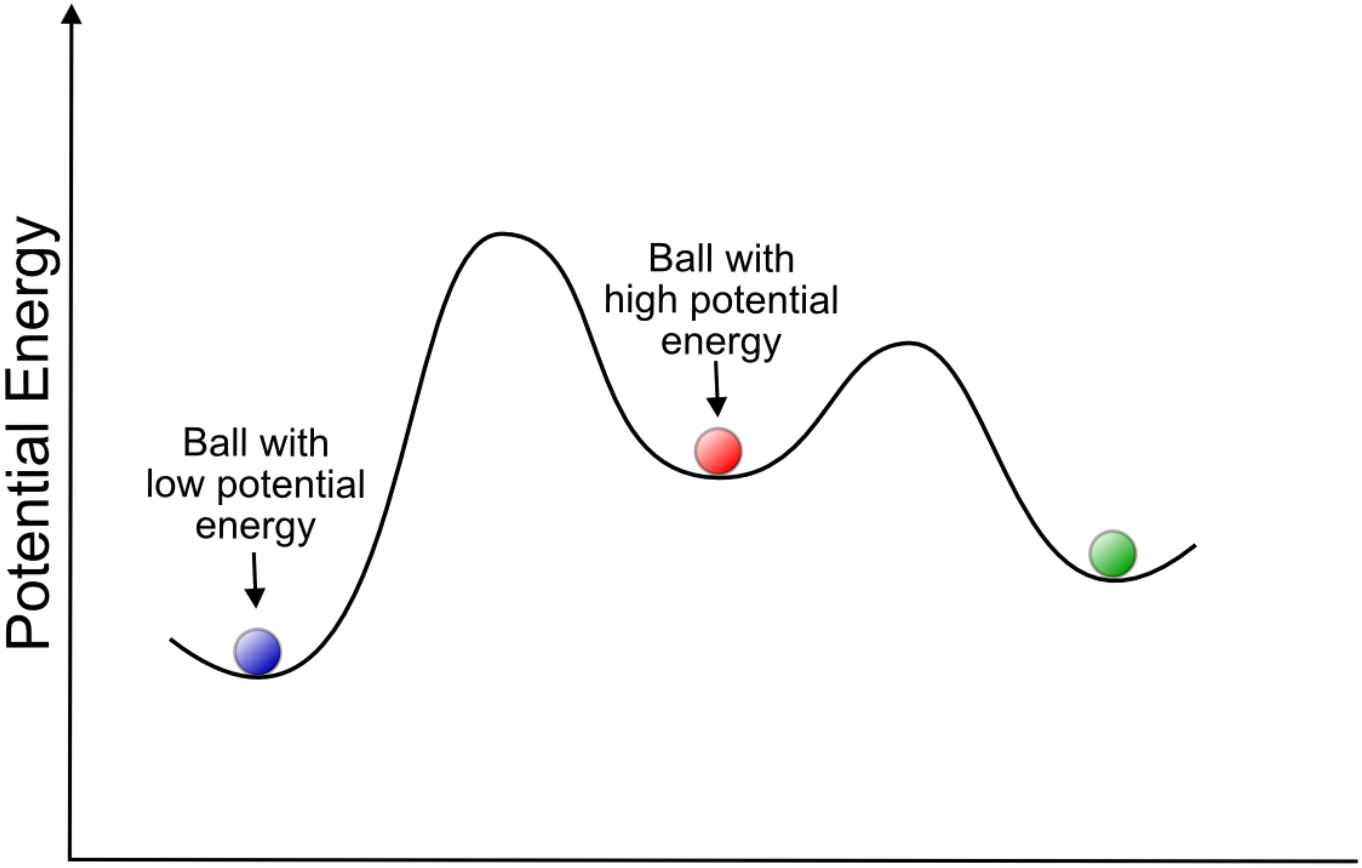
Chem 1032 Thermochemistry Review

Thermochemistry is the study of how heat is absorbed and released during chemical and physical processes. Thermochemistry is a branch of another subject, **Thermodynamics**, which is the study of heat, work, and energy.

Energy

Energy is the capacity to do **work(w)** (or supply heat). Work can be understood as an energy transfer, this can be something like applying a force to move an object (work is applied to inflate a bike tire) or more abstractly energy transfered to the surroundings. In thermodynamics, the **system** is are the molecules in a reaction and the **surroundings** are...everything else.

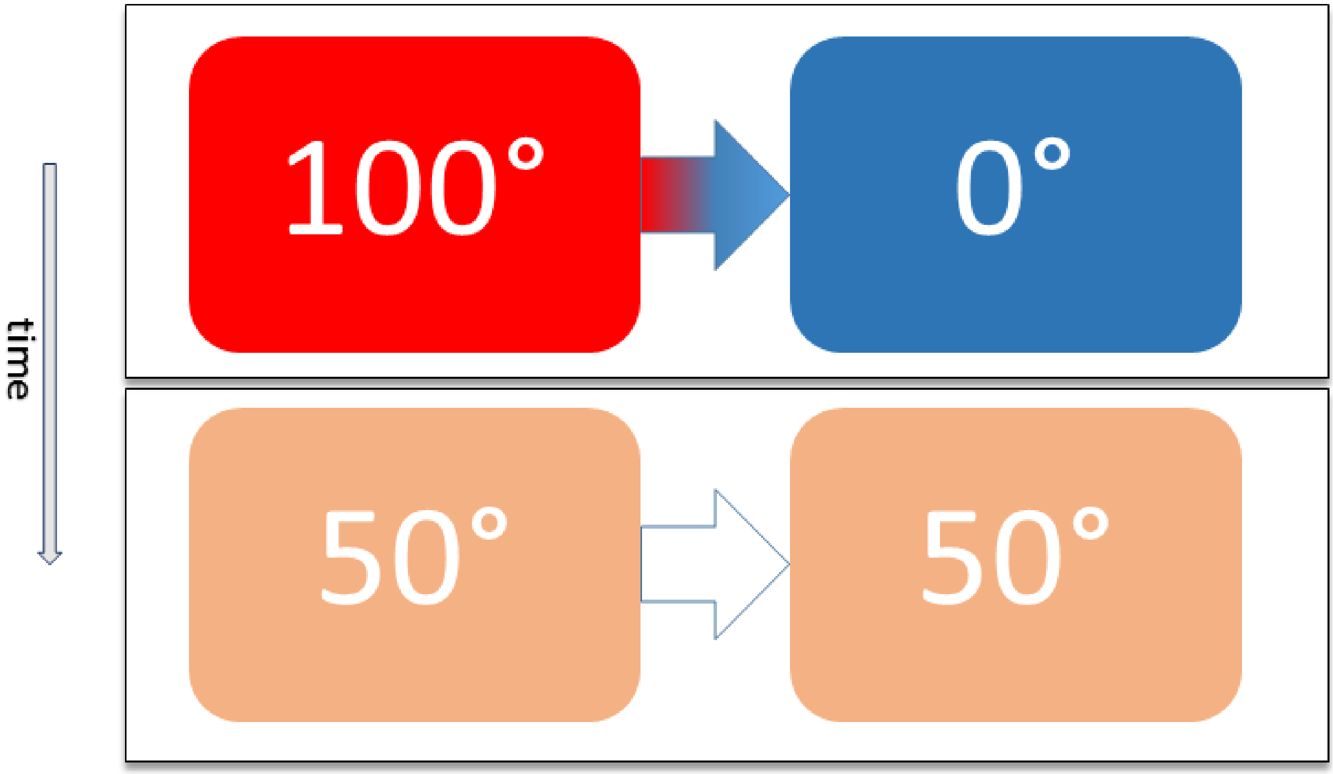
There are 2 kinds of energy, **potential energy**, which is the ability to do work, and **kinetic energy**, the energy that is due to the motion of an object. The way that energy tranfer works, potential energy can be converted into kinetic energy and vis a versa. This interconversion can be understood through the concept of objects falling do to gravity. Say you were to hold a ball on a hill. It possesses potential energy because of the height. Once you let go, that potential energy will be converted into kinetic energy and the ball will roll down the hill. The ball with come to a standstill again once all of its kinetic energy has been converted into potential energy or transfered somehow. This new steady state will be at a lower potential energy that the on top of the hill state, and thus more stable. (note: the energy in this case is transferred in other ways as well and this simple picture neglects the role that different forces (i.e. gravity,friction) play into the picture...but that's a topic for another time.)



Thermal Energy and Heat

Thermal Energy is the kinetic energy of random atomic/molecular movement, the average of which is the **temperature** of a system. Thus, in a hot sustem, atoms/molecules are moving faster than in a cold system.

Heat(q) is the transfer of energy between 2 bodies. Heat will transfer from a warmer system to a cooler system spontaneously to reach a thermal equilibrium, unless work is applied to do the opposite. Think about how your house gets hot in the summer naturally, but to cool it down you have to use energy to do the work of cooling it down via air conditioning. An **endothermic reaction** is one with a *positive* q and an **exothermic** reaction is one with a *negative* q. So an exothermic reaction loses heat to the surroundings and an endothermic reaction requires external heat.



The **heat capacity (C)** of a material is its ability to retain heat given a change in temperature;

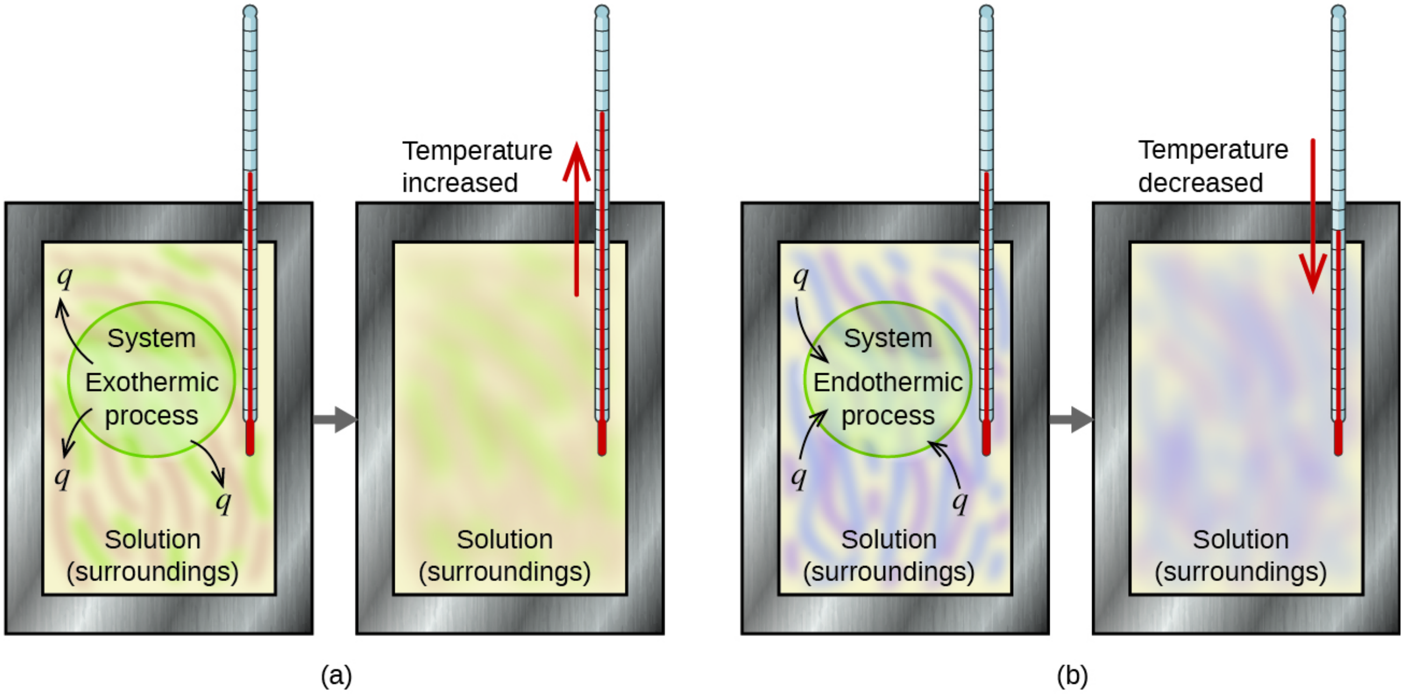
$$C = \frac{q}{\Delta T}$$

The **specific heat capacity (specific heat, c)** is the same concept , but it is related to heat retention and mass.

$$c = \frac{q}{m\Delta T}$$

Calorimetry

A **calorimeter** is a device that that is used to measure the heat of a reaction by measuring the temperature change of heat transfer from the system (reaction) to the surroundings (solution);



Since energy is conserved, in this setup, $q_{sys} + q_{surr} = 0$, the heat absorbed by the calorimeter is negligible. This fact allows us to use the specific heat of the solution to measure the heat of the reaction through a rearangement of the specific heat equation;

$$q_{rxn} = -q_{sol}$$

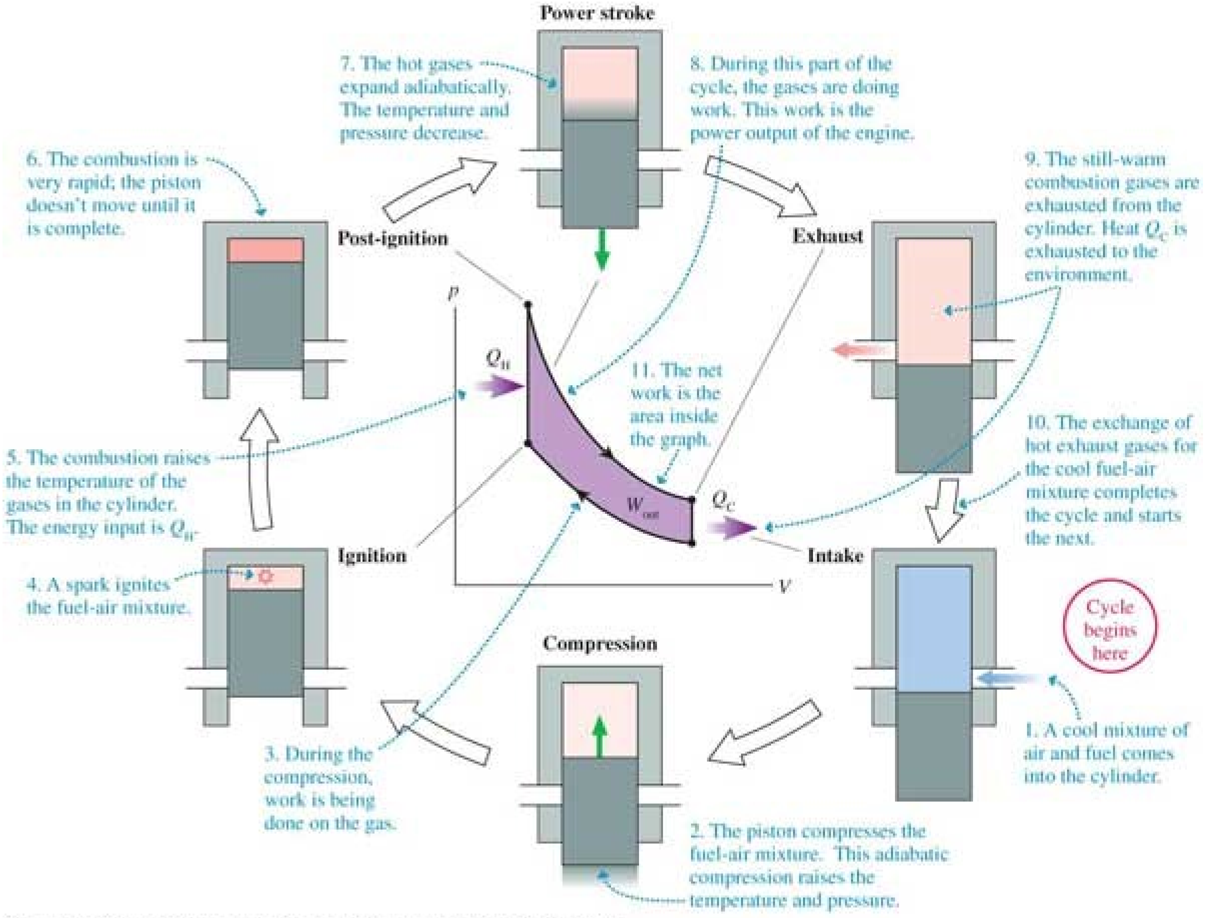
$$q_{sol} = c \cdot m \cdot \Delta T = -q_{rxn}$$

Enthalpy

The **internal energy (U or E)** of a system is the sum of all energies in a system. As the system goes through changes, energy can be transferred from the system to the surroundings. The description of this energy transfer leads to one formulation of the **first law of thermodynamics**;

$$\Delta U = q + w$$

A type of work is **expansion work (pV work)**. You can think of it like this. Say you a deflated balloon that you want to blow up. You must do work to blow into the balloon, but also the physical balloon is doing work against the surroundings (air pressure, gravity, etc.) in order to occupy the new volume it needs to. Another example would be the combustion engine,the combustion reaction of gasoline is exothermic, producing heat, and also does the work of moving the engines pistons to get the car to move.



Internal energy is a **state function**, meaning the path that the system takes from its initial to final state does not matter, only the initial and final states matter.

Enthalpy (H) can describe the thermodynamics of a chemical and physical process;

$$H = U + pV$$

Enthalpy is also a state function. Enthalpy can not be measured directly, but the ΔH can be determined experimentally. For a process at constant pressure;

$$\Delta H = \Delta U + p\Delta V$$

Recall earlier where we discussed pV work and the definition of U;

$$p\Delta V = -w$$

$$\Delta H = q_p + w - w$$

$$\Delta H = q_p$$

This can be understood as, under constant pressure, the only work done is by expansion or contraction, thus the enthalpy change is simply the heat of the system, q_p.

The **standard state** of a system is the reference point for the system, the thermodynamic properties under a certain set of conditions. These conditions typically are **1 bar and 1M**, temperature, while not explicitly defined, is typically **298.15 K**. The symbol for the standard state thermodynamic property is a degree symbol (i.e. ΔH^o)

Standard Enthalpy of Combustion ΔH_C^o

At 298.15 k and 1 bar;

$$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_2 + 3H_2O_{(l)} \qquad \Delta H^o = \; -1366.8 \; kJ$$

So under standard conditions, the system loses 1366.8 kJ to the surroundings, per mole.

Standard Enthalpy of Formation ΔH_f^o

This is the ΔH in which 1 mole of substance is formed from its pure components, at standard conditions.

This reaction would be exothermic;

$$C_{(s)} + O_{2(g)} \;\longrightarrow\; CO_{2(g)} \qquad \Delta H_f^o = \Delta H^o = \; -393.5 \; kJ$$

While this reaction would be endothermic;

$$0.5N_{2(g)} + O_{2(g)} \;\longrightarrow\; NO_{2(g)} \qquad \Delta H_f^o = \Delta H^o = \; 33.2 \; kJ$$

Hess's Law... Putting it all together

As stated before, we can measure the change in enthalpy experimentally, but we can also calculate it from standard enthalpies. There are a wide number of standard enthalpy tables available, with ΔH^o for most of your typical molecules.

Hess's Law simply states that the enthalpy change of a stepwise process is the summation of each of its parts.

Consider this reaction;

$$C_{(s)} + O_{2(g)} \;\longrightarrow\; CO_{2(g)} \qquad \Delta H^o = \; -394 \; kJ$$

We can calculate that -394 kJ from the ΔH^o of the individial reactions need for this reaction;

$$C_{(s)} + 0.5O_{2(g)} \;\longrightarrow\; CO_{(g)} \qquad \Delta H^o = \; -111 \; kJ$$

$$CO_{(g)} + 0.5O_{2(g)} \;\longrightarrow\; CO_{2(g)} \qquad \Delta H^o = \; -283 \; kJ$$

by adding these reactions together;

$$C_{(s)} + 0.5O_{2(g)} \longrightarrow \cancel{CO_{(g)}} \qquad \Delta H^o = \ -111\ kJ$$

$$+\ \cancel{CO_{(g)}} + 0.5O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^o = \ -283\ kJ$$

$$=\ C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^o = \ -394\ kJ$$

Two facts to keep in mind regarding enthalpy.

1.) The enthalpy is proportional to the number of moles participating in the reaction. i.e. doubling the amount of moles participating in a reaction will double the enthalpy change.

$$2(C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}) \qquad \Delta H^o = \ -788\ kJ$$

2.) The reverse reaction has an enthalpy change that is equal to the negative of that of the forward reaction.

$$CO_{2(g)} \longrightarrow C_{(s)} + O_{2(g)} \qquad \Delta H^o = \ 394\ kJ$$

Additional Problems:

1.)An aluminum kettle weighs 1.05 kg.

(a) What is the heat capacity of the kettle?

(b) How much heat is required to increase the temperature of this kettle from 23.0 °C to 99.0 °C?

(c) How much heat is required to heat this kettle from 23.0 °C to 99.0 °C if it contains 1.25 L of water (density of 0.997 g/mL and a specific heat of 4.184 J/g °C)?

2.) When a 0.740-g sample of trinitrotoluene (TNT), C7H5N2O6, is burned in a bomb calorimeter, the temperature increases from 23.4 °C to 26.9 °C. The heat capacity of the calorimeter is 534 J/°C, and it contains 675 mL of water. How much heat was produced by the combustion of the TNT sample?

3.) What mass of carbon monoxide must be burned to produce 175 kJ of heat under standard state conditions?

4.) How much heat is produced when 100 mL of 0.250 M HCl (density, 1.00 g/mL) and 200 mL of 0.150 M NaOH (density, 1.00 g/mL) are mixed?

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)} \qquad \Delta H^o \ = \ -58\ kJ$$

5.) Before the introduction of chlorofluorocarbons, sulfur dioxide (enthalpy of vaporization, 6.00 kcal/mol) was used in household refrigerators. What mass of SO2 must be evaporated to remove as much heat as evaporation of 1.00 kg of CCl2F2 (enthalpy of vaporization is 17.4 kJ/mol)? The vaporization reactions for SO2 and CCl2F2 are $SO_{2(l)} \longrightarrow SO_{2(g)}$ and $CCl_2F_{(l)} \longrightarrow CCl_2F_{2(g)}$, respectively.

6.) The following sequence of reactions occurs in the commercial production of aqueous nitric acid:

$$4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(l)} \qquad \Delta H \ = \ -907\ kJ$$

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)} \qquad \Delta H = \ -113\ kJ$$

$$3NO_2 + H_2O_{(l)} / \longrightarrow /2HNO_{3(aq)} + NO_{(g)} \qquad \Delta H \ = \ -139 \ kJ$$

Determine the total energy change for the production of one mole of aqueous nitric acid by this process.