoning.