

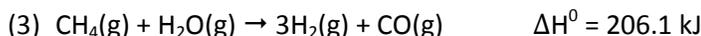
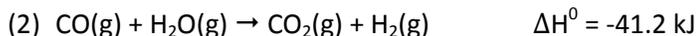
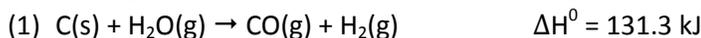
Four Ways to Solve for Heat of a Reaction

1. Hess's Law

Given: A bunch of different reactions that have the reactants and products of the desired reaction.

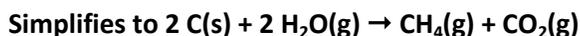
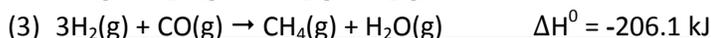
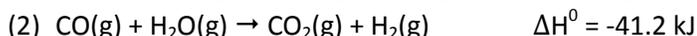
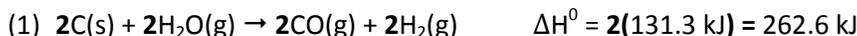
Solution: Rearrange the provided equations so that they can be added together to produce the desired equation. If the coefficients need to be changed, you need to multiply the ΔH given by the same factor. If the equation needs to be flipped, you need to change the sign of the ΔH given.

Example: The combination of coke and steam produces a mixture called coal gas, which can be used as a fuel or as a starting material for other reactions. If we assume coke can be represented by graphite, the equation for the production of coal gas is: $2 \text{C(s)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CH}_4\text{(g)} + \text{CO}_2\text{(g)}$. Determine the standard enthalpy change for this reaction from the following standard reaction enthalpies.



Solution: Notice that the methane, graphite, and carbon dioxide are only present in one equation. You will use these substances for Hess's Law. The water is found in all three; therefore, after you rearrange the equations, the correct coefficient for water should be found.

Equation #1 needs to be multiplied by a factor of **two** because the desired reaction has 2 moles of C(s) reacting. Equation #2 has the carbon dioxide on the correct side of the equation and the correct number of moles of $\text{CO}_2\text{(g)}$ formed, so nothing needs to be done to the second equation. Equation #3 has the methane on the wrong side of the equation, so the equation must be reversed and the sign of the ΔH° changed; however, the correct number of moles of $\text{CH}_4\text{(g)}$ is present in the third equation, so nothing else needs to be done to it.



2. Heats of Formation

Given: The heats of formation of the reactants and products of a given reaction.

Solution: Use the formula: $\Delta H_{\text{rxn}} = \sum n\Delta H^\circ(\text{products}) - \sum m\Delta H^\circ(\text{reactants})$, where n and m are the coefficients of the products and reactants, respectively, in the balanced chemical equation. Remember that the heat of formation of a *reactant* is zero if the reactant is present in its standard state condition.

Example: Determine the heat of combustion of pentaborane, $\text{B}_5\text{H}_9\text{(g)}$, given the following heats of formation at 298 K and 1 atm.

| Substance | $\text{B}_5\text{H}_9\text{(g)}$ | $\text{B}_2\text{O}_3\text{(g)}$ | $\text{H}_2\text{O(g)}$ |
|-----------------------|----------------------------------|----------------------------------|-------------------------|
| ΔH_f (kJ/mol) | 73.2 | -1272.77 | -241.82 |

Solution: The balanced equation of the combustion of pentaborane is:



Therefore, $\Delta H_{\text{rxn}} = (5\Delta H_{\text{f}}(\text{B}_2\text{O}_3) + 9\Delta H_{\text{f}}(\text{H}_2\text{O})) - (2\Delta H_{\text{f}}(\text{B}_5\text{H}_9) + 12\Delta H_{\text{f}}(\text{O}_2))$

$$\Delta H_{\text{rxn}} = (5(-1272.77 \text{ kJ}) + 9(-241.82 \text{ kJ})) - (2(73.2 \text{ kJ}) + 12(0 \text{ kJ})) = -8686.6 \text{ kJ}$$

3. Calorimetry

Given: The temperature change of either water or a bomb calorimeter due to a chemical reaction.

Solution #1: Coffee-Cup Calorimeter (constant pressure)

- Use $q = mc\Delta T$ to determine the amount of energy gained/lost by the water and/or solution. **N.B. If the problem involves dissolving a salt, you must use the mass of the solution (the sum of the water and the salt) in this step!**
- Use $q_{\text{cal}} = -q_{\text{rxn}}$ to determine the amount of energy lost/gained by the reaction. This is the First Law of Thermodynamics.
- Use $q_{\text{rxn}} = n\Delta H_{\text{rxn}}$ to determine the heat of the reaction, where n is the number of moles of the substance used in the reaction.

Example #1: In one experiment, a student placed 50.0 mL of 1.00 M HCl in a coffee-cup calorimeter and carefully measured its temperature to be 25.5°C. To this was added 50.0 mL of 1.00 M NaOH solution whose temperature was also 25.5°C. The mixture was quickly stirred and the student noticed that the temperature of the mixture rose to 32.4°C. What is the heat of the reaction, in kJ/mol? Assume that the density of the solutions is 1.00 g/mL and the specific heat capacity of the mixture is 4.18 J/gK.

- Use $q = mc\Delta T$ to determine the energy gained by the mixture. The total mass of the mixture can be determined using the density of the mixture.
 $q = (100.0 \text{ g})(4.18 \text{ J/gK})(6.9 \text{ K}) = 2884 \text{ J}$
- Therefore, the reaction must have released the same amount of energy, -2884 J.
- Use $q_{\text{rxn}} = n\Delta H_{\text{rxn}}$ to determine the heat of the reaction. 0.0500 moles of both HCl and NaOH are used. Since they have a 1:1 mole ratio in the balanced equation, they are both used up completely with no excess reactants. ($\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$)
 $\Delta H_{\text{rxn}} = -2.884 \text{ kJ} / 0.0500 \text{ moles} = -57.7 \text{ kJ/mol}$

Solution #2: Bomb Calorimeter

- Use $q = C_p\Delta T$ to determine the amount of energy gained by the calorimeter, where C_p is the heat capacity of the calorimeter. You may be given a known reaction ΔH_{rxn} to determine the C_p of the calorimeter first. Use the mass/moles of the given reactant to determine the amount of energy lost by the reaction so that the heat capacity of the calorimeter can be found.
- Use $q_{\text{cal}} = -q_{\text{rxn}}$ to determine the amount of energy lost/gained by the reaction. This is the First Law of Thermodynamics.
- Use $q_{\text{rxn}} = n\Delta H_{\text{rxn}}$ to determine the heat of the reaction, where n is the number of moles of the substance used in the reaction.

Example #2: A bomb calorimeter was calibrated by burning a sample of benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, whose heat of combustion is -3227 kJ/mol. When 1.890 grams of benzoic acid is burned in the calorimeter, the temperature increases by 8.32°C. When 2.680 grams of the rocket fuel hydrazine, N_2H_4 , is burned in the

same calorimeter, the temperature rises from 24.62°C to 33.87°C. Calculate the molar heat of combustion of hydrazine, in kJ/mol.

- The heat capacity of the calorimeter is not given, but can be figured out by the benzoic acid information.
 - The amount of heat released by the sample can be determined by $q = n\Delta H_{\text{rxn}}$.
The number of moles of benzoic acid = (1.890 g)/(122.12 g/mol) = 0.0155 moles
The amount of heat released by the sample: $q = (0.0155 \text{ moles})(-3227 \text{ kJ/mol}) = -50.0 \text{ kJ}$
 - The calorimeter would therefore absorb 50.0 kJ of energy during the combustion.
 - The heat capacity of the calorimeter can now be determined using $q = C_p\Delta T$
 $C_p = (50.0 \text{ kJ})/(8.32^\circ\text{C}) = 6.01 \text{ kJ}/^\circ\text{C}$
- Using the same heat capacity of the bomb calorimeter, the amount of heat absorbed by the calorimeter when the hydrazine is burned can be calculated.
 - $q_{\text{rxn}} = (6.01 \text{ kJ}/^\circ\text{C})(9.25^\circ\text{C}) = 55.6 \text{ kJ}$
 - The reaction must have released -55.6 kJ of energy.
 - Use $q_{\text{rxn}} = n\Delta H_{\text{rxn}}$ to determine the heat of the reaction.
The number of moles of hydrazine = (2.680 g)/(32.05 g/mol) = 0.0836 moles
 $\Delta H_{\text{rxn}} = -55.6 \text{ kJ} / 0.0836 \text{ mol} = -665 \text{ kJ/mol}$

4. Bond Enthalpies

Given: The energy needed to break bonds present in the reactants and the products

Solution: Use the formula $\Delta H_{\text{rxn}} = \Sigma(\text{energy bonds broken}) - \Sigma(\text{energy bonds formed})$

Example: Estimate the heat of combustion of butane, in kJ/mol, using the following bond enthalpies.

| Bond | C-C | C-H | O=O | C=O | O-H |
|------------------------|-----|-----|-----|-----|-----|
| Bond Enthalpy (kJ/mol) | 347 | 413 | 495 | 799 | 463 |

The balanced equation for the combustion of butane is $2\text{C}_4\text{H}_{10} + 13\text{O}_2 \rightarrow 8\text{CO}_2 + 10\text{H}_2\text{O}$.

In two moles of butane, there are 6 moles of C-C bonds and 20 moles of C-H bonds to break.

In thirteen moles of oxygen, there are 13 moles of O=O bonds to break.

In eight moles of carbon dioxide, there are 16 moles of C=O bonds to form.

In ten moles of water, there are 20 moles of O-H bonds to form.

$$\Delta H_{\text{rxn}} = \Sigma(\text{energy bonds broken}) - \Sigma(\text{energy bonds formed})$$

$$\Delta H_{\text{rxn}} = (6(347 \text{ kJ}) + 20(413 \text{ kJ}) + 13(495 \text{ kJ})) - (16(799 \text{ kJ}) + 20(463 \text{ kJ})) = -5267 \text{ kJ}$$

However, the above equation is for the combustion of **2 moles of butane**. The question asks for the combustion of butane in terms of kJ **per mole**. You must be careful with combustion reactions to ensure that you are solving for the right quantity!

$$\Delta H_{\text{rxn}} = -5267 \text{ kJ} / 2 \text{ mol} = -2634 \text{ kJ/mol}$$