

Thermochemistry

Principles of Reactivity: Energy and Chemical Reactions

Thermochemistry

Energy
 Potential (mgh)
 Kinetic ($\frac{1}{2}mv^2$)

Unit = Joule (Nm or kgm^2/s^2)
 $w = Fd$
 Energy can be used to do work
 1 calorie = 4.184J
 1kcal = 1Cal = 1,000cal

ENERGY is the capacity to do work or transfer heat.
HEAT is the form of energy that flows between 2 objects because of their difference in temperature.

Other forms of energy —
 light electrical kinetic and potential
 chemical potential energy (stored in the bonds of the compound)

Sunlight pumps energy into ocean water, converting liquid water to water vapor. **ENERGY TRANSFER**

Water vapor condenses to liquid water, forming clouds and transferring energy to the surrounding atmosphere. **STORED ENERGY**

The energy stored in the atmosphere is converted to mechanical energy through wind and waves. **ENERGY TRANSFER** **RELEASED ENERGY**

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Conservation of energy – Energy can be neither created nor destroyed.

First Law of Thermodynamics – The total energy of the universe is constant.

Reactions involve a rearrangement of atoms which coincides with a change in energy.

Reactions in which energy is released are “product favored” reactions.

Reaction 1

Reaction 2

(a) Translational motion (b) Rotational motion (c) Vibrational motion

(d) Intramolecular forces (e) Intermolecular forces

Internal Energy (U) – Total energy of the system
Kinetic (thermal) energy:
 Translational
 Rotational
 Vibrational
Potential energy
 Nuclear forces
 Electrostatic attractions (Chemical energy)
 Intramolecular - Bonds between atoms
 Intermolecular - Attractions between molecules

Temperature and Heat

- Heat is not the same as temperature
- The more thermal energy a substance has, the greater the motion of its atoms and molecules.
- The total thermal energy in an object is the sum of the individual energies of all the atoms, molecules, or ions in that object.

The thermal energy of a given substance depends not only on temperature but also on the amount of substance. (E.g. Warm bath vs. hot coffee)

System: The portion of the universe under study.
Surroundings: Everything else besides the system.
Interaction: Exchange of energy and or matter between the system and its surroundings.
Systems:
Open system: Exchanges both matter and energy with its surroundings.
Closed system: Exchanges only energy with its surroundings.
Isolated system: Exchanges neither energy nor matter with its surroundings.

Thermal Equilibrium

Heat transfer occurs when two objects at different temperatures are brought into contact.

Heat energy is transferred until the system comes to **thermal equilibrium**.

Within a system, the heat lost by the hotter object is equal to the heat gained by the cooler object.

When heat transfer occurs across the boundary between a system and the surrounding, the directionality of the heat transfer is described as:

Exothermic: heat is transferred from a system to the surroundings.
Endothermic: Heat is transferred from the surroundings to the system

Movie

Specific Heat Capacity and Energy Transfer

Specific Heat: The amount of energy required to increase one gram of a substance by 1K (or °C)

Specific heat capacity (J/g · K)		Change in temperature (K)
↓		↓
$q = C \times m \times \Delta T$		
↑		↑
Heat transferred (J)		Mass of substance (g)

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Compare heat capacity (J/K) with specific heat capacity (J/gK) and molar heat capacity J/mol K

Sign of ΔT	Meaning
Positive	$T_{\text{final}} > T_{\text{initial}}$, so T has increased, and q will be positive. Heat has been transferred to the object under study.
Negative	$T_{\text{final}} < T_{\text{initial}}$, so T has decreased, and q will be negative. Heat has been transferred out of the object under study.

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Specific Heat and Energy Transfer

Specific Heat

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Sample Problems:

- In an experiment it was determined that 59.8J was required to change the temperature of 25.0g of ethylene glycol (a compound used as antifreeze in automobile engines) by 1.00K. Calculate the specific heat capacity of ethylene glycol from these data.
- A 15.5g piece of chromium, heated to 100.0°C, is dropped into 55.5g of water at 16.5°C. The final temperature of the metal and the water is 18.9°C. What is the specific heat capacity of chromium? (Assume no heat is lost to the container or to the surrounding air.)
- A piece of iron (400.g) is heated in a flame and then dropped into a beaker containing 1,000.g of water. The original temperature of the water was 20.0°C, and the final temperature of the water and iron is 32.8°C after thermal equilibrium has been attained. What was the original temperature of the hot iron bar? (Assume no heat is lost to the beaker or to the surrounding air.)

Sample Problems:

1. In an experiment it was determined that 59.8J was required to change the temperature of 25.0g of ethylene glycol (a compound used as antifreeze in automobile engines) by 1.00K. Calculate the specific heat capacity of ethylene glycol from these data.

Answer:

Specific Heat Capacity Units = J/gK

$$59.8\text{ J} / [(25.0\text{g})(1.00\text{K})] = 2.39\text{ J/gK}$$

Sample Problems:

2. A 15.5g piece of chromium, heated to 100.0°C, is dropped into 55.5g of water at 16.5°C. The final temperature of the metal and the water is 18.9°C. What is the specific heat capacity of chromium? (Assume no heat is lost to the container or to the surrounding air.)

Answer:

Heat lost by chromium

$$-q = (15.5\text{g})(C)(18.9^\circ\text{C} - 100.0^\circ\text{C}) = -1257.05(C)$$

Heat gained by water

$$q = (55.5\text{g})(4.184\text{J/g}^\circ\text{C})(18.9^\circ\text{C} - 16.5^\circ\text{C}) = 557.309\text{J}$$

$$1257.05\text{g}^{-1}\text{C}^{-1}(C) = 557.309\text{J}$$

$$C = 557.309 / 1257.05 = .443\text{J/g}^\circ\text{C}$$

Sample Problems:

3. A piece of iron (400.g) is heated in a flame and then dropped into a beaker containing 1,000.g of water. The original temperature of the water was 20.0°C, and the final temperature of the water and iron is 32.8°C after thermal equilibrium has been attained. What was the original temperature of the hot iron bar? (Assume no heat is lost to the beaker or to the surrounding air.)

Answer:

You need the specific heat capacity of iron = 0.449J/gK (p243)

$$(400.\text{g})(0.449)(32.8^\circ\text{C} - T_i) = -(1,000.\text{g})(4.184\text{J/g}^\circ\text{C})(32.8^\circ\text{C} - 20.0^\circ\text{C})$$

$$T_i = 330.992^\circ\text{C} = 331^\circ\text{C}$$

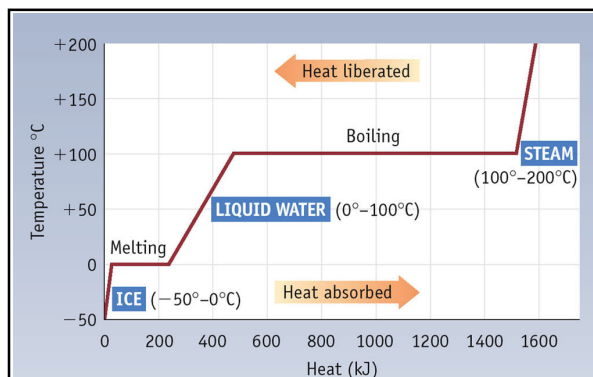
Phase Changes (Change of State)

Solid → Liquid → Gas

Heat of Fusion: Heat required to convert a solid at its melting point to a liquid

Heat of Vaporization: Heat required to convert a liquid at its boiling point to a gas.

Heat of Sublimation: Heat required to take a substance directly from its solid to its gas state.



Note that the temperature of a substance does not change as it is going through a phase change.

Example:

How much heat must be absorbed to warm 25.0g of liquid methanol, CH₃OH, from 25.0°C to its boiling point (64.6°C) and then to evaporate the methanol completely at that temperature? The specific heat capacity of liquid methanol is 2.53J/gK. The heat of vaporization of methanol is 2.00kJ/g

Example:

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Answer:

Step 1

$$q_1 = m(C)(\Delta T) = 25.0g(2.53J/gK)(64.6^\circ C - 25.0^\circ C) = 2504.7J$$

Step 2

$$q_2 = 25.0g(2.00 \times 10^3 J/g) = 50,000J$$

$$\text{Answer} = 52,504.7J = \mathbf{52.5kJ}$$

Pressure – Volume Work

$\Delta E = q + w$ So far we have just considered q

(E = internal energy, q = heat and w = work)

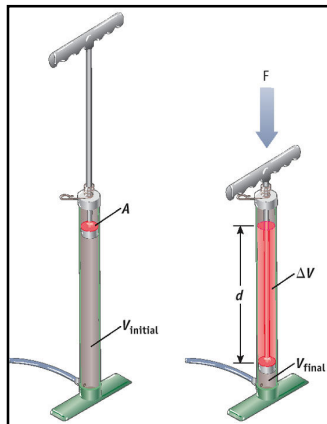
This section focuses on work as it relates to changes in volume against a constant pressure.

The sublimating dry ice (the system) does work on its surroundings (the bag, book and atmosphere



(a) Pieces of dry ice [CO₂(s), -78°C] are placed in a plastic bag. The dry ice will sublime (change directly from a solid to a gas) upon the input of heat.

(b) Heat is absorbed by CO₂(s) when it sublimates and the system (the contents of the bag) does work on its surroundings by lifting the book against the force of gravity.



Recall:

$$\Delta E = q + w$$

$$w = Fd$$

$$P = F/A$$

(P = Constant pressure)

$$w = PAd = P \Delta V$$

$$w = -P \Delta V$$

(by sign convention)

This is pressure-volume work

*See sign conventions in handout.

Heat content of a system at constant pressure is called enthalpy, H

The change in heat content (q_p) is the enthalpy change = ΔH

$$q_p = \Delta H = \Delta E + P \Delta V \quad (\text{From } \Delta E = q_p - P \Delta V)$$

$q_v = \Delta E$ (constant volume, $\Delta V = 0$. P is not constant. No work is done on or by the system.

ΔH and ΔE differ by an amount of work w , done on or by the system

$$q_p = q_v + P \Delta V \quad \text{or} \quad \Delta H = \Delta E + P \Delta V$$

Negative ΔE and ΔH : Energy from system to surroundings

Positive ΔE and ΔH : Energy from surroundings to system

Internal energy (E) is a **state function**.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

A **state function** only depends on the current conditions of the system and not upon how that state was reached.

Cannot measure absolute internal energy, but we usually only care about ΔE

Depends on the present state of the system and not on its history

Heat (q) and work (w) are *not* state functions (They are not contained in the system and exist as a consequence of a change in the system)

For a given change, different combinations of heat and work can lead to the same ΔE .

Functions of state are reversible.

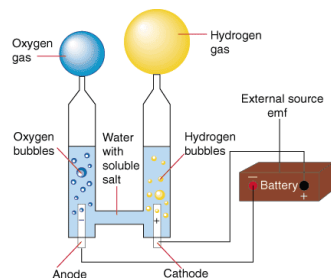
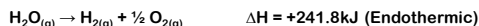


Elevation is a state function, but distance is not.

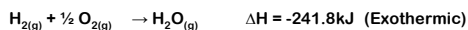
Enthalpy Changes For Chemical Reactions

Enthalpy (heat) of Reactions

Enthalpy changes accompany chemical Reactions:



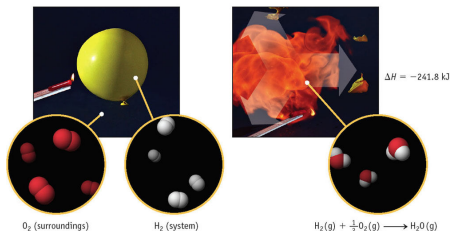
For the opposite reaction (see image)



Note that this is the molar enthalpy for H_2 and H_2O , but not O_2

The molar enthalpy for O_2 would be 2x the reaction, or

$$\Delta H = -483.6 \text{ kJ}$$



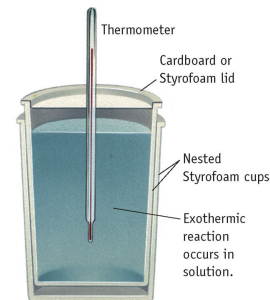
Calorimetry: Using heat transfer and the specific heat (and/or heat capacity) of a known substance to determine the enthalpy change or internal energy change.

Constant Pressure Calorimeter (Coffee Cup Calorimeter):

Determines enthalpy (ΔH) change

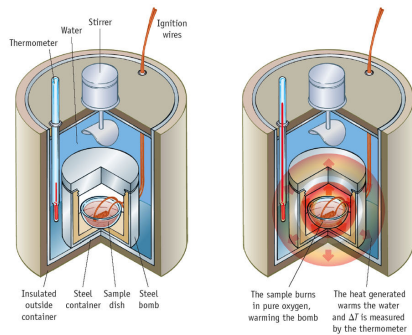
The styrofoam walls are insulating.

The system is open to the air (constant pressure)



Constant Volume Calorimeters ("Bomb" Calorimeters):

Determines the internal energy change (ΔE) of the system.



$$\Delta E = q_v = q_{\text{rxn}} = -(q_{\text{bomb}} + q_{\text{water}})$$

The energy transferred to the bomb is given by the heat capacity (usually in J/K)

The energy transferred to the water is given by the specific heat equation:

$$q_{\text{water}} = m \times C \times \Delta T$$

Watch units of J vs kJ

Example Problems:

1. Assume you mix 200. mL of 0.400M HCl with 200. mL of 0.400M NaOH in a coffee-cup calorimeter. The temperature of the solutions before mixing was 25.10°C; after mixing and allowing the reaction to occur, the temperature is 27.78°C. What is the molar enthalpy of neutralization of the acid? (Assume that the densities of all solutions are 1.00g/mL and their specific heat capacities are 4.20 J/gK)

2. A 1.00g sample of ordinary table sugar (sucrose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is burned in a bomb calorimeter. The temperature of 1.50×10^3 g of water in the calorimeter rises from 25.00°C to 27.32°C. The heat capacity of the bomb is 837J/K, and the specific heat of the water is 4.20J/gK.

- Calculate the heat evolved per gram of sucrose.
- Calculate the heat evolved per mole of sucrose.

Example Problems Answer:

1. Assume you mix 200. mL of 0.400M HCl with 200. mL of 0.400M NaOH in a coffee-cup calorimeter. The temperature of the solutions before mixing was 25.10°C; after mixing and allowing the reaction to occur, the temperature is 27.78°C. What is the molar enthalpy of neutralization of the acid? (Assume that the densities of all solutions are 1.00g/mL and their specific heat capacities are 4.20 J/gK)

Equation:



$$\text{Total volume of solutions} = 200. \text{ mL} + 200. \text{ mL} = 400. \text{ mL}$$

$$\text{Total mass} = 400. \text{ mL} (1 \text{ g/mL}) = 400. \text{ g}$$

$$\text{Moles of HCl and NaOH (each)} = .200 \text{ L} (0.400 \text{ mol/L}) = .0800 \text{ mol}$$

$$q = (400. \text{ g})(4.20 \text{ J/gK})(27.78^\circ\text{C} - 25.10^\circ\text{C}) = 4502.4 \text{ J}$$

$$\text{Molar enthalpy} = 4502.4 \text{ J} / .0800 \text{ mol} = 56,280 \text{ J/mol} = 56.3 \text{ kJ/mol}$$

Example Problems Answer:

2. A 1.00g sample of ordinary table sugar (sucrose $C_{12}H_{22}O_{11}$) is burned in a bomb calorimeter. The temperature of 1.50×10^3 g of water in the calorimeter rises from 25.00°C to 27.32°C . The heat capacity of the bomb is 837J/K , and the specific heat of the water is 4.20J/gK .

- Calculate the heat evolved per gram of sucrose.
- Calculate the heat evolved per mole of sucrose.

a) Temperature change = $27.32^\circ\text{C} - 25.00^\circ\text{C} = 2.32^\circ\text{C}$

$$q_{\text{water}} = (1500\text{g})(4.20\text{J/gK})(2.32^\circ\text{C}) = 14,616\text{J}$$

$$q_{\text{bomb}} = 837\text{J/K}(2.32^\circ\text{C}) = 1,941.84\text{J}$$

$$q_{\text{rxn}} = -(14,616\text{J} + 1,941.84\text{J}) = -16,557.8\text{J} = -16.6\text{kJ/g}$$

b) Moles sucrose = $1.00\text{g} / (342.2965\text{g/mol}) = 2.921 \times 10^{-3}\text{mol}$

$$q_{\text{rxn}} = -16,557.8\text{J} / 2.921 \times 10^{-3}\text{mol} = 5.6685 \times 10^6\text{J/mol} =$$

$$-5.67 \times 10^3\text{kJ/mol}$$

Hess's Law of Heat Summation

The heat of a reaction is constant, whether the reaction is carried out directly in one step or indirectly through a number of steps.

Reversing an equation:

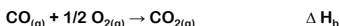
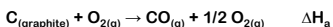
Changes the sign of ΔH

Multiplying coefficients in an equation:

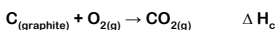
Multiplies the value of ΔH by the same amount.

Multiplying factors may be fractional.

Consider the following reactions:



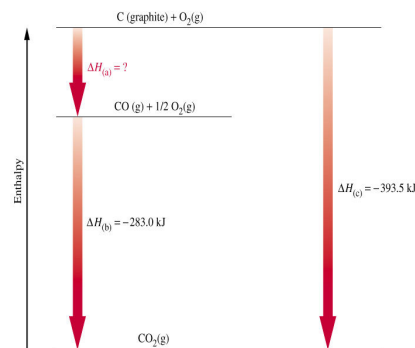
Vs.



Because enthalpy is a state function:

$$\Delta H_a + \Delta H_b = \Delta H_c$$

Whether you get from reactants to products in a two step process or a one step process, the total enthalpy change is the same.

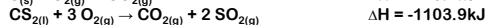


Example: Given the reaction information to the left, determine the unknown enthalpy of reaction "a".

$$\text{Answer: } \Delta H_a + -283.0\text{kJ} = -393.5\text{kJ} \quad \Delta H_a = -110.5\text{kJ}$$

Example:

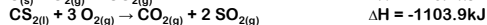
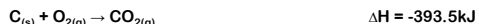
Use Hess's law to calculate the enthalpy change for the formation of $CS_{2(l)}$ from $C_{(s)}$ and $S_{(s)}$ from the following enthalpy values:



Hint: Remember you can reverse and multiply equations through. Whatever you do to the reaction equation, you do to the enthalpy.

Example Answer:

Use Hess's law to calculate the enthalpy change for the formation of $CS_{2(l)}$ from $C_{(s)}$ and $S_{(s)}$ from the following enthalpy values:



Another way to calculate enthalpies of reactions is through the use of

Standard Molar Enthalpies of Formation, ΔH°_f

Definition: The standard molar enthalpy of formation is the enthalpy change for the *formation of 1 mol of a compound directly from its component elements in their standard states*. The standard state of an element or a compound is defined as the *most stable form* of the substance in the physical state that exists *at a pressure of 1 bar (1 atm = 1.013 bar) and at a specified temperature*. Most tables report standard molar enthalpies of formation at 25°C (298K) (From p 265)

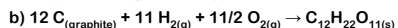
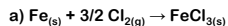
See table 6.2, p266 and Appendix L (pp A-27 to A-32)

The standard enthalpy of formation for any element in its standard state is 0.

Example:

Write equations for the reactions that define the standard enthalpy of formation of $\text{FeCl}_3(\text{s})$ and sucrose (sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$). What are the standard states of the reactants in each equation?

Answer:



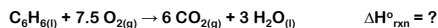
Using this information, the enthalpy of a reaction can be calculated by:

$$\Delta H^\circ_{\text{rxn}} = \sum[\Delta H^\circ_f(\text{products})] - \sum[\Delta H^\circ_f(\text{reactants})]$$

Where \sum means the sum of all the standard enthalpies of formation of the products (times their coefficients in the balanced equation) minus the sum of all the standard enthalpies of formation of the reactants (times their coefficients in the balanced equation)

Sample Problem:

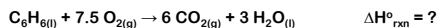
Calculate the standard enthalpy of combustion for benzene, C_6H_6 .



$\Delta H^\circ_f[\text{C}_6\text{H}_6(\text{l})] = +49.0 \text{ kJ/mol}$. Other values needed can be found in Table 6.2 and Appendix L.

Sample Problem Answer:

Calculate the standard enthalpy of combustion for benzene, C_6H_6 .



$\Delta H^\circ_f[\text{C}_6\text{H}_6(\text{l})] = +49.0 \text{ kJ/mol}$. Other values needed can be found in Table 6.2 and Appendix L.

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= [6(-393.51) + 3(-285.83)] - [1(49.0) + 7.5(0)] \\ &= -3,267.55 = -3.27 \times 10^3 \text{ kJ/mol} \end{aligned}$$

Product or Reactant Favored Reactions and Thermochemistry

Recall: Precipitation, gas forming, neutralization, combustion (redox)

Most product favored reactions have $\Delta H^\circ_{\text{rxn}}$ that are negative, and those that are reactant favored are positive.

However, there is another factor; "Entropy", covered in thermodynamics, that will also have to be considered.