

Chapter 5

Distinguish between heat and work.

Work and heat are forms of energy. Work is the energy needed to move an object through a distance and heat is the energy needed to raise its temperature. Although work can be transformed completely into heat, heat cannot be transformed completely into work. One difference between the two is that work is an organized form of energy and can move large objects. For instance, the work done by the expansion of a gas against a fixed pressure is given by $w = P_{\text{ext}} (V_{\text{final}} - V_{\text{initial}})$. Heat is more random and mainly is able to make small particles such as atoms and molecules move more rapidly. Both heat and work appear only during energy changes. We cannot speak of absolute energy, but rather of energy changes.

Define specific heat and state its formula.

Specific heat is the quantity of heat needed to raise the temperature of one gram of substance by one degree Celsius. Specific heat depends on the nature of the substance being heated. The specific heat of water for example is greater than that of iron. Specific heat has the units of $J/(g^{\circ}C)$. The quantity of heat absorbed by an object that undergoes a temperature change is given by $\rightarrow \text{heat absorbed} = \text{mass} \times \text{spht} \times \Delta T$.

Apply the first law of thermodynamics $\Delta E = q + w$

To use the first law of thermodynamics, we need to express work and heat in the same units. In chemistry, we express heat and work as energy flowing into the system. This means that q is the heat absorbed by the system, and w is the work done on the system. The first law can be thought of as an energy bookkeeping equation tracking energy input and output. For example, an apple merchant wishes to keep track of his daily assets, cash (work) and apples (heat). The two assets may be inter-converted, and either cash or apples may be lost or gained by the merchant. The comparison fails in that the “rate of exchange” between heat and work is fixed and in energy systems we do not know the total value of E (the total assets) and can only determine its changes ΔE .

Explain what is meant by a state function.

A state function or state property depends on system's starting point (initial state) and ending point (final state). A state function does not depend on how the change in the system occurred (the pathway). For example, the altitude change from San Francisco to Denver is a state function. The actual mileage traveled depends on the route. The mileage traveled is a path function. Both heat and work are path functions; they can be state functions when the path is specified. An important path is one of constant pressure, a condition frequently encountered in the laboratory. The heat evolved at constant pressure equals a state function, the enthalpy change in a system. For example, a gas at $25^{\circ}C$ has a different energy than a gas at $30^{\circ}C$. It is not about phase, which is the same in both cases. It is about the energy in each system.

Calculate the heat of a reaction at constant volume using a bomb calorimetry data.

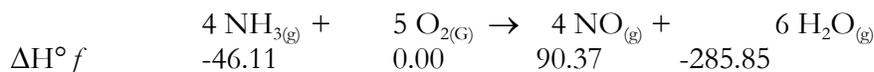
The heat given off by a reaction occurring in a bomb calorimeter increases the temperature of both the bomb and the water surrounding it. When using a bomb calorimeter, unlike a coffee cup calorimeter, the mass of the surroundings is not part of the problem. The C_v represents the amount of energy needed to bring about a change of $1^{\circ}C$ in the calorimeter. The source of the energy for the temperature change is the reaction. The energy that the calorimeter absorbs must equal the energy that the reaction released.

$$-q_v = (C_v) (\Delta T_{\text{bomb}}),$$

The change in the state function internal energy, $\Delta E = qv$, the heat produced at constant volume. Notice that specifying its pathway, one of constant volume, has restricted heat, a path function, so that it equals a state function. The amount of energy difference is very small, so we will consider this as an enthalpy change even though it is not.

Use Hess's law to calculate the standard formation reactions, that is, compute $\Delta H^\circ_{\text{rxn}}$ from $\Delta H^\circ f$ values.

Standard formation reactions greatly simplify the application of Hess's law. For example we can calculate the $\Delta H^\circ_{\text{rxn}}$ in kJ/mol for the oxidation of ammonia in the presence of a platinum catalyst, if we know the products and the reactants and the $\Delta H^\circ f$ respectfully.



Each of the values listed below the compound are for the formation of one mole of that compound. The

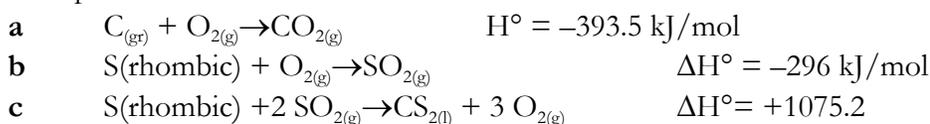
value for oxygen is zero because the product of the formation reaction is an element in its most stable form. In order to use these values instead of writing out each sentence and then invoking Hess's law, we use a modified version of the equation. This equation uses the heats of formations at stable state for each compound in the balanced equation.

$\Delta H^\circ_{\text{rxn}} = \sum A \Delta H^\circ f$ (products) - $\sum B \Delta H^\circ f$ (reactants) ; where A and B stand for the individual stoichiometric coefficients obtained from the balanced equation.

$$\Delta H^\circ_{\text{rxn}} = 4(90.37 \text{ kJ/mol}) + 6(-285.85 \text{ kJ/mol}) - [4(-46.11 \text{ kJ/mol}) + 5(0.00 \text{ kJ/mol})] = -1583.00 \text{ kJ}$$

Write the standard formation reaction for any substance. Combine these types of reactions with others to calculate the heat of reaction for any substance.

To use Hess's law, all reactants and products must be under the same conditions. Consider the Hess's expressions below:



Consider the $\text{CO}_{2(\text{g})}$ produced by reaction **a** and consumed by reaction **c**. If reaction **a** produces $\text{CO}_{2(\text{g})}$ at 298K and 1.00 atm and reaction **c** consumes $\text{CO}_{2(\text{g})}$ at 323 K and 4 atm, then energy is needed to heat and compress the gas. (see Hess's law handout for more problems and information)

On the other hand, if both reactants and products are in a well-defined state at one temperature, no energy is needed for heating and compression (or produced by cooling and expansion). The *standard state* is a pressure of one atmosphere or, for a solute in solution, a concentration of one mole per liter of solution. The degree sign($^\circ$) on the ΔH° indicates that the molar enthalpy change is measured with the reactants and products in their standard states. Note that the standard state does not mention the temperature. Temperature should be written as a subscript in Kelvin, ΔH°_{298} . Often, however, the subscript is omitted and 298 K (25°C) is assumed.

The standard state does not mention anything about the form of a substance. We need to state the form of the matter being used: $\text{O}_{2(\text{g})}$ versus $\text{O}_{3(\text{g})}$ or ozone. Also we can refer to the standard state of steam or water vapor, $\text{H}_2\text{O}_{(\text{g})}$, of ice $\text{H}_2\text{O}_{(\text{s})}$, and of liquid water, $\text{H}_2\text{O}_{(\text{l})}$.

Matter is formed from elements in the most stable state. Standard formation reaction for a substance is one that produces one mole of that substance in its standard state from the elements in their standard states and most stable forms. Most stable forms of elements at 25°C in periodic arrangement (most are crystalline or solid, c or s)

IIB	IVA	VA	VIA	VIIA	VIIIA
	$C_{(\text{graphite})}$	$N_{2(\text{g})}$	$O_{2(\text{g})}$	$H_{2(\text{g})}$	$He_{(\text{g})}$
		$P_{4(\text{S, white})}$	$S_{8(\text{rhombic})}$	$F_{2(\text{g})}$	$Ne_{(\text{g})}$
		$As_{(\text{s, grav})}$	$Se_{(\text{s, grav})}$	$Cl_{2(\text{g})}$	$Ar_{(\text{g})}$
				$Br_{2(\text{l})}$	$Kr_{(\text{g})}$
				$I_{2(\text{s})}$	$Xe_{(\text{g})}$

The standard molar enthalpy of formation is the energy evolved at constant pressure (the enthalpy change) when the standard formation reaction occurs.