
Thermochemistry

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I. What is Energy?

A. Energy is a property of matter that allows 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)**

According to kinetic theory:

- 1. all matter is composed of particles**
- 2. all particles are in motion**
- 3. collisions are elastic**

C. Temperature and Heat

Temperature is the measure of KE

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

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

D. Heat units

- **Joule (J) - the official SI unit defined in terms of force times distance (Nm or kgm^2/s^2)**
- **calorie (cal) - originally defined as the amt. of heat needed to raise 1 g of water 1 C°.**
- **Calorie (Cal) - 1000 calories, 1 kcal, used by nutritionists**

II. Energy changes in a physical change

A. As heat is added to a substance it 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 usually 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.

These factors form the basis for an equation:

$$Q = m C_p \Delta T$$

Q [=] J and is the heat required
m [=] g (usually) and is the amt of substance
DT [=] C° and is the change in temperature
DT also equal $T_f - T_i$ where T_f and T_i represent the
final and initial temperatures

**Note: Q will be positive if the temp is increasing (DT
+) and negative if the temp is decreasing (DT -).**

**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 J/gC° or J/mole C°. 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 the 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 where we heat a solid, liquid or gas. But what happens at the phase change points?

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:

$$Q = m H_f$$

$$Q = m H_v$$

H_f [=] 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 [=] 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 50.0 g of solid ice at -10.0°C to steam at 110.0°C under normal pressure conditions?

$$C_p(\text{solid}) = 2.06 \text{ J/gC}^{\circ}$$

$$H_f = 333 \text{ J/g}$$

$$C_p(\text{liquid}) = 4.18 \text{ J/gC}^{\circ}$$

$$H_v = 2260 \text{ J/g}$$

$$C_p(\text{gas}) = 2.03 \text{ J/gC}^{\circ}$$

III. Mixtures

Concept: Heat energy is transferred from hot to cold until the temperature is the same. This is called thermal equilibrium.

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

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

The experimental technique of calorimetry is used to determine quantitative information such as heat capacity, heat of fusion, heat of vaporization, heat of reaction. Calorimetry is based on the concept of heat exchange in mixtures.

Example: What is the final temperature when a 50.0g block of aluminum at 75°C is put into 25.0 g of water at 50.°C?

IV. Thermodynamics

- A. Thermodynamics is 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).
 - 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 ΔH .

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.

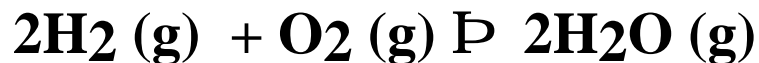
D. Enthalpy Change of a Chemical Reaction

- 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 = 0.

Why is this advantageous?

Let's look at the reaction below



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

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

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

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

DH = H (2 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 DH_f° (or $\Delta_f\text{H}^\circ$) --- 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 bar of pressure. The temperature must be specified but is usually 25°C .

Symbols ΔH = Enthalpy change for any process
 ΔH° = Enthalpy change under standard conditions
 ΔH_f° = Enthalpy change if product is formed from free elements under standard conditions.

By making compounds from their free elements we can tabulate ΔH 's which equal the heat content of the compound. These heats of formation can then be used in more complex reactions to obtain predicted ΔH 's.

Example: What is the enthalpy change for the combustion of C_3H_8 ?

IV. 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: $\text{H}_2\text{O} (\text{l}) \rightarrow \text{H}_2\text{O} (\text{g}) \quad \text{DH} = 44 \text{ kJ}$

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

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

Add both reactions to get

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

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.

V. The Laws of Thermodynamics

A. The First Law - The amount of energy in an isolated system remains constant. If it is not isolated the internal energy can change by the equation below using heat and work

$$DE = q + w$$

B. The Second Law - The sum of the entropy changes for a chemical system and its surroundings must be positive for a process to be spontaneous.

- **entropy - a measure of the numbers of ways that a system can store energy. It is related to the positional disorder of the system. Entropy has the symbol S. The change in entropy would be ΔS .**
- **spontaneous - a term that refers to whether there is a driving force for reactants to become**

products. Processes that are spontaneous are said to be product favored. Processes that are not spontaneous are said to be reactant favored.

$$DS_{\text{system}} + DS_{\text{surroundings}} = DS_{\text{universe}}$$

$$DS_{\text{universe}} > 0 \text{ if spontaneous}$$

C. The Third Law - the entropy of a pure, perfect crystal of a substance at absolute zero (-273°C) is zero. The third law tells us that it is possible to measure the absolute entropy of a substance. It is not possible to measure the absolute internal energy or enthalpy.

D. Gibbs Free Energy (G)

The change in the Gibbs Free Energy (DG) is a measure of the change in the entropy for a system and its surroundings.

$$DG = -TDS_{\text{universe}}$$

The calculation of DG therefore tells us whether there is a driving force for a reaction to occur. If DG is negative the process is spontaneous; if DG is positive the process is not spontaneous.

For a reaction where the temperature and pressure does not change there is a simple relation between DG, DH_{sys} , and DS_{sys} .

$$DG = DH - TDS$$

This equation gives us a way to relate the enthalpy change (DH) and entropy change (DS) and determine if a process is spontaneous.

DH	DS	DG	Spontaneous?
+	+	- or +	yes or no, maybe at high T
+	-	+	no
-	+	-	yes, at all T
-	-	- or +	yes or no, maybe at low T

It is important to see that there are two “driving forces” for a reaction, enthalpy and entropy. If a reaction is to be spontaneous it must have one of the following characteristics: it must either be exothermic or it must have a positive entropy change.