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# Thermochemistry

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## What is Energy?

A. Energy is a property of matter that allows for work to be done

B. Potential and Kinetic

Potential energy is energy of position (interparticle forces or intraparticle forces)

Kinetic energy is energy of motion (translational, rotational, vibrational)

Review - according to kinetic theory:

1. all matter is composed of particles
2. all particles are in motion
3. collisions are elastic
4. all particles at a given temp don't have the same KE

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Slide 1

## C. Temperature and Heat

Temperature is the measure of average KE. (°C)

Thermal energy (heat content) is a measure of the KE and PE of a group of particles. (J)

Heat is thermal energy which moves from one place to another. (J)

Other heat units would be the calorie (cal) and the British Thermal Unit (BTU)

The study of heat changes during physical and chemical changes is called thermochemistry.

The technique of measuring these heat changes is called calorimetry.

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## Energy changes in a physical change

A. As heat is added to a substance the substance undergoes temperature changes (KE changes) and phase changes (PE changes).

B. Temp changes

As we add heat to a solid, liquid or gas the temperature changes. The amount of heat needed depends to change the temp depends on 3 factors:

- (1) the amount of material,
- (2) what the material is,
- (3) the amount of temperature change needed.

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Slide 3

These factors form the basis for an equation:

$$Q = m C_p \Delta T$$

$Q [=] \text{ J}$  and is the heat required  
 $m [=] \text{ g}$  (usually) and is the amt of substance  
 $\Delta T [=] \text{ C}^\circ$  and is the change in temperature

$\Delta T$  also equals  $T_f - T_i$  where  $T_f$  and  $T_i$  represent the final and initial temperatures

Note:  $Q$  will be positive if the temp is increasing ( $\Delta T +$ ) and negative if the temp is decreasing ( $\Delta T -$ ).

$C_p$  is the amount of heat needed to change a unit mass of material by a unit temperature change. It is called the specific heat capacity. Most commonly the units are  $\text{J/gC}^\circ$  or  $\text{J/mole C}^\circ$ .

The value of  $C_p$  changes from one phase to another and from one substance to another. The subscript  $p$  refers to the fact that this is the heat capacity at constant pressure - a situation that is commonly encountered when processes occur that are open to the atmosphere.

### C. Phase changes

The above equation can be used for any temperature change to usually either calculate heat needed for a process or the temp change that will result from the addition or subtraction of a given amount of heat. What happens at the phase change point?

The important point is that when a solid changes to a liquid or a liquid to a gas, the temp does not change until all the pure substance has undergone the phase change. Thus we add heat to a solid at the MP and the temp does not change. Likewise we add heat to a liq at the BP and the temp does not change.

The equations that govern these changes are:

$$Q = m H_f \qquad Q = m H_v$$

$H_f [=] \text{ J/g}$  and is the heat of fusion, the amount of heat needed to change 1 g of solid to liquid. This is a positive number. The value for the change from liq to solid is a negative number.

$H_v [=] \text{ J/g}$  and is the heat of vaporization, the amount of heat needed to change 1 g of liquid to gas. This is a positive number. The value for the change from gas to liquid is a negative number.

### D. The Importance of the algebraic sign of $Q$

A positive value of  $Q$  means that heat is following into the substance. This is called an endothermic process.

A negative value of  $Q$  means that heat is following out of the substance. This is called an exothermic process.

## E. The Big Picture

We can put all these changes into a graph of Q versus T to see the big picture. To go from a solid below the freezing point all the way to a gas above the boiling point requires 5 steps or transitions. We can label these as  $Q_1$  to  $Q_5$ .

$Q_1$ ,  $Q_3$ , and  $Q_5$  are temperature changes;  $Q_2$  and  $Q_4$  are phase changes.

To calculate the amount of heat needed to go from one temp to another, you must:

- Identify the phase you are in at the beginning temp.
- Identify the phase you are in at the end temp.
- Use the appropriate steps (transitions) to get from the beginning to the end. Add the various steps together to get the total.

Example: How much heat is needed to change 10.0 g of solid ice at  $0.0^\circ\text{C}$  to steam at  $105.0^\circ\text{C}$  under normal pressure conditions?

$$\begin{array}{ll} C_p(\text{solid}) = 2.06 \text{ J/gC}^\circ & H_f = 333 \text{ J/g} \\ C_p(\text{liquid}) = 4.18 \text{ J/gC}^\circ & H_v = 2260 \text{ J/g} \\ C_p(\text{gas}) = 2.03 \text{ J/gC}^\circ & \end{array}$$

## Mixtures

**Concept:** Heat energy is transferred from hot to cold until the temperature is the same. This is called thermal equilibrium. The technique of calorimetry uses this to find properties of substances or mixtures. A calorimeter is the device which holds the substances where the heat transfer is occurring.

If we say that objects that lose heat have negative Q values and objects that gain heat have positive Q values then

$$Q_{\text{lost}} + Q_{\text{gained}} = 0$$

Example: What is the final temperature when a 50.0 g block of aluminum at  $75^\circ\text{C}$  is put into 25.0 g of water at  $50.^\circ\text{C}$ ?

## Thermodynamics

A. Thermodynamics involves the study of heat and work.

- Two of the terms we use in thermodynamics are "internal energy" and "enthalpy". They refer to the energy content of a substance in slightly different ways. This energy content changes by the general processes of heat transfer and work (q and w). Internal energy can be thought of as the thermal energy of the system – the sum of PE and KE of the particles.
- The "enthalpy change" is a measure of the heat transfer into or out of a system at constant pressure. Any process occurring that is open to the atmosphere is operating at constant pressure so this is a useful concept. "Enthalpy change" has the symbol  $\Delta H$ .

## B. Endothermic processes

- Endothermic processes are those in which the enthalpy of products is greater than the enthalpy of reactants.  $\Delta H > 0$  and heat is absorbed from the surroundings. If a chemical reaction takes place, the "pot" feels cold. Melting is a physical change that is endothermic.

## C. Exothermic processes

- Exothermic processes are those in which the enthalpy of the products is less than the enthalpy of the reactants.  $\Delta H < 0$  and heat is given up to the surroundings. If a chemical reaction takes place, the "pot" feels hot. Freezing is a physical change that is exothermic.

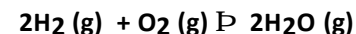
## D. Enthalpy Change of a Chemical Reaction

- It is impossible to measure the absolute amount of heat content (H) that a substance has. We can only measure changes in heat content (DH). We therefore set an arbitrary zero point for heat content and define all other enthalpies to it.

Define: The heat content of any free element at  $25^{\circ}\text{C} = 0$ .

Why is this advantageous?

Let's look at the reaction below



$$\Delta H = H(\text{final}) - H(\text{initial})$$

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

$$\Delta H = H(2 \text{ moles of water}) - [H(2 \text{ moles of hydrogen}) + H(1 \text{ mole of oxygen})]$$

We can measure the DH by experiment for this reaction. We cannot measure directly the absolute heat contents of hydrogen, oxygen or water. But if we have defined the H of any free element (hydrogen and oxygen) to be zero then

$$\Delta H = H(2 \text{ moles of water})$$

We see that the DH that we measure for this experiment is equal to the heat content of 2 moles of water. This DH is thus a measure of the heat content of water and is given a special symbol  $\Delta H_f^{\circ}$  --- the "f" representing formation and the superscript " $^{\circ}$ " indicating that the reaction was run using pure reactants to produce pure products in their standard states. Reactant and product gases are at one atmosphere of pressure. The temperature must be specified but is usually  $25^{\circ}\text{C}$ .

Symbols  $\Delta H$  = Enthalpy change for any process  
 $\Delta H^{\circ}$  = Enthalpy change under standard conditions

$\Delta H_f^{\circ}$  = Enthalpy change if product is formed from free elements under standard conditions.

- By making compounds from their free elements we can tabulate  $\Delta H_f^{\circ}$ 's which "equal" the heat content of the compound. These heats of formation can then be used in more complex reactions to determine DH for the complex reaction.
- The DH for a reaction can also be used as a conversion factor in stoichiometry problems.

Examples: What is the enthalpy change for the combustion of propane ( $\text{C}_3\text{H}_8$ )?

How much heat would be given off if you burn 50.0 g of  $\text{C}_3\text{H}_8$

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## Hess's Law

**Concept:** If a reaction can be written as the sum of 2 or more reactions, the enthalpy change (DH) for the overall process is the sum of the DH's for the individual reactions.

**Example:**  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$  DH= 44 kJ

$\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$  DH= 242 kJ

What is the DH for  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$  ?

Add both reactions to get

$\text{H}_2\text{O}(\text{l}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) + \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$

This gives the desired reaction, so add the DH's to get 286 KJ as the DH for the reaction.

**Remember:** (1) If a reaction must be multiplied by a whole number, the DH for that reaction is also multiplied.

(2) If a reaction is reversed, the sign of DH is reversed.

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## Special $\Delta H$ 's

### Heat of Solution

The heat or enthalpy of solution is the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent.

When an ionic compound dissolves in water the process can be broken down into 2 major steps:

(1) The ions are removed from the crystal lattice – this is an endothermic process.

(2) The ions attract and are surrounded by water molecules – this is an exothermic process.

Thus heats of solution can be endothermic or exothermic.

### Heat of Dilution

Diluting a solute in a solvent can also lead to energy changes for the same reasons given above for the heat of solution. Thus dilution can be either an endothermic or exothermic process.

Diluting concentrated sulfuric acid (or phosphoric acid) is very dangerous because of the extremely high exothermic heat of dilution. Always add concentrated acid to water while stirring and not water to concentrated acid.