

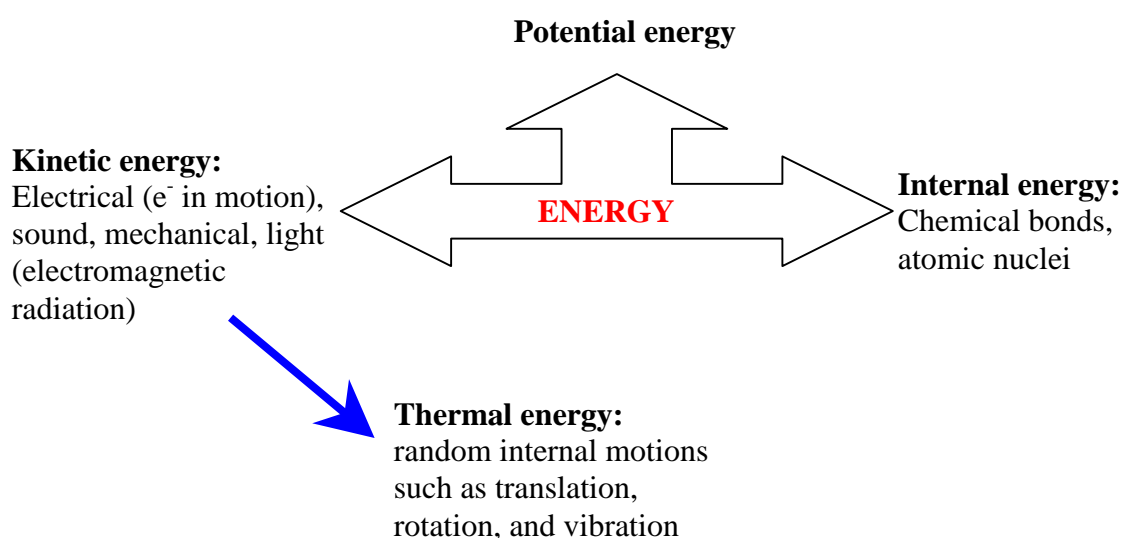
Thermochemistry

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Thermochemistry is concerned with the observation, measurement and prediction of energy changes accompanying chemical reactions.

Some terminology

The reaction and its immediate vicinity we consider is called the **system**. The area around the system is called the **surroundings**. If an **energy** is transferred from the system to the surroundings, **work** is done. Energy is thus the ability to do work. There are four types of energy: kinetic energy, potential energy, thermal and internal energy.



The **kinetic energy** is related with motion, however the potential energy (stored energy) can be stored as an object is displaced against gravity. A special kind of kinetic energy is the thermal energy (random internal motions such as translation, rotation, and vibration). If the temperature is higher these motions are faster. The **internal energy** of a system is the sum of all possible forms of energy in the system. The internal energy is a **state function**: its value depends only on the state of the system, not on how the system arrived at that state.

There are three systems: open system, close system and isolated system. **Open system** both energy and matter can be transferred from the system to the surroundings. In a **close system** energy can be transferred but not matter, however in an **isolated system** neither energy nor matter can be transferred.

Heat

Energy transferred between system and surroundings due to temperature differences is heat energy, Q

Heat capacity

The molar heat capacity, C is the amount of heat energy necessary to change one mole of a substance one Celsius degree temperature. The heat capacity depends on both the chemical composition of the material as well as the phase it is in (solid, liquid, etc.).

FIRST LAW OF THERMODYNAMICS (law of conservation of energy).

A mathematical statement of the First Law of Thermodynamics is

$$\Delta U = Q + W$$

where ΔU is the change in internal energy, Q is the heat exchanged between system and surroundings, and W is the work exchanged between system and surroundings. The sign conventions for heat (Q) and work (W) are very important and must be learned:

- Q is positive: means that the system takes in heat from the surroundings (endothermic process)
- Q is negative: means that the system loses heat to the surroundings (exothermic process)
- W is positive: means that **work is done on the system**
- W is negative: means that **work is done by the system**

By definition, work is force (F) applied over a distance (D), i.e. $W = F \times D$. There are several types of work possible, but the only significant source of work for most chemical processes and reactions is pressure-volume work defined as:

$$W = -p \times \Delta V$$

where p is the external pressure on the system, ΔV is the change in volume, defined as $V_{\text{final}} - V_{\text{initial}}$.

Constant Volume Processes

It should be clear that if the volume of a system doesn't change, then there can be no pressure-volume work, since ΔV is zero. Under these conditions, the first law can be written:

$$\Delta U = Q_v - p \times \Delta V = Q_v - 0 = Q_v$$

Thus, the heat exchanged (Q_v) between system and surroundings at constant volume is equal to the change in internal energy.

Enthalpy and Constant Pressure Processes

If a process takes place at constant pressure, then pressure-volume work results if the volume of the system changes. We can re-write the first law under these conditions as:

$$\Delta U = Q_p - p \times \Delta V \Rightarrow Q_p = \Delta U + p \times \Delta V$$

By definition, the state function **enthalpy** is defined as $H = U + p \times V$. Thus, for a process which takes place at constant pressure, the heat exchanged between system and surroundings at constant pressure is the enthalpy:

$$Q_p = \Delta H$$

Since almost all common chemical processes occur at constant pressure, hence the enthalpy is a very useful function because we only need to measure the heat absorbed or evolved; we don't need to worry about the pressure-volume work.

Hess' Law

The enthalpy, similar like internal energy, is a state function. Hess' Law states that the enthalpy change for a reaction is the same whether the reaction occurs directly or in steps.

Applications of Hess' Law

- 1) One of the applications of Hess' Law is to determine the enthalpy change for a reaction by combining other reactions to get the desired reaction, then combining the enthalpy changes for the reactions to get ΔH for the reaction under consideration.
- 2) Another application of Hess' Law is to pretend that the reactants are broken up into the elements which make them up, then these elements are combined to form the products. This results in the following useful equation:

$$\Delta H_r^0 = \sum n\Delta H_{f, products}^0 - \sum n\Delta H_{f, reactants}^0$$

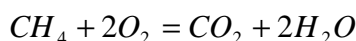
where n represents the stoichiometric coefficient and ΔH_f is the **enthalpy of formation** of the substance: the enthalpy change for the reaction where *one mole* of the substance in its standard state is formed from the constituent elements in their standard states. Remember that by definition, **the enthalpy of formation of an element in its standard state is zero**. The index ⁰ indicates that the process occurs at the standard conditions (i.e. T=298K and p=101325 Pa).

Problems and solutions

Problem 1.

When 1 mol of methane is burned at constant pressure, 890.3kJ of energy is released as heat. Calculate ΔH for a process in which a 1kg sample of methane is burned at constant pressure. Atomic mass for carbon is 12u, hydrogen 1u, oxygen 16u.

Methane is burned according to the reaction:



$$1\text{mol}CH_4 = 16\text{g}$$

$$1\text{kg} = 1000\text{g}$$

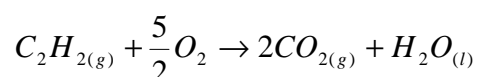
$$x\text{mol}CH_4 = \frac{1000\text{g} \times 1\text{mol}}{16\text{g}} = 62.5\text{mol}CH_4$$

If 1mol of methane is burned, 890.3kJ of energy is released, hence burning 62.5mol(1kg) of methane $62.5 \times 890.3\text{kJ} = 55643.75\text{kJ}$ of energy is released.

Problem 2

The heat of formations of $CO_{2(g)}$, $H_2O_{(l)}$ and $C_2H_{2(g)}$ are -394kJ/mol , -285.8kJ/mol and 226.7kJ/mol , respectively. Calculate the heat of combustion reaction of $C_2H_{2(g)}$.

The combustion reaction of $C_2H_{2(g)}$:



According to the Hess' law, the heat (ΔH_r^0) of this reaction is:

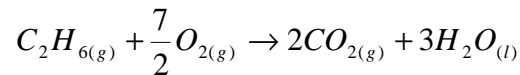
$$\Delta H_r^0 = \left(2 \times \Delta H_{fCO_{2(g)}} + \Delta H_{fH_2O_{(l)}} \right) - \Delta H_{fC_2H_{2(g)}}$$
$$\Delta H_r^0 = \left[2 \times \left(-394 \frac{\text{kJ}}{\text{mol}} \right) + \left(-285.8 \frac{\text{kJ}}{\text{mol}} \right) \right] - 226.7 \frac{\text{kJ}}{\text{mol}} = -2601 \frac{\text{kJ}}{\text{mol}}$$

During the combustion reaction of $C_2H_{2(g)}$ $-2601 \frac{\text{kJ}}{\text{mol}}$ heat is released.

Problem 3

The heat of formations of $CO_{2(g)}$, $H_2O_{(l)}$ and $C_2H_{6(g)}$ are -394kJ/mol , -285.8kJ/mol and -85kJ/mol , respectively. Calculate the heat released during combustion 2m^3 of ethan $C_2H_{6(g)}$.

The combustion reaction of $C_2H_{6(g)}$:



According to the Hess' law, the heat (ΔH_r^0) of this reaction is:

$$\Delta H_r^0 = (2 \times \Delta H_{fCO_{2(g)}} + 3\Delta H_{fH_2O_{(l)}}) - \Delta H_{fC_2H_{6(g)}}$$
$$\Delta H_r^0 = \left[2 \times \left(-394 \frac{\text{kJ}}{\text{mol}} \right) + 3 \times \left(-285.8 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left(-85 \frac{\text{kJ}}{\text{mol}} \right) = -1560.4 \frac{\text{kJ}}{\text{mol}}$$

Using Clapeyron equation we calculate the mol's numer in 2m^3 of ethan $C_2H_{6(g)}$:

$$pV = nRT$$

where: p-pressure, V-volume, n-mol's number, R-gas constante $8.314 \frac{\text{J}}{\text{mol} \times \text{K}}$, T-temperature.

$$n = \frac{pV}{RT} = \frac{101325\text{Pa} \times 2\text{m}^3}{8.314 \frac{\text{J}}{\text{mol} \times \text{K}} \times 298\text{K}} = 81.83\text{mol}$$

During combustion 2m^3 of ethan $C_2H_{6(g)}$ $81.83\text{mol} \times \left(-1560.4 \frac{\text{kJ}}{\text{mol}} \right) = -127692.5\text{kJ}$ heat is released.

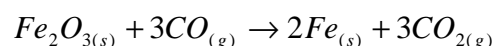
Problems

1)

The heat (enthalpy) of formations of $CO_{2(g)}$ is -394kJ/mol . Calculate the heat of combustion 10kg of carbon. Atomic mass of carbon is $12u$.

2)

The heat (enthalpy) of formations of $CO_{2(g)}$ and $CO_{(g)}$ are -394kJ/mol , -110kJ/mol , respectively. Calculate the heat of reduction raction of 5kg $Fe_2O_{3(s)}$ proceeds according with reaction:



3)

Calculate the heat released during combustion of:

a) 1kg ethanol $C_2H_5OH_{(l)}$

b) 1kg bezene $C_6H_{6(l)}$

The enthalpy of formations of $CO_{2(g)}$, $H_2O_{(l)}$, $C_2H_5OH_{(l)}$, $C_6H_{6(l)}$ are -394kJ/mol , -285.8kJ/mol , -228kJ/mol , 49kJ/mol , respectively. The atomic mass of elements are: $C-12u$, $H-1u$, $O-16u$.

4)

Calculate the heat of combustion of 1m^3 mixture contains 40vol% of propane C_3H_8 and 60vol.% of butane $C_4H_{10(g)}$. The enthalpy of formations of $CO_{2(g)}$, $H_2O_{(l)}$, $C_3H_{8(g)}$, $C_4H_{10(g)}$ are -394kJ/mol , -285.8kJ/mol , -104kJ/mol , -132kJ/mol , respectively.

5)

The heat of combustion of propanol is -1875kJ . Calculate the enthalpy of formation of propanol. The enthalpy of formations of $CO_{2(g)}$, $H_2O_{(g)}$ are -394kJ/mol , -241kJ/mol .