

THERMOCHEMISTRY



Objectives for Unit 5:

- To know the meaning of the terms kinetic energy, potential energy, system, surroundings, internal energy, and heat.
- To be able to state the First Law of Thermodynamics.
- To know how ΔH and ΔU are related to heat effects.
- To know the meaning of the terms endothermic and exothermic.
- To know the significance of a state function, and that ΔH is the heat absorbed or released at constant pressure.
- To be able to calculate the ΔH of a related reaction, given the ΔH for one reaction, .
- To use the $\Delta H/\text{mol}$ and previous stoichiometric concepts to calculate the heat involved in a chemical reaction when any amount reacts.
- To be able to work problems involving heat capacity and specific heat.
- To use calorimetry data to calculate enthalpy or internal energy changes for chemical reactions or heat exchange processes.
- To be able to use Hess's law.
- To calculate the heat of a reaction from standard enthalpies of formation or determine the standard enthalpy of formation from the heat of a reaction and other heats of formation.
- To be familiar with how the thermochemistry of food and fuel relates to every day life.

Energy and Its Units

ENERGY (U)

Energy is an inherent property of a system. Any system at a given set of conditions (e.g. pressure and temperature) has a certain energy content. The concept of energy invented to describe a number of processes such as conversion of work to heat. The SI unit of energy is joule (J).

Units:

1 calorie = heat required to raise temp. of 1.00 g of H_2O by 1.0 °C.

1000 cal = 1 kilocalorie = 1 kcal

1 kcal = 1 Calorie (a food "calorie")

But we use the unit called the JOULE

source: <http://www.taftan.com/thermodynamics/ENERGY.HTM>



Kinetic: Energy associated with motion.

Kinetic Energy Equation (E_k)

Kinetic Energy is equal to $\frac{1}{2}$ mass \times velocity²

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$$E_k = \frac{1}{2} mv^2$$

Calculate the kinetic energy (in J and cal) of an electron.

Mass = 9.11×10^{-31} kg, velocity = 5.0×10^5 m/s

$$E_k = \frac{1}{2} mv^2 = \frac{1}{2} (9.11 \times 10^{-31} \text{ kg}) \times (5.0 \times 10^5 \text{ m/s})^2$$

$$E_k = 1.1 \times 10^{-19} \text{ kg m}^2/\text{s}^2 = 1.1 \times 10^{-19} \text{ J}$$

$$E_k = 2.7 \times 10^{-20} \text{ cal}$$



Potential: Energy that is stored as a function of position.

Potential Energy Equation (E_p)

Potential Energy is equal to mass \times acceleration due to gravity \times height

$$E_p = mgh$$

$$g = 9.8 \text{ m/s}^2$$

Consider a 165 lb. Person on a 15 ft. diving board.

$$E_p = mgh = (75.0 \text{ kg}) \times (9.8 \text{ m/s}^2) \times (4.6 \text{ m})$$

$$E_p = 3.4 \times 10^3 \text{ kg m}^2/\text{s}^2 = 3.4 \text{ kJ}$$

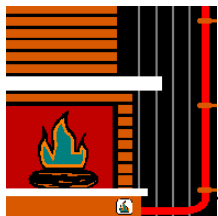
Internal Energy (U)

The sum of the kinetic and potential energies making up a substance is referred to as the INTERNAL ENERGY (U).

Studying the TOTAL ENERGY (E_{tot}) gives: $E_{\text{tot}} = E_k + E_p + U$

If the laboratory conditions: $E_k = 0$ and $E_p = 0$ $E_{\text{tot}} = U$

THE 1ST LAW OF THERMODYNAMICS



This is the Law of Conservation of Energy.

Energy may be created from one form to another, but the total quantity of energy remains constant (that is the net energy change is zero).

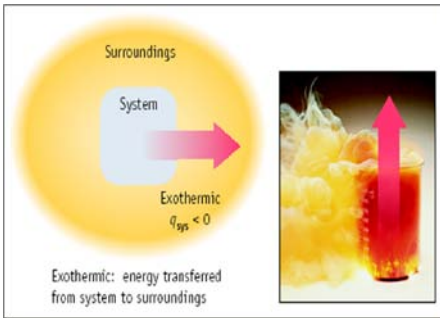
HEAT OF REACTION



System and Surroundings

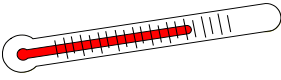
There are two ways energy is transferred between a system and its surrounding when a system changes from one state to another.

EXOTHERMIC:



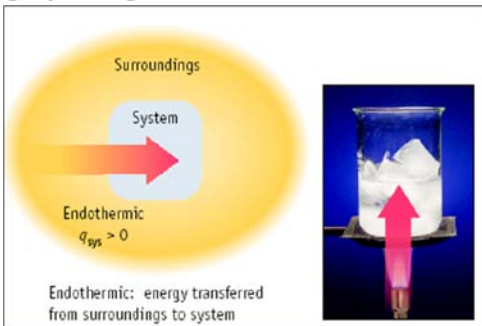
Heat always transfer from hotter object to cooler one.

- **EXO**thermic: heat transfers from **SYSTEM** to **SURROUNDINGS**.



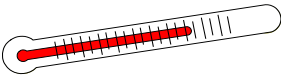
T(system) goes down, T(surr) goes up

ENDOTHERMIC:



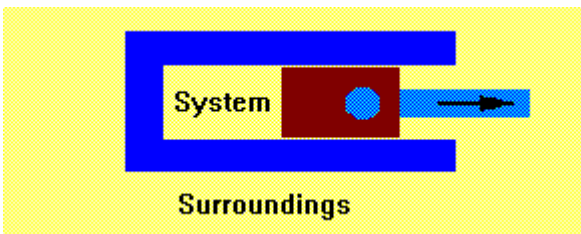
Heat always transfer from hotter object to cooler one.

- **ENDO**thermic: heat transfers from **SURROUNDINGS** to the **SYSTEM**.



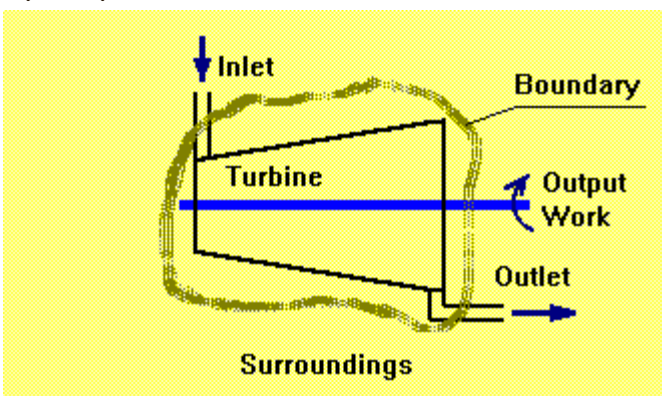
T(system) goes up, T (surr) goes down

Closed System



In closed systems, nothing leaves the system boundaries.

Open System



In open systems there is a mass transfer across the system's boundaries; for instance the steam flow through a steam turbine at any instant may be defined as an open system with fixed boundaries.

source: <http://www.taftan.com/thermodynamics/SYSTEM.HTM>

When $\Delta U = 0$ (no net change in total energy), the work done by the **system** is equal to the heat energy that the system absorbed from the **surroundings**.

Δ means final minus initial.

For reactions: Δ means products minus reactants

HEAT (q)



Heat is a form of energy that is transferred from one body (system) to another body (system or surroundings).

Heat transfer can occur when there is a temperature difference. Assume two bodies with different temperatures are brought into contact with each other. The heat transfers from the hotter body to the colder one. This will continue until the temperature of the bodies are the same (thermal equilibrium). The SI unit of heat is joule (J). Other units are:

- 1 cal (calorie) = 4.1868 J
- 1 Btu (British thermal unit) = 1055.05 J
- 1 thermie = 4.184E6 J
- 1 kJ = 1000 J
- 1 hp.h (horsepower. hour) = 2.6845×10^6 J
- 1 kWh = 3.6×10^6 J

source: <http://www.taftan.com/thermodynamics/HEAT.HTM>

Heat (q) and Energy (U) are transfer units.

ENDOTHERMIC AND EXOTHERMIC CHANGES

Endothermic Reaction



Endothermic Reaction: occurs when heat (energy) is absorbed from the surroundings. **q is positive**

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Exothermic Reaction



Exothermic Reaction: occurs when heat (energy) is released into the surroundings. **q is negative.**

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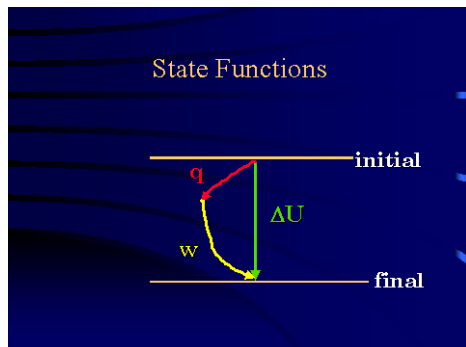
ENTHALPY AND ENTHALPY CHANGE

ENTHALPY is the heat content of a system at CONSTANT PRESSURE.

Enthalpy is a STATE FUNCTION.

A State function only depends upon the present state of the system and not on how that state was reached. That is, depends only upon the initial state (reactants) and the final state (products).

Example: Internal Energy (U)



source: <http://www.uow.edu.au/~wprice/thermo213/sld018.htm>

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CALCULATE ENTHALPY

Since it is impossible to measure the enthalpy of a system, we measure the CHANGES in enthalpy.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

ENTHALPY CHANGE: $\Delta H = q_p$ (heat at constant pressure)

Example:



Rockets require the following fuel:

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note 1: For chemical reactions that are the reverse of each other, ΔH is the same value, but opposite in sign.

note 2: The value of ΔH is always associated with a balanced equation so the coefficients are read as moles in its simplest form.

HEAT STOICHIOMETRY

Using a Chemical Equation to calculate heat and moles:

Example:



How much heat is evolved when 10.0 grams of N_2H_4 is involved in the following reaction:

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CALORIMETRY

MEASURING HEAT: Use a **CALORIMETER** to measure temperature changes during a physical or chemical change. **HEAT CAPACITY** is the amount of heat energy required to raise the temperature of a given amount of substance by one degree Celsius.

- **SPECIFIC HEAT:** Is the amount of heat needed to raise 1 gram of a substance, 1°C .
 - Units: *In Class*
- **MOLAR HEAT:** Is the amount of heat needed to raise 1 mole of a substance 1°C .
 - Units: *In Class*
- **ABSOLUTE HEAT:** Is the amount of heat needed to raise a substance 1°C .
 - Units: *In Class*

Example:

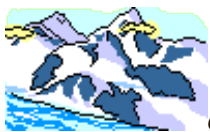


52.3 grams of a metal was heated with 3675 joules of heat. This caused a temperature change from 10.0°C to 30.0°C . Calculate the specific heat of this metal (in $\text{J/g}^{\circ}\text{C}$).

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Energy can be measured when a substance changes its physical state.

- **HEAT OF FUSION:** The amount of heat required (solid to liquid)
 - *In Class*
- **HEAT OF VAPORIZATION:** The amount of heat required (liquid to gas).
 - *In Class*
- **HEAT OF CONDENSATION:** The amount of heat required (gas to liquid).
 - *In Class*
- **HEAT OF CRYSTALLIZATION:** The amount of heat required (liquid to solid).
 - *In Class*



Calculate the amount of heat (in cal. and J) required to vaporize a 20.0 gram sample of ice from -15°C to 115°C .

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To determine the enthalpy in a chemical reaction, use a CALORIMETER.

A good source to look at for simulating a calorimetry experiment: [Click Here](#)

Example:

25.0 grams of a metal was heated to $100.^{\circ}\text{C}$. This metal was placed into a calorimeter containing 35.0 grams of water. The temperature in the calorimeter rose from $25.^{\circ}\text{C}$ to $35.^{\circ}\text{C}$. What is the specific heat (in $\text{J/g}^{\circ}\text{C}$) of the metal?

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A bit more complicated:



Propane, C_3H_8 burns in air to yield CO_2 and H_2O .



If we heat 1000. grams of water from $20.^{\circ}\text{C}$ to $100.^{\circ}\text{C}$ and then boil it at $100.^{\circ}\text{C}$ to generate the necessary heat, how many grams of propane must we use?

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HESS'S LAW



Germain Hess (1802-1805)

source: http://www.chemistry.co.nz/hess_law.htm

Thermochemical equations can be rearranged, terms can be cancelled, and the equations can be added to give heats for reactions not included in the data tables. The basis for this type of calculation is known as HESS'S LAW.

source: Tzimopoulos, Metcalfe, Williams, and Castka Modern Chemistry; Holt, Rinehart, and Winston, Orlando, Florida; 1993. p. 531

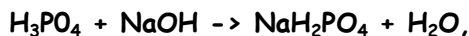
There are two aspects of the law:

1. When several reactions are summed to get a new reaction, we add the ΔH 's for the reaction to get the ΔH for the new reaction.

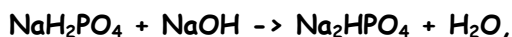
According to Hess's Law:

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

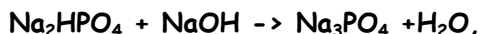
For Example:



this is step one, and will give X amount of heat.



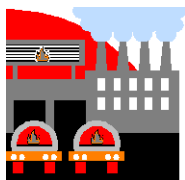
this is step two, and will give Y amount of heat.



this is step three, and will give Z amount of heat.

Therefore X+Y+Z will give the total heat or the constant summation of heat.

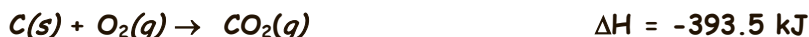
Example Reaction:



The enthalpy change for methane: $\text{CH}_4(g) \rightarrow \text{C}(g) + 4 \text{H}(g)$

Experimentally, this is difficult to isolate hydrogen as just H. Also, CH_4 gets broken down by combustion, not by this reaction. But, we can look at a series of reactions to figure out the ΔH for the above reaction.

These include:



Work with the equations for summation to obtain the original equation:

Add the following:

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Standard Enthalpies of Formation

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

$$\Delta H = (\text{sum of } \Delta H \text{ products}) - (\text{sum of } \Delta H \text{ of reactants})$$

We have a scale known as ENTHALPIES OF FORMATION : ΔH_f°

ΔH_f° is written per one mole of the substance in its standard states.

Refer to Table 6.2 p. 247 and Appendix C.

Here is a list of all the different ΔH° :

$\Delta H_{\text{rxn}}^\circ$ is the ENTHALPY CHANGE FOR A REACTION

$$\Delta H_{\text{rxn}}^\circ = (\text{sum of } \Delta H_f^\circ \text{ products}) - (\text{sum of } \Delta H_f^\circ \text{ of reactants})$$

ΔH_f° is the STANDARD MOLAR ENTHALPY OF FORMATION

1 mole of a substance has been formed.

$\Delta H_{\text{vap}}^\circ$ is the STANDARD MOLAR ENTHALPY OF VAPORIZATION

1 mole of a substance has been vaporized

$\Delta H_{\text{combustion}}^\circ$ is the STANDARD MOLAR ENTHALPY OF COMBUSTION

1 mole of a substance has been burned

note 1: ΔH_f° for elements and diatomics is zero.

note 2: Most ΔH_f° are negative (formation is an exothermic process).

Example:



The decomposition of baking soda



To solve : Simply look up Table values of all the substances involved and calculate $\Delta H_{\text{rxn}}^\circ$.

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Fuels

A bit more complicated:

The combustion of 1mole of benzene, $\text{C}_6\text{H}_6(l)$, to produce carbon dioxide and water liberates 3271 kJ when the product returns to 25°C and 1 atm (standard). What is the ΔH_f° of benzene in kJ/mol?