Energy

The capacity to do work or to produce heat.

Law of Conservation of Energy

Energy can be converted from one form to another but can neither be created nor destroyed.

($E_{universe}$ is constant)

The Two Types of Energy

Potential: due to position or composition - can be converted to work

Kinetic: due to motion of the object

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

(m = mass, v = velocity)

Temperature v. Heat

Temperature reflects random motions of particles, therefore related to kinetic energy of the system.

Heat involves a transfer of energy between 2 objects due to a temperature difference

State Function

Depends only on the present state of the system - not how it arrived there.

It is independent of pathway.

System and Surroundings

System: That on which we focus attention

Surroundings: Everything else in the universe

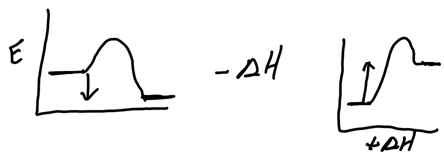
Universe = System + Surroundings

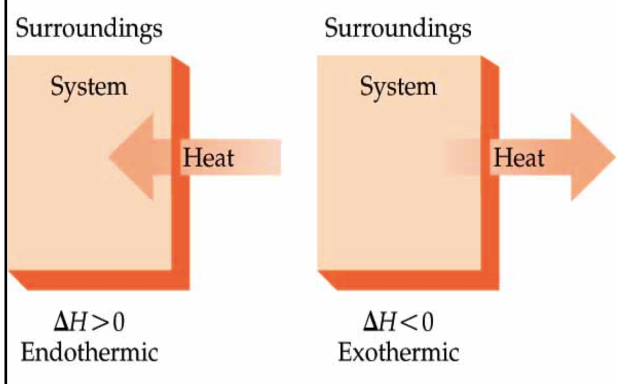
Exo and Endothermic

Heat exchange accompanies chemical reactions. Enthalpy (ΔH)

Exothermic: Heat flows out of the system (to the surroundings). $-\Delta H$

Endothermic: Heat flows into the system (from the surroundings). $+\Delta H$





First Law

First Law of Thermodynamics: The energy of the universe is constant.

First Law

$$\Delta E = q + w$$

ΔE = change in system's internal energy

q = heat

w = work

6.1 Why do heat (q) and work (w) have positive values when entering a system and negative values when leaving?

6.9 A system receives 425 J of heat from and delivers 425 J of work to its surroundings. What is the change in internal energy of the system (in J)? A:

$\Delta E = q + w$

$425 J + (-425 J) = 0$

The SI unit of energy is the **joule (J)**, a derived unit composed of three base units:

$$1\ J = 1\ kg{\cdot}m^2/s^2$$

$1\ J = 1\ \frac{kg \cdot m^2}{s^2}$

Both heat and work are expressed in joules. Let's see why the joule is the unit for work. The work (w) done on a mass is the force (F) times the distance (d) that the mass moves: $w = F \times d$. A *force* changes the velocity of a mass over time; that is, a force *accelerates* a mass. Velocity has units of meters per second (m/s), so acceleration (a) has units of meters per second per second (m/s^2). Force, therefore, has units of mass (m, in kilograms) times acceleration:

	$F = m \times a$	has units of	$kg{\cdot}m/s^2$
Therefore,	$w = F \times d$	has units of	$(kg{\cdot}m/s^2) \times m = kg{\cdot}m^2/s^2 = J$

The **calorie (cal)** is an older unit defined originally as the quantity of energy needed to raise the temperature of 1 g of water by 1°C (specifically, from 14.5°C to 15.5°C). The calorie is now defined in terms of the joule:

$$1\ cal \equiv 4.184\ J \quad \text{or} \quad 1\ J = \frac{1}{4.184}\ cal = 0.2390\ cal$$

Since the quantities of energy involved in chemical reactions are usually quite large, chemists use the kilojoule (kJ) or, in earlier sources, the kilocalorie (kcal): Page 262

$$1\ kJ = 1000\ J = 0.2390\ kcal = 239.0\ cal$$

The nutritional Calorie (note the capital C), the unit that measures the energy available from food, is actually a kilocalorie:

$$1\ Cal = 1000\ cal = 1\ kcal = 4184\ J$$

1 Cal = 1000 cal

The *British thermal unit (Btu)*, a unit that you may have seen used for the energy output of appliances, is the quantity of energy required to raise the temperature of 1 lb of water by 1°F; *1 Btu is equivalent to 1055 J*. In general, the SI unit (J or kJ) is used in this text. Some interesting quantities of energy are featured in **Figure 6.5**.

6.14 Thermal decomposition of 5.0 metric tons of limestone to lime and carbon dioxide absorbs 9.0×10^6 kJ of heat. Convert this energy to (a) joules; (b) calories; (c) British thermal units.

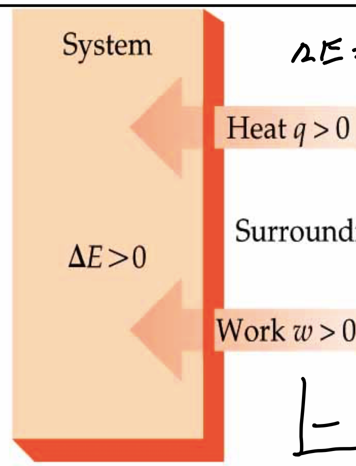
Energy 1cal = 4.184 J

Food 1Cal = 1000 cal

British Thermal Units (BTU) 1 BTU = 1055 J

$9.0 \times 10^6 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 9.0 \times 10^9 \text{ J}$

$9.0 \times 10^9 \text{ J} \times \frac{1 \text{ cal}}{4.184 \text{ J}} = 2.15 \times 10^9 \text{ cal}$



$\Delta E = q + w$

Work

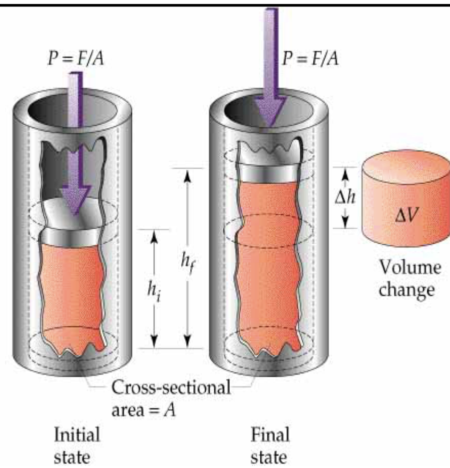
work = force × distance

since pressure = force / area,

work = pressure × volume

atm press

$w_{system} = -P\Delta V$



Enthalpy

Enthalpy = $H = E + PV$

$\Delta E = \Delta H - P\Delta V$

$\Delta H = \Delta E + P\Delta V$

At constant pressure,

$q_P = \Delta E + P\Delta V$,

where $q_P = \Delta H$ at constant pressure

ΔH = energy flow as heat (at constant pressure)

Problem 5.37

$2Mg(s) + O_2(g) \longrightarrow 2MgO(s) \quad \Delta H = -1204 \text{ kJ}$

(a) Is this reaction exothermic or endothermic?

(b) Calculate the amount of heat transferred when 2.4 g of Mg(s) reacts at constant pressure.

(c) How many grams of MgO are produced during an enthalpy change of −96.0 kJ?

(d) How many kilojoules of heat are absorbed when 7.50 g of MgO(s) is decomposed into Mg(s) and O_2(g) at constant pressure?

sys → surr

$2Mg + O_2 \rightarrow 2MgO + \text{heat}$

$2.4 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.3 \text{ g Mg}} \times \frac{1204 \text{ kJ}}{2 \text{ mol Mg}} = 59.4 \text{ kJ}$

$96.0 \text{ kJ} \times \frac{2 \text{ mol MgO}}{1204 \text{ kJ}} \times \frac{40.3 \text{ g MgO}}{1 \text{ mol MgO}} = 6.43 \text{ g MgO}$

6.61 Liquid hydrogen peroxide, an oxidizing agent in many rocket fuel mixtures, releases oxygen gas on decomposition:

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g) \quad \Delta H = -196.1\ \text{kJ}$$

How much heat is released when 652 kg of H_2O_2 decomposes?

6.62 Compounds of boron and hydrogen are remarkable for their unusual bonding (described in Section 14.5) and also for their reactivity. With the more reactive halogens, for example, diborane (B_2H_6) forms trihalides even at low temperatures:

$$B_2H_6(g) + 6Cl_2(g) \longrightarrow 2BCl_3(g) + 6HCl(g) \quad \Delta H = -755.4\ \text{kJ}$$

What is ΔH per kilogram of diborane that reacts?

6.61

$$652\ kg\ H_2O_2 \times \frac{1000\ g\ H_2O_2}{1\ kg} \times \frac{1\ mol\ H_2O_2}{34.02\ g\ H_2O_2} \times \frac{196.1\ kJ}{2\ mol\ H_2O_2} = -1.88 \times 10^6\ kJ$$

6.62 $1.0\ kg\ B_2H_6$

Heat Capacity

$$C = \frac{\text{heat absorbed}}{\text{increase in temperature}} = \frac{J}{°C} \text{ or } \frac{J}{K}$$

Some Heat Exchange Terms

specific heat capacity

heat capacity per gram = J/° C g or J/K g

$\frac{J°}{g\ °C}$

molar heat capacity

heat capacity per mole = J/° C mol or J/K mol

$\frac{J°}{g\ °C}$ $\frac{J}{°C \cdot mol}$

6.40 A 27.7-g sample of the radiator coolant ethylene glycol releases 688 J of heat. What was the initial temperature of the sample if the final temperature is 32.5°C (c of ethylene glycol = 2.42 J/g·K)?

$$E = s \times m \times \Delta T$$

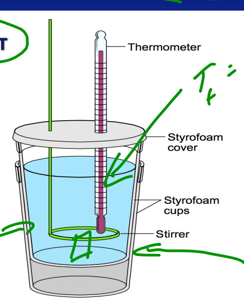
$$688\ J = \left(2.42 \frac{J}{g\ °C}\right)(27.7\ g)\Delta T$$

$$\Delta T = 10.3\ °C$$

$$T_i = 42.8\ °C$$

Constant Pressure Calorimetry

E= s × m × ΔT



$T_f = 25\ °C$

23 °C

100 °C metal

$$E_{H_2O} = S_{H_2O} \times m_{H_2O} \times \Delta T \quad (25 - 23)$$

$$E_{metal} = S_{metal} \times m_{metal} \times \Delta T \quad (100 - 25\ °C)$$

$$E_{H_2O} = E_{metal}$$

6.47 When 25.0 mL of 0.500 M H_2SO_4 is added to 25.0 mL of 1.00 M KOH in a coffee-cup calorimeter at 23.50°C, the temperature rises to 30.17°C. Calculate ΔH in kJ per mole of H_2O formed. (Assume that the total volume is the sum of the volumes and that the density and specific heat capacity of the solution are the same as for water.)

$$E = s \times m \times \Delta T$$

$$E = \left(\frac{4.184\ J}{g\ °C}\right)(50.0\ g)(30.17 - 23.50°)$$

50 mL

$$E = 1395.36\ J \times \frac{1\ kJ}{1000\ J} = 1.395\ kJ$$

$$H_2SO_4 + KOH \rightarrow H_2O + SO_4^{2-} + K^+$$

$$H^+ + OH^- \rightarrow H_2O$$

mol 0.025 0.025

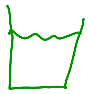
$$0.025\ mol\ OH^- \times \frac{1\ mol\ H_2O}{1\ mol\ OH^-} = 0.025\ mol\ H_2O$$

$$25\ mL\ KOH \times \frac{1.00\ mol\ KOH}{1000\ mL} = 0.025\ mol\ OH$$

$$\Delta H = \frac{1.395\ kJ}{0.025\ mol} = -55.8\ kJ/mol$$

A 15.0 g sample of nickel is heated to 99.8 °C and placed in a coffee cup calorimeter. The calorimeter contains 150.0 g of water at 23.5 °C. After allowing the two substance to equilibrate the final temperature was 25.0 °C.

What is the specific heat of the metal?



$E_{H_2O} = (4.184 \frac{J}{°C\,g})(150.0\,g)(25.0-23.5°C)$

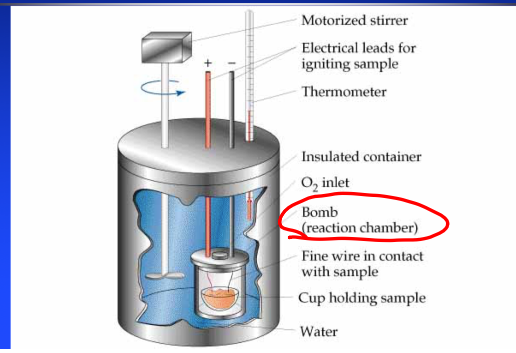
$'' = 941.4\ J$

$E_{metal} = S_{metal} \times m \times \Delta t$

$941.4J = S_{metal} \times 15.0\,g \times (99.8-25°C)$

$S_{metal} = \frac{941.4J}{(15.0g)(99.8-25°C)} = 0.839 \frac{J}{g°C}$

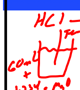
Constant Volume Colorimetry



$MgO_{(s)} + 2H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_2O_{(l)}$

1.234 g of MgO was combined with 60.0 mL HCL in a constant pressure calorimeter. The initial temperature of the solution was 21.2 °C and the final temperature was 24.6 °C. Calculate the Enthalpy (ΔH) for this reaction. (The specific heat for the solution is 4.184 J °C^{-1} g^{-1})

$HCl \rightarrow H^+ + Cl^-$



$E = S \times m_{soln} \times \Delta T$

$= (4.184 \frac{J}{°C\,g})(60\,g + 1.234\,g)(24.6-21.2°C)$

$E = 871.09\ J = 0.871\ kJ$

$\Delta H = \frac{0.871\ kJ}{0.031\ mol} = -28.097 \frac{kJ}{mol}$

$1.234\,g\ MgO \times \frac{1\ mol\ MgO}{40.3\,g\ MgO} = 0.031\ mol\ MgO$

Problem

When 3.88 g of solid ammonium nitrate dissolves in 60.0 g of water in a coffee-cup calorimeter, the temperature drops from 23.0 °C to 18.4 °C.

a. Calculate the enthalpy (in kJ/mole of ammonium nitrate) for the solvation process (The specific heat for the solution is 4.184 J °C^{-1} g^{-1}).

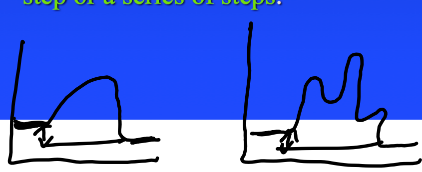
b. Is the process endothermic or exothermic?

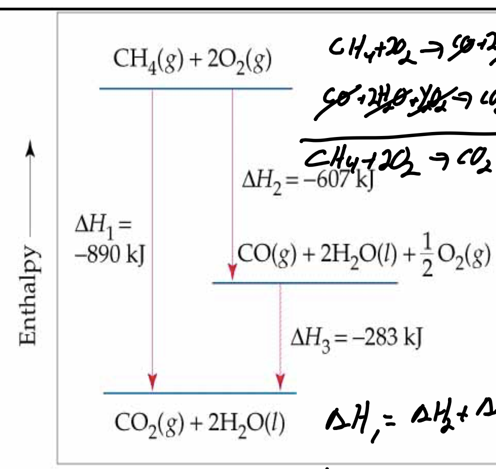
$NH_4NO_3 \rightarrow NH_4^+ + NO_3^-$

Hess's Law

Reactants → Products

The change in enthalpy is the same whether the reaction takes place in one step or a series of steps.





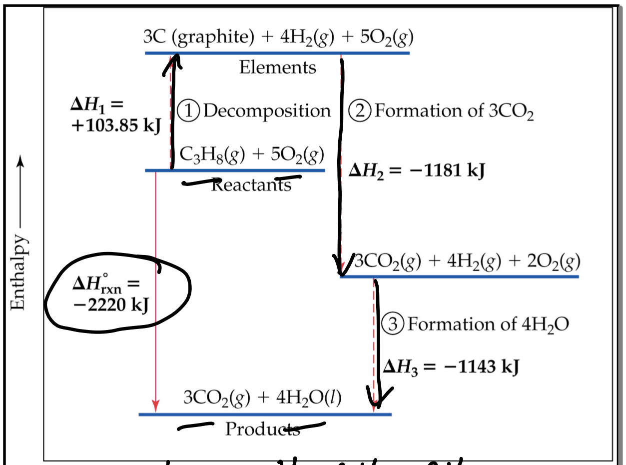
$CH_4 + 2O_2 \rightarrow CO + 2H_2O + \frac{1}{2}O_2$

$CO + 2H_2O + \frac{1}{2}O_2 \rightarrow CO_2 + 2H_2O$

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$\Delta H_1 = \Delta H_2 + \Delta H_3$

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



$\Delta H_{Rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3$

Calculations via Hess's Law

1. If a reaction is reversed, ΔH is also reversed.

   $N_2(g) + O_2(g) \rightarrow 2NO(g) \quad \Delta H = 180\ kJ$

   $2NO(g) \rightarrow N_2(g) + O_2(g) \quad \Delta H = -180\ kJ$

2. If the coefficients of a reaction are multiplied by an integer, ΔH is multiplied by that same integer.

   $6NO(g) \rightarrow 3N_2(g) + 3O_2(g) \quad \Delta H = -540\ kJ$

$\times 3$ $\quad 3(-180) = -540$

Problem

Calculate the enthalpy change for the reaction

$P_4O_6(s) + 2O_2(g) \rightarrow P_4O_{10}(s)$ $\quad \Delta H_{Rxn} = ?$

given the following enthalpies of reaction:

$P_4(s) + 3O_2(g) \rightarrow P_4O_6(s) \quad \Delta H = -1640.1\ kJ$

$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s) \quad \Delta H = -2940.1\ kJ$

$P_4O_6 \rightarrow P_4 + 3O_2 \quad \Delta H = 1640\ kJ$

$P_4 + 5O_2 \rightarrow P_4O_{10} \quad -2940.1\ kJ$

$P_4O_6 + 2O_2 \rightarrow P_4O_{10} \quad \Delta H_{Rxn} = -1300\ kJ$

Problem ΔH

Use Hess's Law to calculate the standard enthalpy of formation of solid $Mg(OH)_2$ given the following data:

$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$	$\Delta H° = -1203.6\ kJ$
$Mg(OH)_2(s) \longrightarrow MgO(s) + H_2O(l)$	$\Delta H° = +37.1\ kJ$
$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$	$\Delta H° = -571.7\ kJ$

$Mg_{(s)} + O_{2(g)} + H_{2(g)} \rightarrow Mg(OH)_{2(s)} \quad \Delta H_{Rxn} = ?$

$H_2O + MgO \rightarrow Mg(OH)_2 \quad -37.1\ kJ$

$\frac{2}{2}Mg + \frac{1}{2}O_2 \rightarrow \frac{2}{2}MgO \quad \frac{-1203.6}{2}$

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \frac{-571.7}{2}$

$Mg + H_2 + O_2 \rightarrow Mg(OH)_2$

$\Delta H_{Rxn} = -924.75\ kJ$

Problem

Given the data

$N_2(g) + O_2(g) \longrightarrow 2NO(g)$	$\Delta H = +180.7\ kJ$
$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$	$\Delta H = -113.1\ kJ$
$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$	$\Delta H = -163.2\ kJ$

use Hess's law to calculate ΔH for the reaction

$N_2O(g) + NO_2(g) \rightarrow 3NO(g)$

$\Delta H_{Rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3$

Standard Enthalpies of Formation

Change in enthalpy that accompanies the formation of one mole of substance from its elements, with all substances in their standard states.

$\Delta H_f^o = -601\ kJ/mol$

$Mg_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow MgO_{(s)}$

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	$HF(g)$	−268.6
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	−1207.1	Methane	$CH_4(g)$	−74.8
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

$\frac{1}{2} N_{2(g)} + \frac{3}{2} H_{2(g)} \rightarrow NH_{3(g)}$

Standard States

Compound

- For a gas, pressure is exactly 1 atmosphere.
- For a solution, concentration is exactly 1 molar.
- Pure substance (liquid or solid), it is the pure liquid or solid.

Element

- The form [$N_2(g)$, $K(s)$] in which it exists at 1 atm and 25° C.

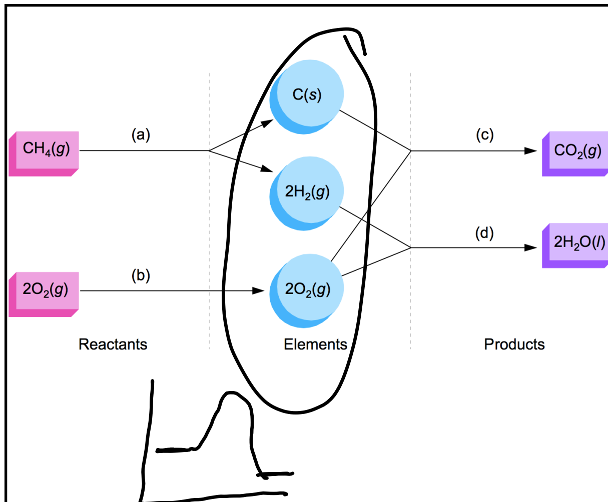
Change in Enthalpy

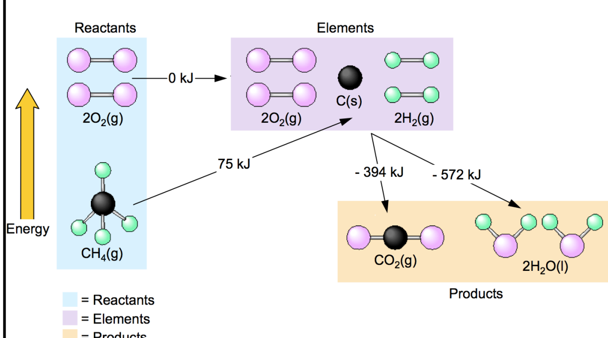
Can be calculated from enthalpies of formation of reactants and products.

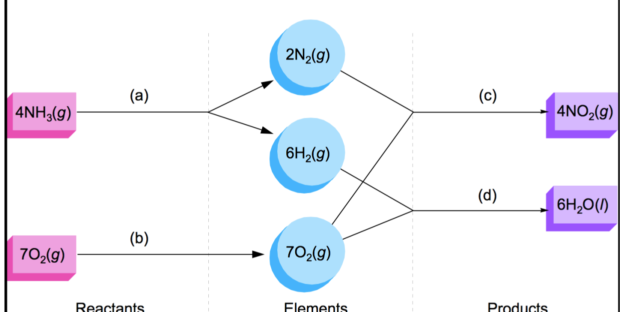
$$\Delta H_{rxn}^\circ = \Sigma n_p \Delta H_f^\circ(\text{products}) - \Sigma n_r \Delta H_f^\circ(\text{reactants})$$

$\Delta H^\circ_{rxn} = \Sigma n_p \Delta H^\circ_{f\,p} - \Sigma n_r \Delta H^\circ_{f\,r}$

$E = s \times m \times \Delta T$







6.77 What is the difference between the standard enthalpy of formation and the standard enthalpy of reaction?

6.78 How are ΔH_f° values used to calculate ΔH_{rxn}°?

$$\Delta H_{Rxn}^\circ = \sum n_p \Delta H_{f_p}^\circ - \sum n_r \Delta H_{f_r}^\circ$$

$$M_{(s)} + \tfrac{1}{2}O_{2(g)} \rightarrow MO_{(s)}$$

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Hydrogen bromide	$HBr(g)$	−36.23	Water vapor	$H_2O(g)$	−241.8

$$2CH_3OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(g)}$$

$$\Delta H_{Rxn} = \sum n_p \Delta H_p^\circ - \sum n_r \Delta H_r^\circ$$

$$= \left[2\,mol\,CO_2\left(\frac{-393.5\,kJ}{mol}\right) + 4\,mol\,H_2O_g\left(\frac{-241.8\,kJ}{mol}\right)\right] - \left[2\,mol\,CH_3OH\left(\frac{-238.6\,kJ}{mol}\right) + 3\,mol\,O_2\left(\frac{0\,kJ}{mol}\right)\right]$$

$$\Delta H_{Rxn} = -1277\,kJ$$

$$1.0\,kg\,CH_3OH \times \frac{1000\,g}{1\,kg} \times \frac{1\,mol\,CH_3OH}{32\,g\,CH_3OH} \times \frac{1277\,kJ}{2\,mol\,CH_3OH} = 1.99 \times 10^4\,kJ$$

Problem

a. Calculate the heat of combustion of methanol, $CH_3OH(l)$ in air. The products are carbon dioxide gas and ~~liquid~~ gas water.

b. How much energy is generated by the combustion of 1.0 kg of methanol in air?

6.84 Copper(I) oxide can be oxidized to copper(II) oxide:

$$Cu_2O(s) + \tfrac{1}{2}O_2(g) \longrightarrow 2CuO(s) \qquad \Delta H_{rxn}^\circ = -146.0\text{ kJ}$$

Given ΔH_f° of $Cu_2O(s) = -168.6$ kJ/mol, find ΔH_f° of $CuO(s)$.

$$\Delta H_{Rxn} = \sum n_p \Delta H_{f_p} - \sum n_r \Delta H_{f_r}$$

$$-146.0\,kJ = \left[2\,mol\,CuO\left(\Delta H_{f_{CuO}}\right)\right] - \left[1\,mol\,Cu_2O\left(\frac{-168.6\,kJ}{mol}\right) + \tfrac{1}{2}\,mol\,O_2\left(\frac{0\,kJ}{mol}\right)\right]$$

$$\Delta H_{f_{CuO}} = -157.3\,kJ/mol$$

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Calculate the heat of combustion of ethanol, $C_2H_5OH(l)$ in air. The products are carbon dioxide gas and liquid water. Use this information to answer the following question. A batch of Sauvignon Blanc wine contains 10.6% ethanol by mass. Assuming the density of the wine to be 1.0 g/mL, what caloric content does the alcohol (ethanol) in a 6-oz glass of wine (177 mL) have? (1 Cal = 4.184 kJ)