Thermochemistry

Brown, LeMay Ch 5
AP Chemistry
Monta Vista High School

5.1: Thermochemistry

James Prescott Joule (1818-1889)

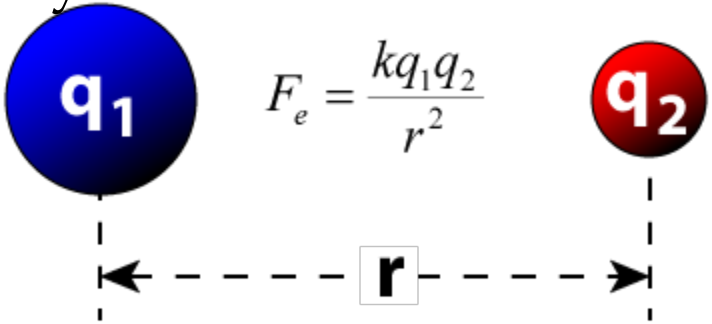
- From Greek *therme* (heat); study of energy changes in chemical reactions
- ***Energy:*** capacity do work or transfer heat
  - Joules (J), kilo joules (kJ) or calories (cal); 1 cal = 4.184 J

Kinetic: energy of motion; dependent on mass & velocity

Energy used to cause the temperature of an object to rise is called heat. Temperature change is associated with Kinetic energy and phase change (breaking/forming bonds) is associated with Potential energy. That is why temperature does not change during a phase change even though heat is given.

$$\boxed{KE = \frac{1}{2}mv^2}$$

•In chemistry KE is generally used for calculating e velocity in photoelectric effect, in molecular motion in gases and KE is directly proportional to the temperature.

2. ***Potential:*** stored in "fields" (gravitational and electrical/magnetic); dependant on position relative to another object
   - Applies to large objects where gravity is overriding force, but not significantly to molecules where gravity is negligible and electrostatic forces dominate
   - Associated with chemical energy; stored in arrangement of atoms or subatomic particles (electrostatic & nuclear forces, bonding between atoms). In chemistry, described by coulomb's law
   - 

$$F_e = \frac{kq_1q_2}{r^2}$$

Credit: Google Images

   - **Coulomb's Law is used in explaining properties such as strength of ionic bond, metallic bond, covalent bond, ionization energy and electron affinity.**

Vocabulary

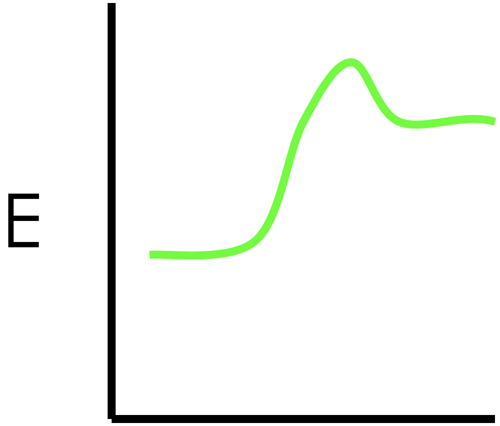
- ***System:*** "isolated" portion of study (typically just the chemicals in a reaction)
- ***Surroundings:*** everything else (container, room, Earth, etc.)

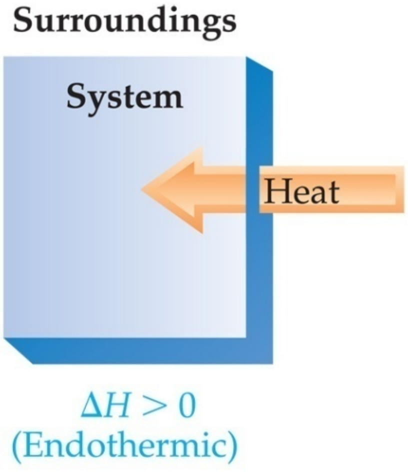
Closed system: easiest to study because exchanges *energy* with surroundings but *matter* is not exchanged.

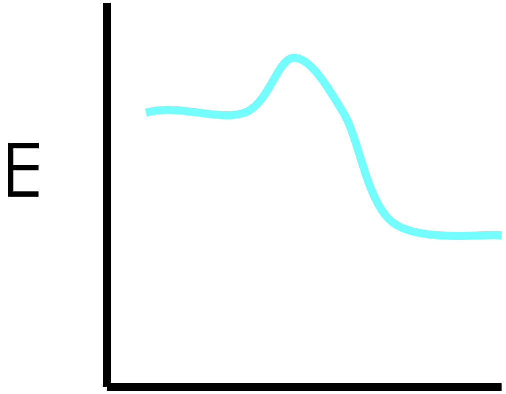
The system includes the molecules we want to study (here, the hydrogen and oxygen molecules).
The surroundings are everything else (here, the cylinder and piston).

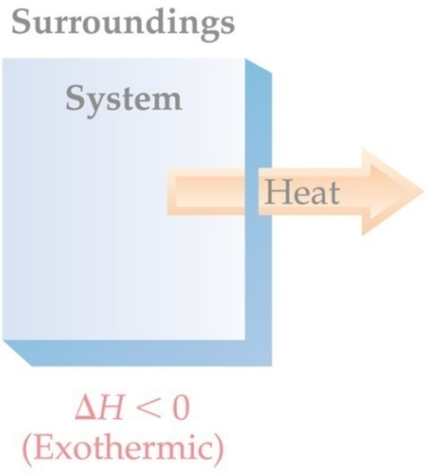
Heat & Reactions

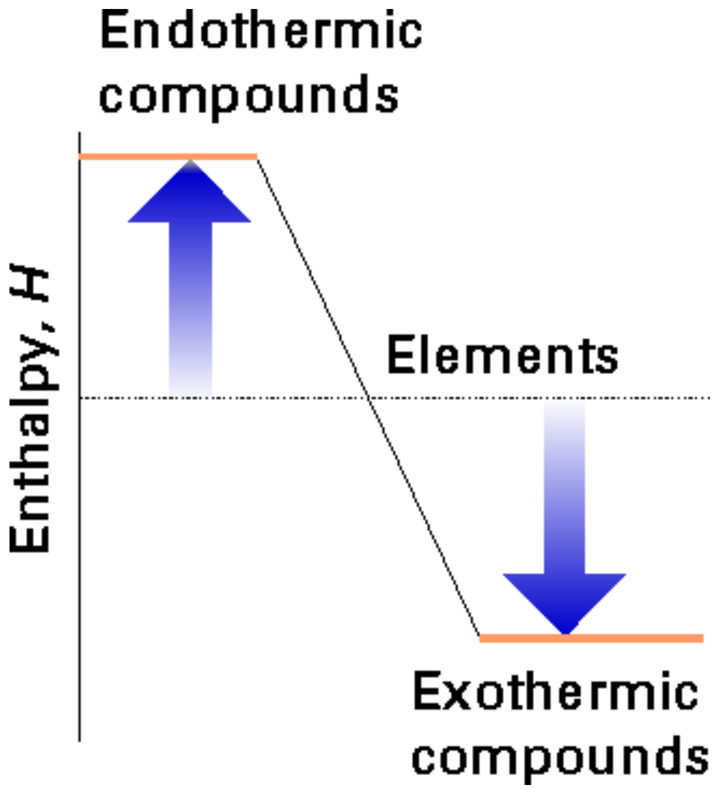
- http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/activa2.swf











if we replace strong
bonds with weak bonds
(or fewer bonds)
then the formation is
ENDOTHERMIC and takes
in heat.

If we replace weak bonds
with strong bonds (or
more bonds)
Then the formation is
EXOTHERMIC and gives off
heat.

Sign Conventions

$q > 0$ Heat is added to system

$q < 0$ Heat is removed from system (into surroundings)

$w > 0$ Work done to system

$w < 0$ System does work on surroundings

Laws of Thermodynamics

- ***"0th Law":*** 2 systems are in thermal equilibrium when they are at the same T.
  - Thermal equilibrium is achieved when the random molecular motion of two substances has the same intensity (and therefore the same T.)

- ***1st Law:*** Energy can be neither created nor destroyed, or, energy is conserved.

- ***2nd and 3rd Laws:*** discussed in Ch. 19

Internal energy, E

- Includes:
  - *Translational* motion
  - *Rotational* motion of particles through space
  - Internal *vibrations* of particles.

- It is difficult to measure all E, so the change in internal energy (ΔE) is typically measured:

$$\mathbf{\Delta E = E_{final} - E_{initial}}$$

$\Delta E > 0$	Increase in energy of system (gained from surroundings)
$\Delta E < 0$	Decrease in energy of system (lost to surroundings)

MATTER, MOTION, AND ENTROPY: A REVIEW

Answers will appear as you click. This is set up as a slide show so it will not print.

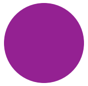
Credit: CHM 102 Sinex

What is the difference between an atomic and molecular substance?

Atomic	Molecular
single atom	multiple atoms
He	N_2
Ar	CO_2
Fe	C_6H_{12}

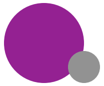
Describe the types of motion

- Translational



whole atom or molecule changes its location in three dimensional space

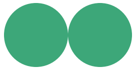
- Rotational



whole molecule spins around an axis in three dimensional space

Motion of whole molecule

- Vibrational



← Motion within molecule

motion that changes the shape of the molecule – stretching, bending, and rotation of bonds

Which type of motion contributes the most to the entropy of a substance?

Translational motion

Which type of motion is the cause of collisions?

Translational motion

Which type of motion influences the orientation for an effective collision?

Rotational motion

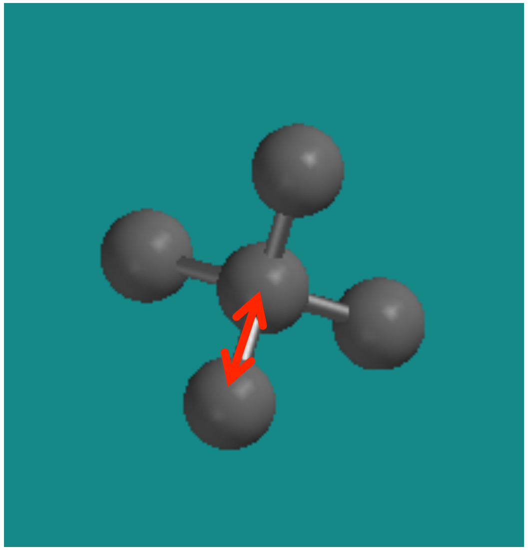
Types of Motion and the States of Matter

Matter		Mode		
State	Type	Translation	Rotation	Vibration
Gas	Atomic			
	Molecular			
Liquid	Atomic			
	Molecular			
Solid	Atomic			
	Molecular			

Types of Vibrations

Vibration	Minimum number of atoms	How atoms are connected	What changes?
Stretching			
Bending			
Internal rotation			

In solids such as the carbon tetrahedron from the diamond structure, how would you describe the motion of the atoms?



As the carbon atoms vibrate, all the bond lengths vary about an average value.

First Law of Thermodynamics

- When a system undergoes a chemical or physical change, the change in **internal energy (E) is equal to the heat (q)** added or liberated from the system **plus the work (w)** done on or by the system:

$$\Delta E = q + w$$

Example:

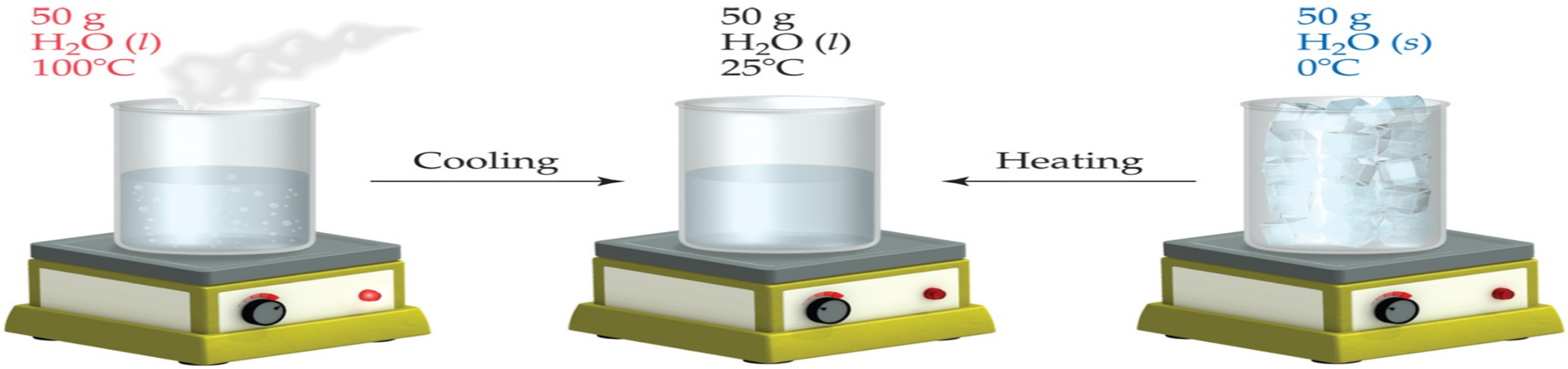
- Octane and oxygen gases combust within a closed cylinder in an engine. The cylinder gives off 1150 J of heat and a piston is pushed down by 480 J during the reaction. What is the change in internal energy of the system?
  - q is (-) since heat leaves system; w is (-) since work is done by system. Therefore,

    $\Delta E = q + w = (-1150\text{ J}) + (-480\text{ J}) = -1630\text{ J}$
  - 1630 J has been liberated from the system (C_8H_{18} and O_2) added to the surroundings (engine, atmosphere, etc.)

State functions

- Property of a system that is determined by specifying its condition or its “state”
  - The value of a state function depends only on its present state and not on the history of the sample.
  - T & E are state functions

    Consider 50 g of water at 25°C: E_{H2O} does not depend on how the water got to be 25°C (whether it was ice that melted or steam that condensed or…)



  - Work (w) and heat (q) are not state functions because the ratio of q and w are dependent on the scenario

    Consider the combustion of gasoline in a car engine vs. burning in the open.

Thermochemical Equation

- **Thermochemical equation:** A chemical equation that shows the enthalpy relation between products and reactants is called a thermochemical equation.

- Ex. $H_{2\,(g)} + Cl_{2\,(g)} \rightarrow 2\,HCl_{\,(g)} \quad \Delta H = -185\ kJ$
- If you reverse an equation, value of ΔH is reversed.
- If you double a rxn, value of ΔH is doubled.

Heat of Reaction

- Reactions either absorb PE (endothermic, +ΔH) or release PE (exothermic, -ΔH)

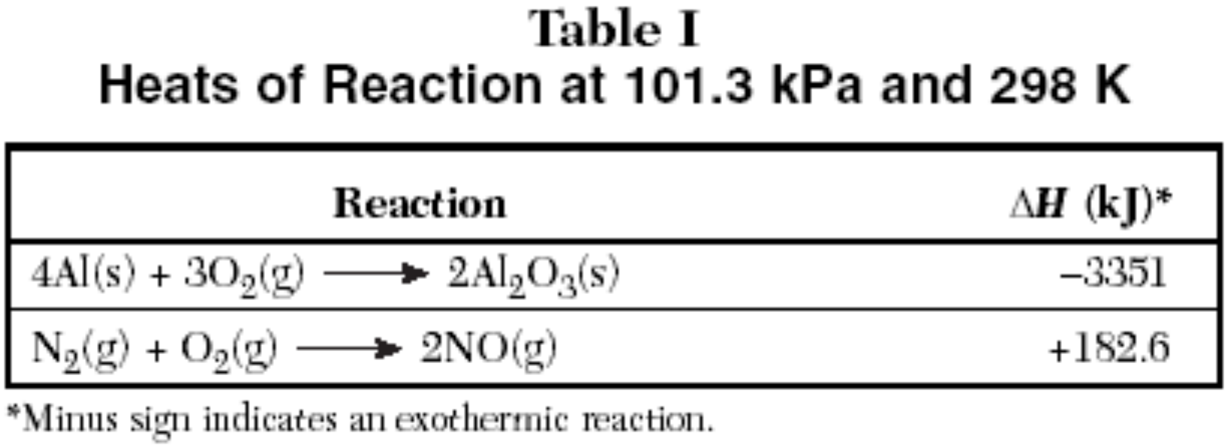


Table I

Heats of Reaction at 101.3 kPa and 298 K

Reaction	ΔH (kJ)*
$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$	–3351
$N_2(g) + O_2(g) \longrightarrow 2NO(g)$	+182.6

*Minus sign indicates an exothermic reaction.

Rewriting the equation with heat included:

$4\,Al(s) + 3\,O_2(g) \rightarrow 2\,Al_2O_3(s) + 3351\text{ kJ}$

$N_2(g) + O_2(g) + 182.6\text{ kJ} \rightarrow 2\,NO(g)$

Enthalpy

- **Enthalpy (H) is defined** as the heat content of a system at constant pressure.
- It is an extensive property.
- It is not possible to measure the heat content of the system only the changes in the heat content of the system can be measured. **Enthalpy change** is defined as the amount of heat absorbed or lost by a system during a process at constant pressure.
- **Heat of reaction and change in enthalpy are used interchangeably.**
- **Units**: kJ/mol
- Q_{reaction} at constant pressure= ΔH(change in enthalpy) = H (products) – H (reactants)

The Truth about Enthalpy

-Enthalpy is an extensive property. hence it is proportional to the amount of reactants and products. e.g. for decomposition of two moles of water twice as much energy is needed as for one mole of water.

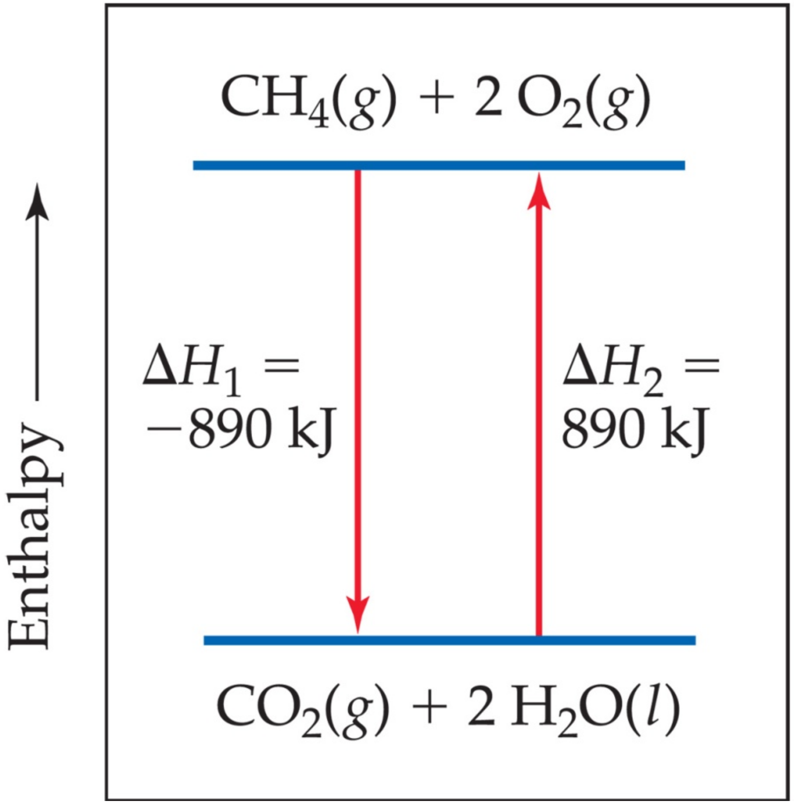
-ΔH for a reaction in the forward direction is equal in size, but opposite in sign, to ΔH for the reverse reaction. Reversing a reaction changes the sign of enthalpy. $A \rightarrow B$ 10kJ, then $B \rightarrow A$ –10kJ

-ΔH for a reaction depends on the state of the products and the state of the reactants. (different values of dH for $H_2O_{(l)}$ and $H_2O_{(g)}$)

Enthalpy of Reaction

The *change* in enthalpy, ΔH, is the enthalpy of the products minus the enthalpy of the reactants:

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



Standard Enthalpies of Formation:

-It is amount of heat absorbed or released when 1 mole of a compound is formed from its constituent elements

-ΔHf is 0 from pure elements in their natural state.

-Standard enthalpies of formation, ΔH_f°, are measured under standard conditions (25 °C and 1.00 atm pressure).

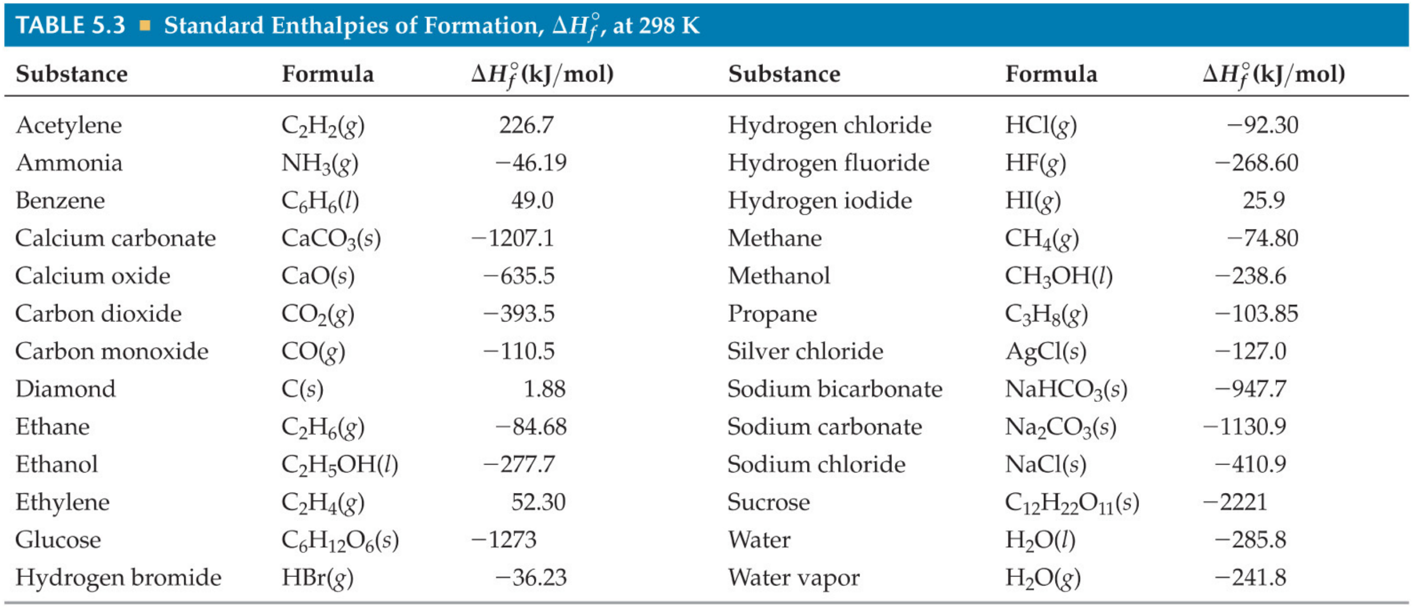


TABLE 5.3 ■ **Standard Enthalpies of Formation, ΔH_f°, at 298 K**

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	−92.30
Ammonia	$NH_3(g)$	−46.19	Hydrogen fluoride	$HF(g)$	−268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	−1207.1	Methane	$CH_4(g)$	−74.80
Calcium oxide	$CaO(s)$	−635.5	Methanol	$CH_3OH(l)$	−238.6
Carbon dioxide	$CO_2(g)$	−393.5	Propane	$C_3H_8(g)$	−103.85
Carbon monoxide	$CO(g)$	−110.5	Silver chloride	$AgCl(s)$	−127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	−947.7
Ethane	$C_2H_6(g)$	−84.68	Sodium carbonate	$Na_2CO_3(s)$	−1130.9
Ethanol	$C_2H_5OH(l)$	−277.7	Sodium chloride	$NaCl(s)$	−410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	−2221
Glucose	$C_6H_{12}O_6(s)$	−1273	Water	$H_2O(l)$	−285.8
Hydrogen bromide	$HBr(g)$	−36.23	Water vapor	$H_2O(g)$	−241.8

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Enthalpy of Formation (ΔH_f)

- ***Formation:*** a reaction that describes a substance formed from its elements

  Ex: $2\ N_2\ (g) + 4\ H_2\ (g) + 3\ O_2\ (g) \rightarrow 2\ NH_4NO_3\ (s)$

- Standard enthalpy of formation ($\Delta H_f°$): forms 1 mole of compound from its elements in their standard state (at 298 K)

  $2\ C\ (graphite) + 3\ H_2\ (g) + ½\ O_2\ (g) \rightarrow C_2H_5OH\ (l)$

  $\Delta H_f° = -\ 277.7$ kJ

  - $\Delta H_f°$ of the most stable form of any element equals zero.
    H_2, N_2, O_2, F_2, Cl_2 (g)
    Br_2 (l), Hg (l)
    C (graphite), P_4 (s, white), S_8 (s), I_2 (s)

Enthalpy of Combustion (ΔH_c)

- **Enthalpy of Combustion** is the heat released by the complete combustion of one mole of a substance. ΔHc
- **Example:** Write a thermochemical equation for combustion of C_6H_6, if ΔHc for C_6H_6 is –3169.0 kJ/mol.

Enthalpy of Vaporization ΔH_{vap}

- **Enthalpy of Vaporization**: Amount of heat required to boil (or condense) 1 mol of a substance at its boiling point. ***ΔH_{vap} for water= 40.7 kJ/mol, what would $\Delta H_{condensation}$ be for water?***

Example:

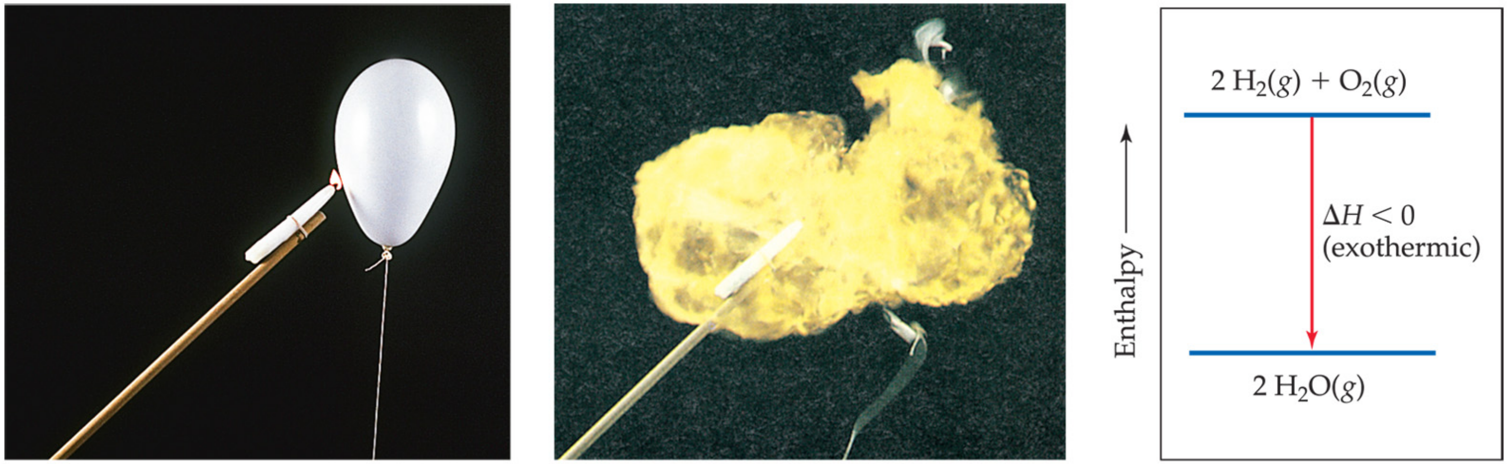
- How much heat is required to vaporize 5 moles of water at its B.P.?

Enthalpy of Fusion ΔH_{fus}

- **Enthalpy of Fusion:** Amount of heat required to melt (or freeze) 1.00 mol of a substance at its freezing point. ΔH_{fus} ***for water=6.02kJ/mol***

Enthalpy of Reaction

This quantity, ΔH, is called the enthalpy of reaction, or the heat of reaction.



Enthalpy of Reaction (ΔH_{rxn})

- Also called ***heat of reaction:***

1. Enthalpy is an extensive property (depends on amounts of reactants involved).

Ex: $CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(l)$

$\Delta H_{rxn} = -\,890.\text{ kJ}$

- Combustion of 1 mol CH_4 produces 890. kJ

… of 2 mol CH_4 → (2)(-890. kJ) = -1780 kJ

What is the ΔH of the combustion of 100. g CH_4?

2. $\Delta H_{\text{reaction}} = - \Delta H_{\text{reverse reaction}}$

$CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (l)$

$\Delta H = -\ 890.\ \text{kJ}$

$CO_2\ (g) + 2\ H_2O\ (l) \rightarrow CH_4\ (g) + 2\ O_2\ (g)$

$\Delta H = +890.\ \text{kJ}$

Hess' Law

Germain Hess (1802-1850)

If a rxn is carried out in a series of steps,

$$\Delta H_{rxn} = \Sigma\,(\Delta H_{steps}) = \Delta H_1 + \Delta H_2 + \Delta H_3 + \ldots$$

Ex. What is ΔH_{rxn} of the combustion of propane?

$$C_3H_8\,(g) + 5\,O_2\,(g) \rightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$$

$3\,C\,(s) + 4\,H_2\,(g) \rightarrow C_3H_8\,(g)$ $\Delta H_1 = -103.85$ kJ

$C_3H_8\,(g) \rightarrow 3\,C\,(s) + 4\,H_2\,(g)$ $\Delta H_1 = +103.85$ kJ

$3[\,C\,(s) + O_2\,(g) \rightarrow CO_2\,(g)\,]$ $\Delta H_2 = 3(-393.5$ kJ$)$

$4[\,H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightarrow H_2O\,(l)\,]$ $\Delta H_3 = 4(-285.8$ kJ$)$

$$\Delta H^\circ_{rxn} = 103.85 + 3(-\,393.5) + 4(-\,285.8) = -\,2219.8 \text{ kJ}$$

Calculation of ΔH

We can use Hess's law in this way:

$$\Delta H = \Sigma\, n\, \Delta H_f^\circ{}_{\text{products}} - \Sigma\, m\, \Delta H_f^\circ{}_{\text{reactants}}$$

where *n* and *m* are the stoichiometric coefficients.

Hess' Law (again): Heat of formations can be used to calculate heat of reaction.

Ex. Combustion of propane:

$C_3H_8\ (g) + 5\ O_2\ (g) \longrightarrow 3\ CO_2\ (g) + 4\ H_2O\ (l)$

Given:

Compound	ΔH°_{rxn} (kJ/mol)
C_3H_8 (g)	-103.85
CO_2 (g)	-393.5
H_2O (l)	-285.8
H_2O (g)	-241.82

$$\Delta H^\circ_{rxn} = [3(-393.5) + 4(-285.8)] - [1(-103.85) + 5(0)]$$

$$= -2219.8\ \text{kJ}$$

Calorimetry

- Measurement of heat flow
- ***Heat capacity, C:*** amount of heat required to raise T of an object by 1 K

$$\mathbf{q = C\,\Delta T}$$

- ***Specific heat*** (or ***specific heat capacity,*** **c**): heat capacity of 1 g of a substance

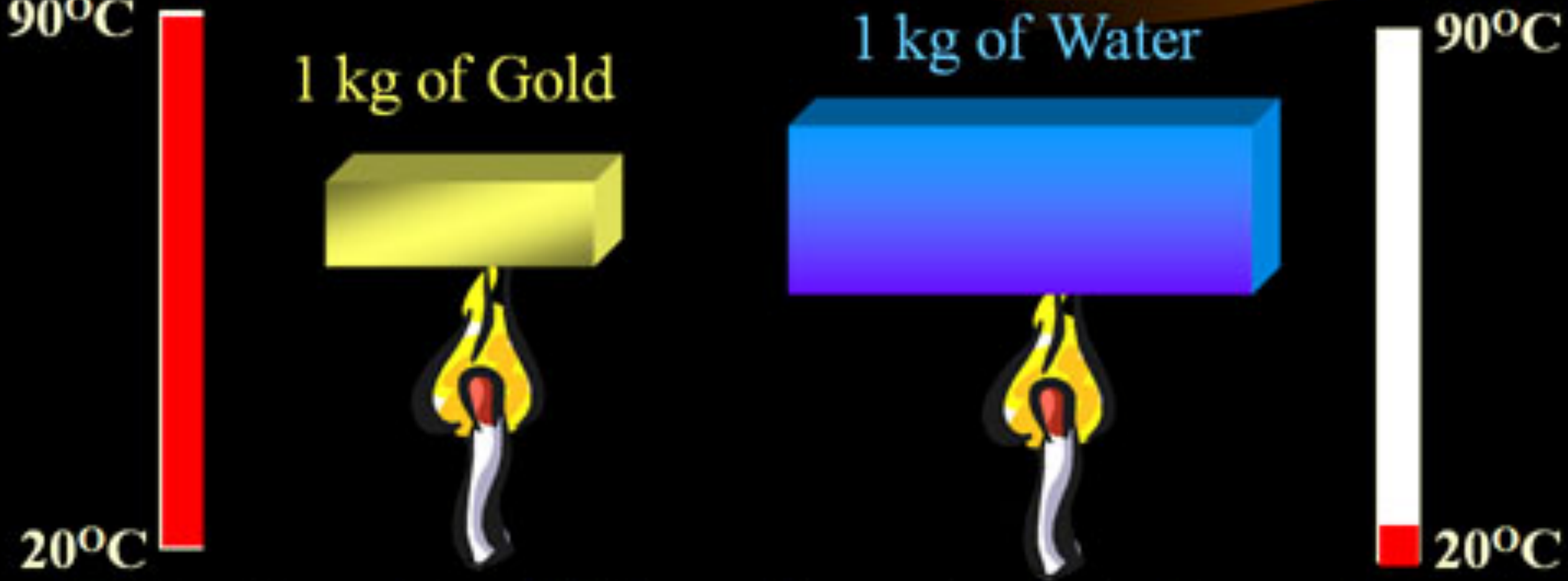
$$\mathbf{q = m\,c\,\Delta T}$$

Ex: How much energy is required to heat 40.0 g of iron (c = 0.45 J/(g K) from 0.0°C to 100.0°C?

$$q = m\,c\,\Delta T = (40.0\text{ g})(0.45\text{ J/(g K)})(100.0 - 0.0\ {}^{o}\text{C})$$

$$= 1800\text{ J}$$

Different materials store different amounts of heat energy.



Water takes about 30 times longer to heat than gold, meaning it stores about 30 times more calories.

- **Calorimetry** is an experimental technique used to measure the heat transferred in a physical or chemical process.
- The apparatus used in this procedure is called as a "**Calorimeter**". There are two types of calorimeters- Constant pressure (coffee cup) and constant volume (bomb calorimeter). We will discuss constant pressure calorimeter in detail.
- **Constant Pressure Calorimeter**: The coffee cup calorimeter is an example of this type of calorimeter. The system in this case is the "contents" of the calorimeter and the surroundings are cup and the immediate surroundings.
- **qrxn + q soln + q cal =0**

During the rxn:

$$q_{rxn} + q_{solution} = 0$$

- where q_{rxn} is the heat gained or lost in the chemical reaction and $q_{solution}$ is the heat gained or lost by solution. Heat exchange in this system (q_{rxn}), is equal to enthalpy change. Assuming no heat transfer takes place between the system and surroundings, $q_{rxn} + q_{solution} = 0$

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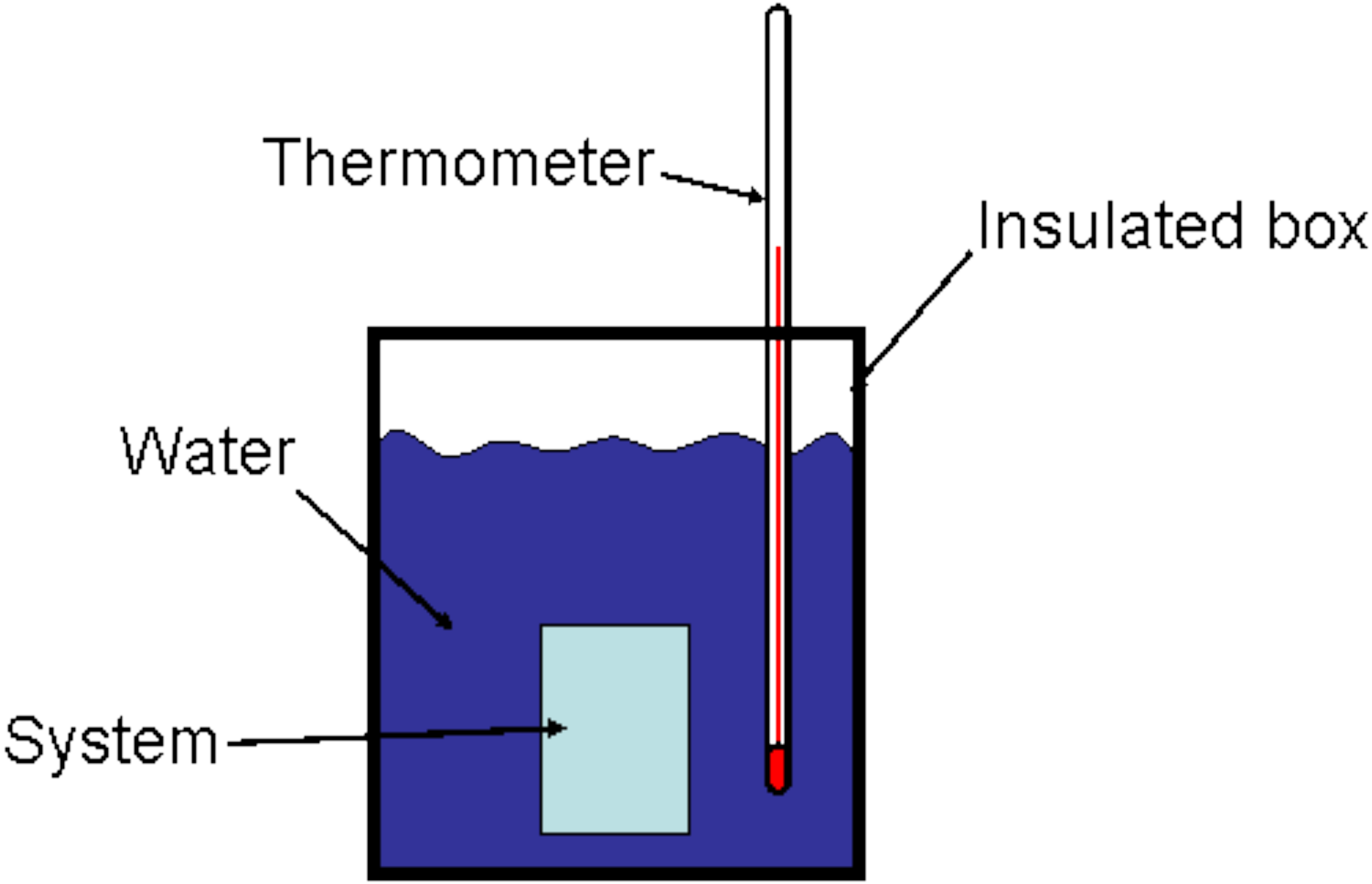
Constant Pressure Calorimetry

By carrying out a reaction in aqueous solution in a simple calorimeter such as this one, one can indirectly measure the heat change for the system by measuring the heat change for the water in the calorimeter.



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Sample Problem #1:

1. 0.500g of magnesium chips are placed in a coffee-cup calorimeter and 100.0 ml of 1.00 M HCl is added to it. The reaction that occurs is:

$Mg\ (s) + 2HCl\ (aq) \rightarrow H_2\ (g) + MgCl_2\ (aq)$

The temperature of the solution increases from 22.2^oC (295.4 K) to 44.8 ^oC (318.0 K). What's the enthalpy change for the reaction, per mole of Mg? (Assume specific heat capacity of solution is 4.20 J/(g * K) and the density of the HCl solution is 1.00 g/ml.)

Ans. -4.64×10^5 *J/mol Mg*

Sample Problem #2:

200. ml of 0.400 M HCl is mixed with the same amount and molarity of NaOH solution, inside a coffee-cup calorimeter. The temperature of the solutions before mixing was 25.10 ^{o}C, and 27.78 ^{o}C after mixing and letting the reaction occur. Find the molar enthalpy of the neutralization of the acid, assuming the densities of all solutions are 1.00 g/ml and their specific heat capacities are 4.20 J/(g * K).

Heat Transfer (Heating and Cooling Curves)

- **Heat Transfer** : Heating and cooling curves can be used to calculate heat exchange during phase changes
- http://www.dlt.ncssm.edu/tiger/Flash/phase/HeatingCurve.html (Heating/Cooling Curve Animation)

For Calculating Energy at Phase Change

- During phase changes all the heat is used for breaking the bonds. To calculate amount of heat absorbed/released during phase changes (q), the following formula is used: **$Q = m.\ \Delta H$ (or $n.\ \Delta H$)**
- Value of ΔH changes with phase change. ΔH of water has following values:
- **H_{fusion} = 334 J/g (6.02 kJ/mol), $H_{freezing}$ = - 334 J/g (-6.02 kJ/mol),**
- **$H_{vaporization}$ = 2260 J/g (40.7 kJ/mol), $H_{condensation}$ = -2260 J/g (-40.7 kJ/mol)**

For Calculating Energy other than at phase change

- Use the formula **$Q=m \times c \times \Delta t$**
- Total energy change can be calculated by adding all the energy changes.

Ex. How much heat is needed to vaporize 5.0 g of ice at -5 degree C to steam at 110 degree C?