

ALE 26. Energy Changes (ΔE) and Enthalpy Changes (ΔH) in Chemical Reactions
(Reference: Chapter 6 - Silberberg 5th edition)

Important!! For answers that involve a calculation you must show your work neatly using dimensional analysis with correct significant figures and units to receive full credit. No work, no credit. Report numerical answers to the correct number of significant figures. **CIRCLE ALL NUMERICAL RESPONSES.**

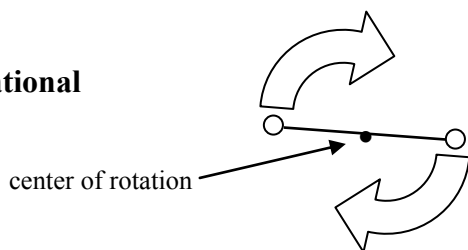
The Model: Internal Energy and the First Law of Thermodynamics

Each particle in a system has potential energy (E_p) and kinetic energy (E_k), the sum of these energies for all particles in the system is the, **internal energy**, E (some textbooks use the symbol, U) of a system is understood to be all of the energies of the molecules in the system. There are three kinds of kinetic energy:

translational 

vibrational 

rotational



The **First Law of Thermodynamics** says that the change in the internal energy of a system is dependent on two things:

- 1) the system exchanging heat (q) with the surroundings and
- 2) the system either doing work (w) on the surroundings or the surroundings doing work on the system.

$$\Delta E = q + w$$

If a system undergoes no exchange of heat with the surroundings, and if the system neither does work on nor is worked upon by the surroundings, then the internal energy of the system will not change.

Key Questions

1. Explain how **each** of the sign conventions for q and w makes sense as far as E increasing or decreasing when the system:
 - a. accepts heat from the surroundings. (Is $q > 0$ or is $q < 0$? How does this impact ΔE ?)
 - b. releases heat into the surroundings. (Is $q > 0$ or is $q < 0$? How does this impact ΔE ?)
 - c. does work on the surroundings. (Is $w > 0$ or is $w < 0$? How does this impact ΔE ?)
 - d. is worked upon by the surroundings. (Is $w > 0$ or is $w < 0$? How does this impact ΔE ?)

- 2a. What happens to the various internal energies of the molecules when the system accepts heat from the surroundings (and no work is performed)? (Circle the correct response.)
- Molecules move at faster speeds, rotate faster, vibrate more, and may even be found in excited electronic states.
 - Molecules move at slower speeds, rotate slower, vibrate less, and more molecules are found in the ground (*i.e.*, lowest energy) electronic state.
- b. What happens to the various internal energies of the molecules when the system does work on the surroundings (and no heat is exchanged)? (Circle the correct response.)
- molecules move at faster speeds, rotate faster, vibrate more, and may even be found in excited electronic states.
 - molecules move at slower speeds, rotate slower, vibrate less, and more molecules are found in the ground electronic state.

Exercise

- A. A system releases 406 J of energy into the surroundings and at the same time does 217 J of work on the surroundings. What is the value of the change in internal energy of the system, ΔE ? What is the significance if ΔE is a negative value? A positive value?

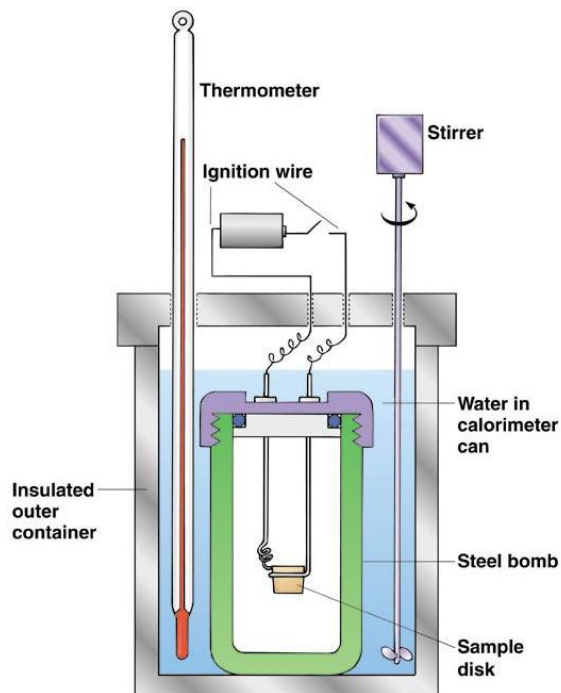
Constant-Volume Calorimetry

Where do heats of combustion (*i.e.* enthalpy of combustion, $\Delta H_{\text{combustion}}$) come from?

The Model: Bomb Calorimetry

A schematic of the typical constant-volume (or “bomb”) calorimeter is shown to the right. A sample (perhaps weighing 1 gram) is placed in the sample disk and the ignition wire is put in contact with the sample. The “bomb” (a machine-crafted, quarter-inch-thick stainless steel container) is closed (rather like a jar with a screw-on lid) and several (~20) atmospheres of oxygen gas are pumped into the bomb. The bomb is then placed in (typically) 2.00-L of H_2O , in which is a thermometer and a motorized stirrer. The insulated outer container is closed and the stirrer turned on. The system is allowed to reach thermal equilibrium and the initial temperature is measured.

When the system has reached thermal equilibrium, a switch is thrown which completes the circuit and a spark is sent down the ignition



wire. When the spark comes into contact with the sample in the O₂-rich bomb, the sample is combusted completely. A by-product of all combustion reactions is heat. The heat disperses throughout the bomb and the water surrounding the bomb. The temperature of the water increases and the thermometer responds. If the outer container is perfectly insulating, the system will again reach thermal equilibrium and the final temperature can easily be measured.

Key Questions

3. When pressure is a constant, the physical definition of pressure-volume work is: $w = -P \Delta V$
 - a. How much change occurs to the volume of the machine-crafted, quarter-inch-thick stainless steel bomb when a sample is combusted in it?

 - b. Assuming the volume within the bomb is the same before and after the combustion, how much work is done by the chemical system inside the bomb when the sample combusts?

4. In *constant-volume* calorimetry, the change in internal energy for a combusted material is simply equal to the amount of heat exchanged:

$$\Delta E = q$$

Explain where this equation comes from. (*Hint*: What did we learn about what the First Law of Thermodynamics says a change in internal energy is equal to?)

5. In the last ALE, we saw that the amount of heat needed to change the temperature of a mass m by ΔT is:

$$q = C \cdot m \cdot \Delta T \text{ (where } \Delta T = t_f - t_i)$$

Because the mass of the constant-volume calorimeter is a constant from one experiment to the next, instead of having a specific heat (C), the calorimeter has a heat capacity (C_{cal}). The equation relating the change in internal energy of the combusted sample with the change in temperature of the calorimeter is:

$$\Delta E = -C_{cal} \Delta T$$

- a. What are the units of the calorimeter's heat capacity?

- b. Why is there a negative sign in the equation? (*Hints*: Where is the thermometer that the temperature readings are made: in the system itself, or in the surroundings of the system? The combustion reaction is exothermic, so what is the sign of ΔT going to be?)

Exercise

- B. Before a bomb calorimeter can be used to analyze the heat of combustion of an unknown, the heat capacity of the calorimeter must be determined. One standard that is used in bomb calorimetry is 2,2,4-trimethylpentane (“isooctane”, C_8H_{18}). The change in internal energy (ΔE) per gram of combusted isooctane is -47.71 kJ/g . Suppose 0.692 g of octane is combusted in a bomb calorimeter with a heat capacity of $9.98 \text{ kJ/}^\circ\text{C}$. The initial temperature of the calorimeter before the combustion is $25.00 \text{ }^\circ\text{C}$. Assuming no heat is lost to the outside of the calorimeter, what should be the final temperature of the calorimeter after the reaction? (*Hints*: ① How much heat is released when 0.692 g of isooctane is combusted? ② What is the change in temperature of the calorimeter when the isooctane is combusted? ③ Does the temperature of the calorimeter rise or fall when the isooctane is combusted? Find T_f .)

The Model: Enthalpy

Enthalpy (or “heat content”) is symbolized by H and is defined as

$$H = E + PV$$

where E is internal energy, P is pressure, and V is volume of the system. A change in enthalpy is, therefore, related to the change in internal energy and the change in the product of the system’s pressure and volume:

$$\Delta H = \Delta E + \Delta(PV) \quad \text{(Equation 1)}$$

Key Questions

- 6a. Finish the following equation of state for n moles of an ideally-behaving gas at absolute temperature T :

$$PV = \underline{\hspace{2cm}}$$

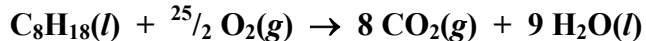
- b. When converting from the change in internal energy to the change in enthalpy for a combustion reaction, it is typical to use eqn 2

$$\Delta H = \Delta E + \Delta n_{\text{gas}} R T_i \quad \text{(Equation 2)}$$

where Δn_{gas} is the number of moles of gaseous products minus the number of moles of gaseous reactants in the combustion reaction, and T_i is the *absolute* temperature at which the combustion was initiated. Use eqn 1 and your answer to [Question 6a](#) to derive eqn 2.

Exercises

C. ① The complete combustion of isooctane at 25 °C may be represented by:



Calculate Δn_{gas} when 0.692 g of isooctane (114.23 g/mol) is completely combusted.

Hints: $\Delta n_{\text{gas}} = n_{\text{gaseous products}} - n_{\text{gaseous reactants}}$

Calculate the number of moles of isooctane. Calculate the number of moles of oxygen that would react with that amount of isooctane, and calculate the number of moles of carbon dioxide that would be produced from that amount of isooctane. Circle your answer.

② Calculate $\Delta n_{\text{gas}} R T_i$ when 0.692 g of isooctane is completely combusted at 25.0 °C. (This quantity should have units of J, so $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$.) Circle your answer.

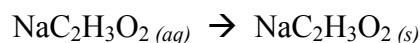
③ Use eqn 2 to calculate ΔH when 0.692 g of isooctane is completely combusted at 25 °C. (ΔE was calculated in Exercise B. Be mindful of units!) Circle your answer.

④ Calculate the heat of combustion of isooctane in kJ/mol at 25 °C. The heat of combustion of a substance is simply a ratio of the change in enthalpy when that substance was combusted to the number of moles of the substance that was combusted (*i.e.*, $\Delta H_{\text{combustion}} = \Delta H / n$). Circle your answer.

- D. "Hot packs" used by skiers, climbers and others for warmth are based on the crystallization of sodium acetate from a highly concentrated solution.
- a.) What is the sign of ΔH for this crystallization? Explain why.

b.) Is the reaction exothermic or endothermic? Explain why.

- c.) Is heat a reactant or a product? Answer this question by writing heat in the appropriate place in the reaction below.



- E. A chemical engineer studying the properties of fuels placed 1.500 g of a hydrocarbon in the bomb of a calorimeter and filled it with oxygen gas. The bomb was immersed in 2.500 L of water (assume the density of water is 1.000g/mL) and the reaction initiated. The water temperature rose from 20.00 °C to 23.55 °C. If the calorimeter (excluding the water) had a heat capacity of 403 J/°C, calculate the heat of combustion per gram of the fuel. Hint: heat lost by the combustion reaction = heat gained by the water + heat gained calorimeter