

Thermochemistry



A. Introduction

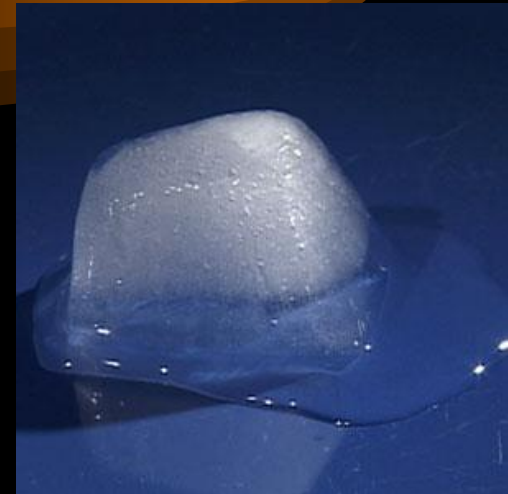
- Many activities involve **energy changes**

a) **Physical changes**

- Melting, boiling, dissolving, etc
- Involves intermolecular forces

- Gas \rightarrow Liquid \rightarrow Solid – heat released
(exothermic)

- Solid \rightarrow Liquid \rightarrow Gas – heat absorbed
(endothermic)



Introduction (energy changes) - continued

b) Chemical reactions

- energy required to break bonds (endothermic) or released when bonds are formed (exothermic) during a reaction
- Involves intramolecular forces (transfer, sharing or rearranging of electrons)
- More energy involved than for physical change

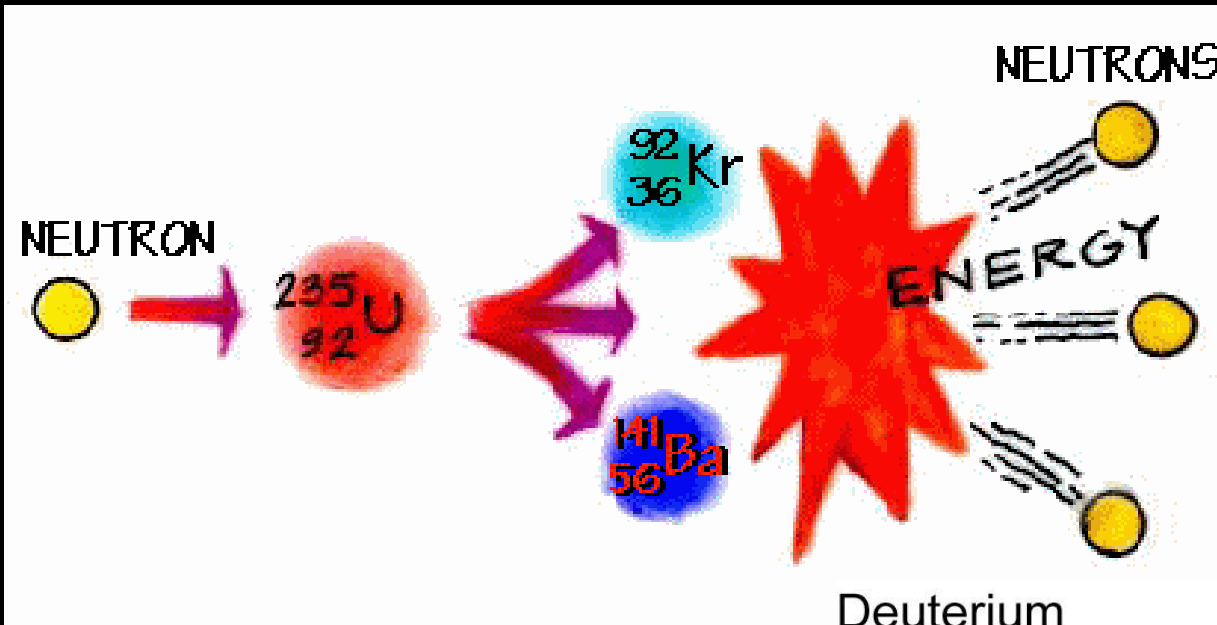


Introduction (energy changes) - continued

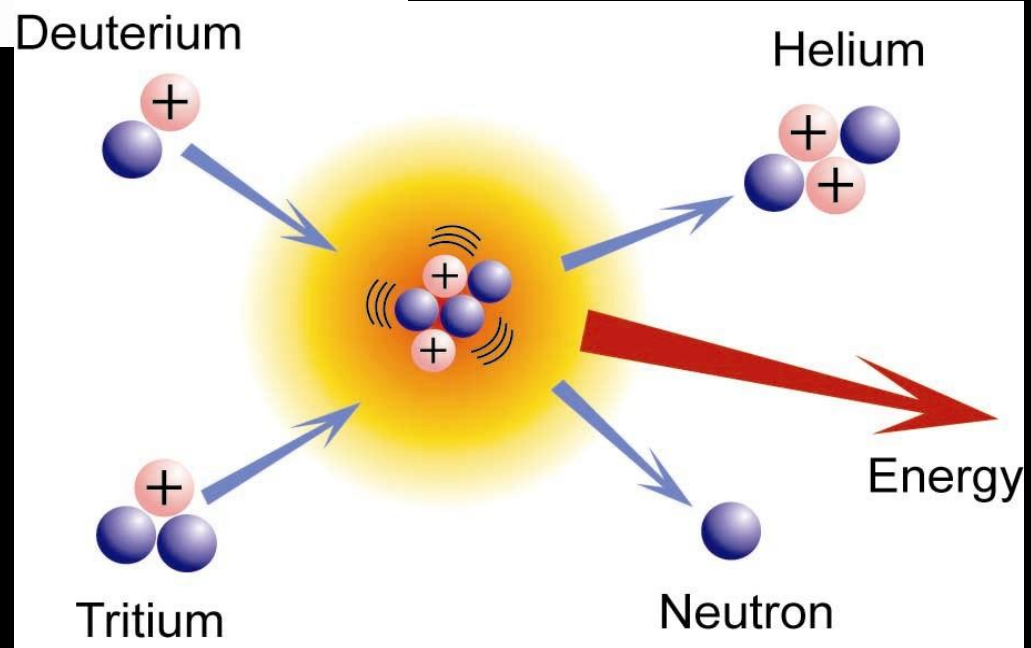
c) Nuclear reactions

- Nucleus of an atom splits (fission) or nuclei are joined (fusion)
- Involves the protons
- Mass is converted into energy and it releases an enormous amount of energy
- Fusion produces relatively harmless products and fission produces radioactive waste

NUCLEAR REACTIONS



FUSION



B. Basic Definitions

Thermochemistry: the study of energy changes that accompany physical or chemical changes of matter.

Thermodynamics: relationships and conversions between heat and other forms of energy.

Thermal Energy: the energy available from a substance as a result of the motion of its molecules.

Chemical System: the set of reactants and products that are being studied (usually represented by a chemical equation)

Surroundings: all matter around the system being studied that is capable of absorbing or releasing energy.

Enthalpy: total (or change in) heat content of a system

C. Thermal Energy Relationships

1. **Temperature** is the average kinetic energy of the particles in a substance.

The atoms in an object are in constant motion.



A When the horseshoe is hot, the particles in it move very quickly.

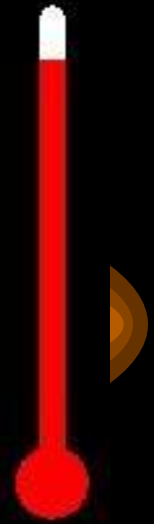


D When the horseshoe has cooled, its particles are moving more slowly.

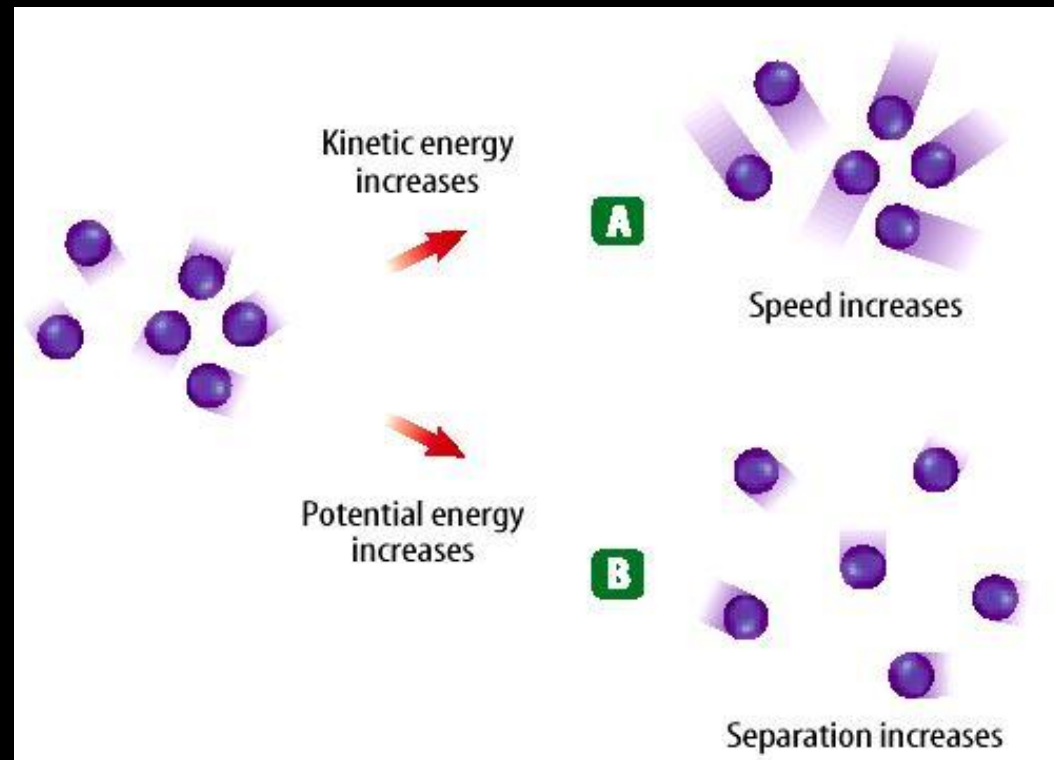
SI unit for temperature is the Kelvin

a. $K = ^\circ C + 273$ ($10\ ^\circ C = 283K$)

b. $^\circ C = K - 273$ ($10K = -263\ ^\circ C$)



2. Thermal Energy
– the total of all the kinetic and potential energy of all the particles in a substance.



Thermal energy relationships - continued

a. As temperature increases, so does thermal energy (because the kinetic energy of the particles increases).

b. Even if the temperature doesn't change, the thermal energy in a more massive substance is **higher** (because it is a **total** measure of energy).

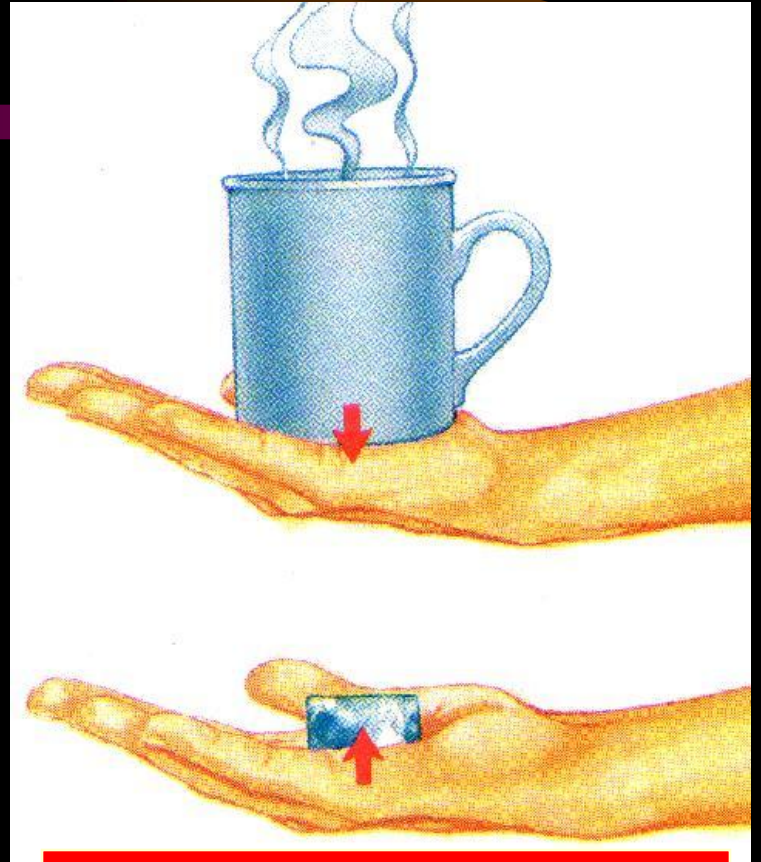


3. Heat

a. The *flow* of thermal energy from one object to another.

b. Heat *always* flows from **warmer** to **cooler** objects.

Cup gets cooler while hand gets warmer



Ice gets warmer while hand gets cooler

4. Specific Heat Capacity

a. Some things **heat up** or **cool down** faster than others.



b. Specific heat capacity is the amount of heat required to raise the temperature of 1 kg (or 1 g) of a material by one degree (C or K).

$$C_{\text{water}} = 4184 \text{ J / kg C}$$

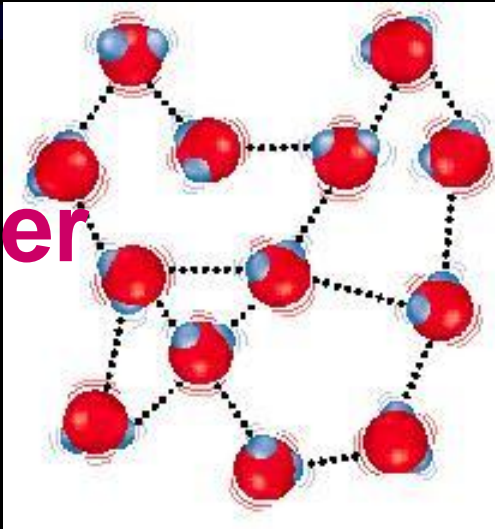
$$= 4.184 \text{ J/g C}$$

$$C_{\text{sand}} = 664 \text{ J / kg C} = 0.664 \text{ J/g C}$$

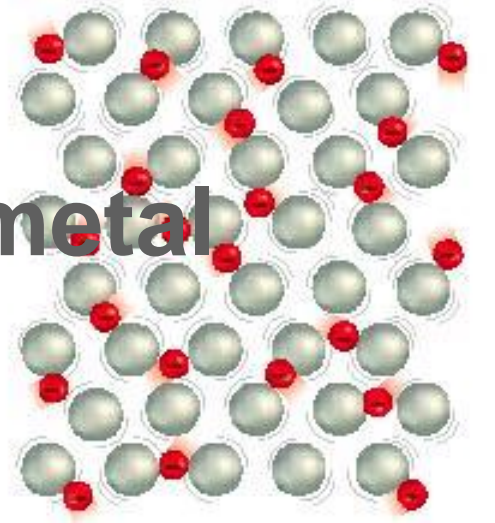
This is why land heats up quickly during the day and cools quickly at night and why water takes longer.

Why does water have such a high specific heat capacity?

water



metal



Water molecules form strong hydrogen bonds with each other; therefore it takes more heat energy to break them. Metals have weak bonds and do not need as much energy to break them.

D. MORE DEFINITIONS:

Recall: Specific heat capacity

The heat needed to \uparrow the temperature of 1 g of a substance by 1 °C. Symbol: c , units: $\text{J}/(\text{g}^\circ\text{C})$.

Heat capacity

The heat needed to \uparrow the temperature of an object by 1 °C. Symbol: $C (=c \times m)$, units: $\text{J}/^\circ\text{C}$

Heat of reaction

The heat released or absorbed during a *chemical reaction*. Symbol: none, units: J.

Specific heat (of reaction)

The heat change during a *chemical reaction* per gram of reactant. Symbol: H , units: J/g .

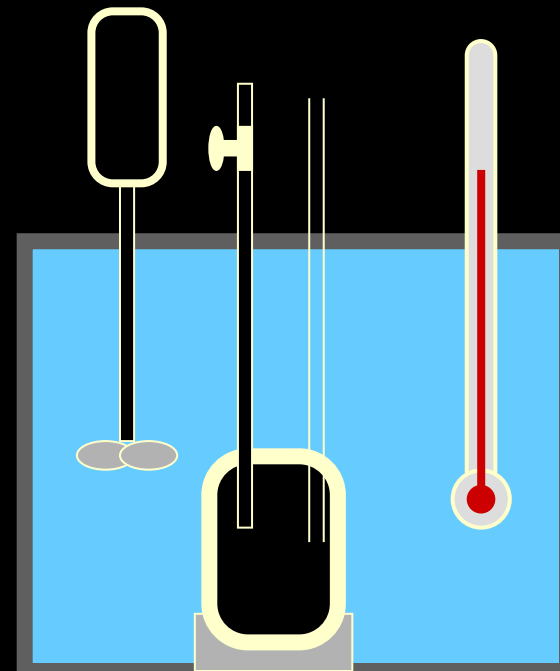
Molar heat of reaction

The heat change during a *chemical reaction* per mole of reactant. Symbol: ΔH , units: J/mol .

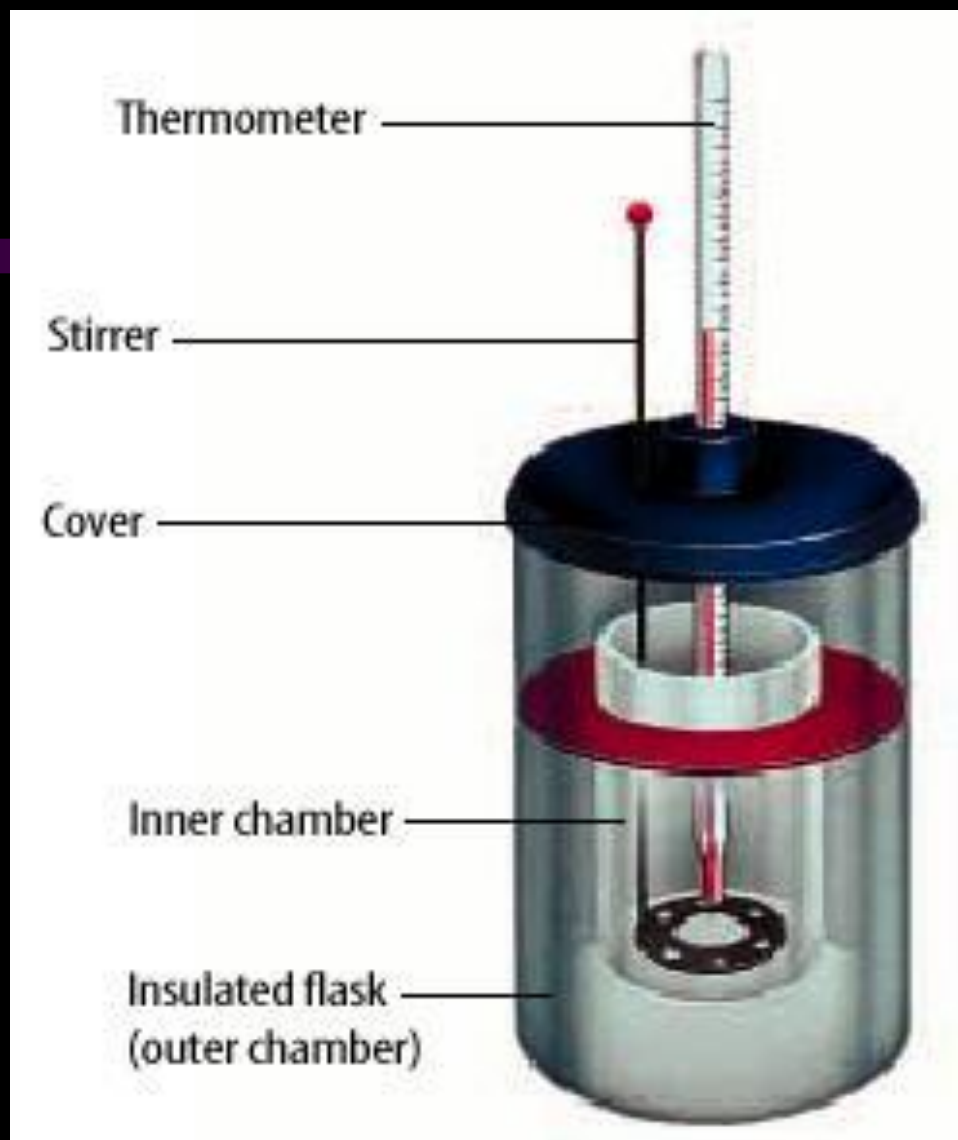
E. Types of Systems

- A chemical system in which energy and matter can move between the system and its surroundings is considered an **OPEN** system (Ex. a reaction taking place in a beaker).
- A **CLOSED** system is one in which matter can not move in or out but energy may (Ex. bomb calorimeter).
- In order to measure energy changes in a chemical system, ideally one needs an **ISOLATED** system in which neither mass or energy can move in or out.
- However, that is impossible so we consider calorimeters to be isolated systems even though they are really closed systems

- Knowing how much energy a fuel provides can tell us if it is useful for a certain application.
- For example, the amount of energy a food releases when burned, can tell us about its caloric content (fats release lots of energy – almost twice as much as carbohydrates or proteins for the same mass).
- Heat energy released during combustion can be measured with a calorimeter.
- A “bomb calorimeter” is shown. It includes water in a heavily insulated container, a stirrer, valve, bomb chamber, ignition wires, and a thermometer.



A calorimeter is used to help measure the specific heat of a substance and the energy of a reaction.



F. Measuring and Calculating Energy Changes

Calorimetry is the process through which energy changes in a chemical system are measured.

The factors that affect energy change in a chemical system are **mass** (m), **temperature change** (ΔT) and the **specific heat capacity** of substance (c).

Heat change in a chemical system (enthalpy) can be calculated using the formula:

$$Q = m \times c \times \Delta T$$

How to calculate changes in thermal energy

$$Q = m \times c \times \Delta T$$

Q = quantity of thermal energy (J)

m = mass of substance (g)

ΔT = change in temperature ($T_f - T_i$) ($^{\circ}\text{C}$)

c = specific heat of substance ($\text{J/g} \times ^{\circ}\text{C}$)

- For a list of “c” values, see back of textbook or handout.

$$Q = m \times c \times \Delta T$$

- This equation makes sense if you consider units

$$J = \frac{J}{g^{\circ}C} \times g \times ^{\circ}C$$

Sample problem: (must know c (water) = 4.184 J/g°C)

When 12 g of a food was burned in a calorimeter, the 100 mL of water in the calorimeter changed from 20°C to 33°C. Calculate the heat released.

$$Q = cm\Delta T = 4.184 \text{ J}/(g^{\circ}C) \times 100 \text{ g} \times 13^{\circ}C = 5.4 \text{ kJ}$$

Examples

1. What is the energy in J, kJ and MJ required to raise the temperature of 2.57 kg of water by 92 °C?
2. What is the final temperature if 1750 kJ of energy is added to 12 500 g of water initially at 5.0°C?
3. How much energy would it take (in kJ and MJ) to raise the temperature of 2500 g of a substance from 20°C to 355°C? The specific heat capacity for the substance is 0.86J/(g°C).
4. What is the total heat required to raise the temperature of both a pot and the water in it by 53°C? The pot weighs 450 g and its specific heat capacity is 0.510 J/g°C. The weight of the pot plus the water is 1650 g.

$$1. \quad Q = cm\Delta T = 4.184 \text{ J/(g}^\circ\text{C)} \times 2570 \text{ g} \times 92 \text{ }^\circ\text{C}$$

$$= 989265 \text{ J} = 989 \text{ kJ} = 0.989 \text{ MJ}$$

$$2. \quad Q = cm\Delta T$$

$$\Delta T = Q/cm = \frac{1\,750\,000 \text{ J}}{4.184 \text{ J/(g}^\circ\text{C)} \times 12500 \text{ g}} = 33.5^\circ\text{C}$$

Since the temperature started at 5.0°C , the final temperature is 38.5°C .

$$3. \quad Q = cm\Delta T = 0.86 \text{ J/(g}^\circ\text{C)} \times 2500 \text{ g} \times 335^\circ\text{C}$$

$$= 720 \text{ kJ or } 0.72 \text{ MJ}$$

4. Total heat = water heat + pot heat

$$= 4.184 \text{ J/(g}^\circ\text{C)} \times 1200 \text{ g} \times 53.0^\circ\text{C} = 266102.4 \text{ J}$$

$$= 0.510 \text{ J/(g}^\circ\text{C)} \times 450 \text{ g} \times 53.0^\circ\text{C} = 12163.5 \text{ J}$$

$$= 278\,265.9 \text{ J}$$

$$= 278 \text{ kJ}$$

Heat Capacity Calculations

- Recall that heat capacity ($\text{J}/^\circ\text{C}$) is different from specific heat capacity ($\text{J}/\text{g}^\circ\text{C}$).
- Heat capacity is sometimes a more useful value
- For example, because a calorimeter includes wires, the stirrer, thermometer, etc. some heat will be transferred to these other materials.
- Rather than having to calculate Q for each material (like question 4) a $\text{J}/^\circ\text{C}$ value is used.

Sample problem: $Q=(cm)\Delta T$

A calorimeter has a heat capacity ($c \times m$) of $2.05 \text{ kJ}/^\circ\text{C}$. How much heat is released if the change in temperature of the calorimeter is 11.6°C ?

$$Q = (cm)\Delta T \quad Q = 2.05 \text{ kJ}/^\circ\text{C} \times 11.6 \text{ }^\circ\text{C} = 23.\underline{8} \text{ kJ}$$

More practice

1. 5.0 g of copper was heated from 20°C to 80°C. How much energy was used to heat the Cu?

$$Q = cm\Delta T = 0.385 \text{ J/(g}^\circ\text{C)} \times 5 \text{ g} \times 60 \text{ }^\circ\text{C} = 115.5 \text{ J}$$

2. If a 3.1 g ring is heated using 10.0 J, its temp. rises by 17.9°C. Calculate the specific heat capacity of the ring. Is the ring pure gold?

$$Q = cm\Delta T$$

$$c = q/m\Delta T = \frac{10.0 \text{ J}}{3.1 \text{ g} \times 17.9^\circ\text{C}} = 0.18 \text{ J/(g}^\circ\text{C)}$$

The ring is not pure. Gold is 0.13 J/(g°C)

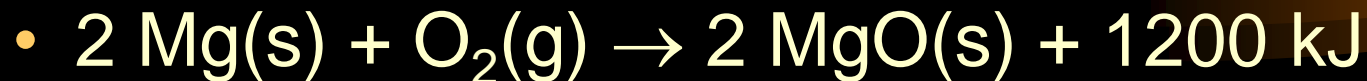
3. Do questions on handout.

G. Thermochemical Equations

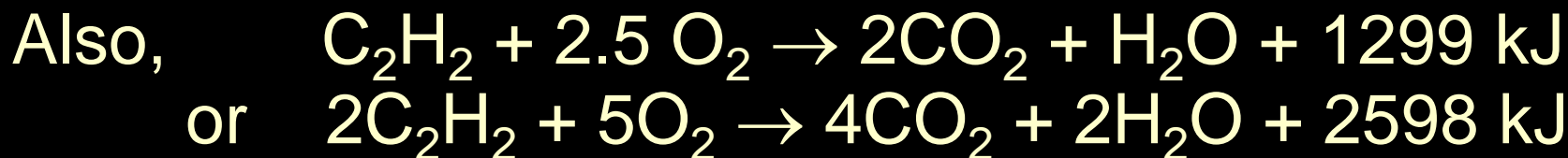
Thermochemical equations are chemical equations with an added heat term.



This is endothermic (heat is absorbed/used)



This is exothermic (heat is produced/released)



Sample problem:

3.00 g of octane was burned in a calorimeter with excess oxygen, the 1000 mL of water in the calorimeter rose from 23.0°C to 57.6°C. Write the thermochemical equation for octane, representing the molar heat of combustion.

Sample: First, calculate the heat released by the combustion reaction via $Q=cm\Delta T$...

$$= 4.184 \text{ J/(g}^\circ\text{C)} \times 1000 \text{ g} \times 34.6 \text{ }^\circ\text{C} = 144\,766.4 \text{ J}$$

Octane (C_8H_{18}) has a molar mass of 114.26 g/mol

We can determine the molar heat of reaction

1) via the specific heat of reaction or 2) directly

$$h = \frac{\text{J}}{\text{g}} = \frac{144\,766.4 \text{ J}}{3.00 \text{ g}} \quad \Delta H = \frac{48.26 \text{ kJ}}{\text{g}} \times \frac{114.26 \text{ g}}{\text{mol}}$$
$$= 48\,260 \text{ J/g} = 48.26 \text{ kJ/g} \quad = 5514 \text{ kJ/mol}$$

$$\text{or } \Delta H = \frac{\text{J}}{\text{mol}} = \frac{144\,766.4 \text{ J}}{0.026256 \text{ mol}} = 5514 \text{ kJ/mol}$$



H. Molar Enthalpies

Molar Enthalpy is the heat (enthalpy) change for a chemical, physical or nuclear change per mole of a substance.

The symbol for Molar Enthalpy is ΔH_x , where x represents the type of reaction and it is measured in J/mol or kJ/mol.

Molar Enthalpy

Energy changes (ΔH) involved for 1 mole of a substance...

- **Solution** (dissolving) (ΔH_{sol})
- **Combustion** (ΔH_{comb})
- **Vapourization** (ΔH_{vap})
- **Fusion (Freezing)** (ΔH_{fus})
- **Neutralization** (ΔH_{neut})
- **Formation** (from elements) (ΔH_{f})

Molar Enthalpies

- We can use these values to calculate total energy required for a specific process if we know:
 - The amount of substance changing
 - The molar enthalpy for that process

Example:

- Vapourization enthalpy (ΔH_{vap}) for Freon is 35kJ/mol
- A refrigerator contains 500g of Freon (121 g/mol)
- Calculate the total energy required

Combined Calculations

- We can combine our equations for Q and ΔH !
- Recall $Q = m c \Delta T$
- $\Delta H_{\text{total}} = n \Delta H_{\text{(for the process)}}$
- Therefore:
- $n \Delta H_{\text{(for the process)}} = m c \Delta T$

TRY THESE!



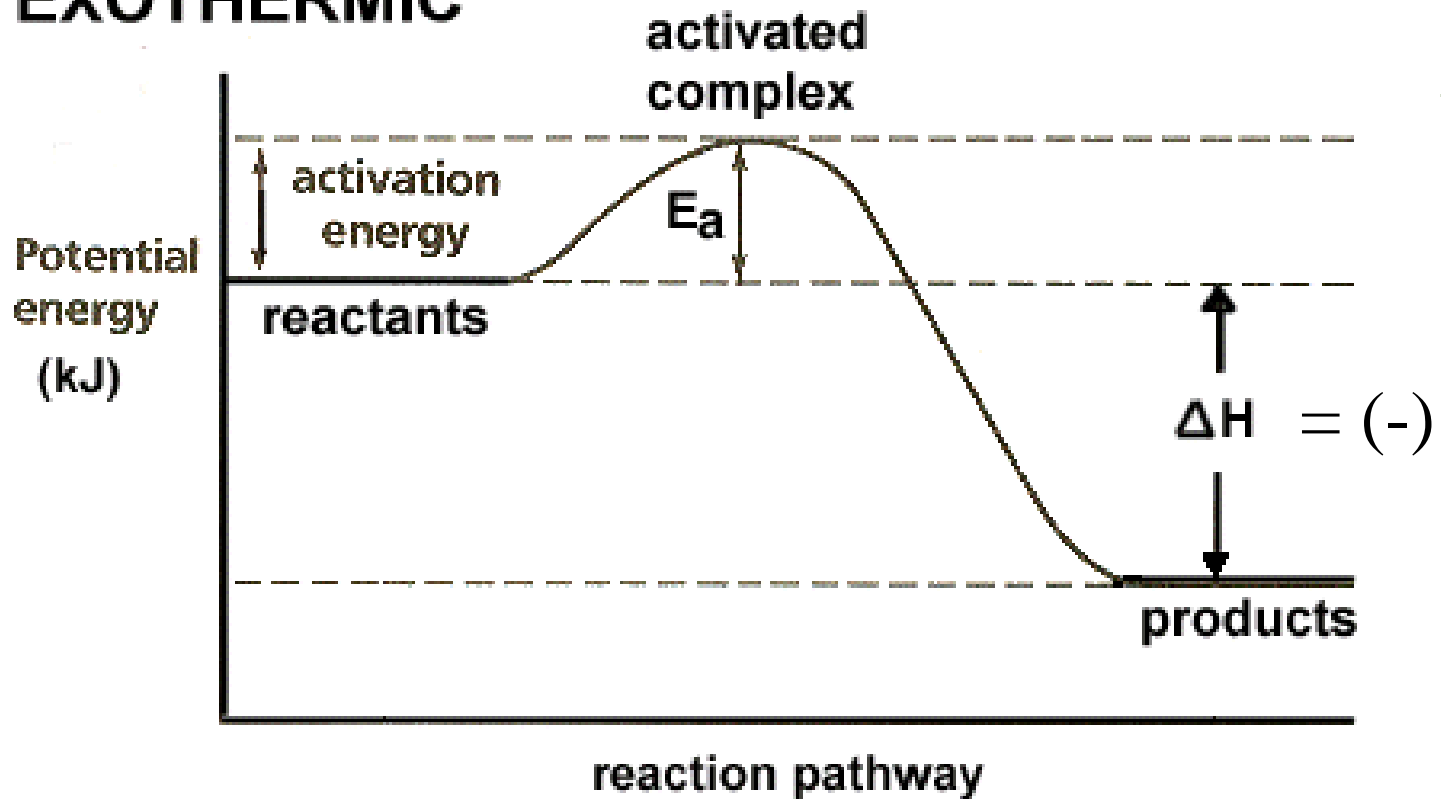
Phase Change Activity

1. Place 40 g of crushed ice into a beaker.
2. Record the temperature of the ice.
3. Stir the ice until it completely melts recording the temperature every minute.
4. Once fully melted, heat the water on a hot plate set to 3 recording the temperature every minute.
5. Once the water has boiled, allow it boil for 5 minutes recording the temperature every minute.
6. When done plot a temperature vs. time graph and calculate the amount of heat absorbed by the “water” during the entire activity.
7. How do your values of the melting and boiling point for water compare to the theoretical values? Account for any differences.

I. More on Energy Changes

- **Endothermic**
 - energy is absorbed by substances/bonds/nucleus
 - temperature of surrounding environment drops
 - value of Q or ΔH is positive
 - energy is written as a reactant
 - energy absorbed by bond breaking is greater than energy released by bond forming
- **Exothermic**
 - energy is released from substances/bonds/nucleus
 - temperature of surrounding environment increases
 - value of Q or ΔH is negative
 - energy is written as a product
 - Energy released by bond forming is greater

EXOTHERMIC



Reactant \Rightarrow Product + Energy (heat)

Reactants contain more stored or potential energy than products

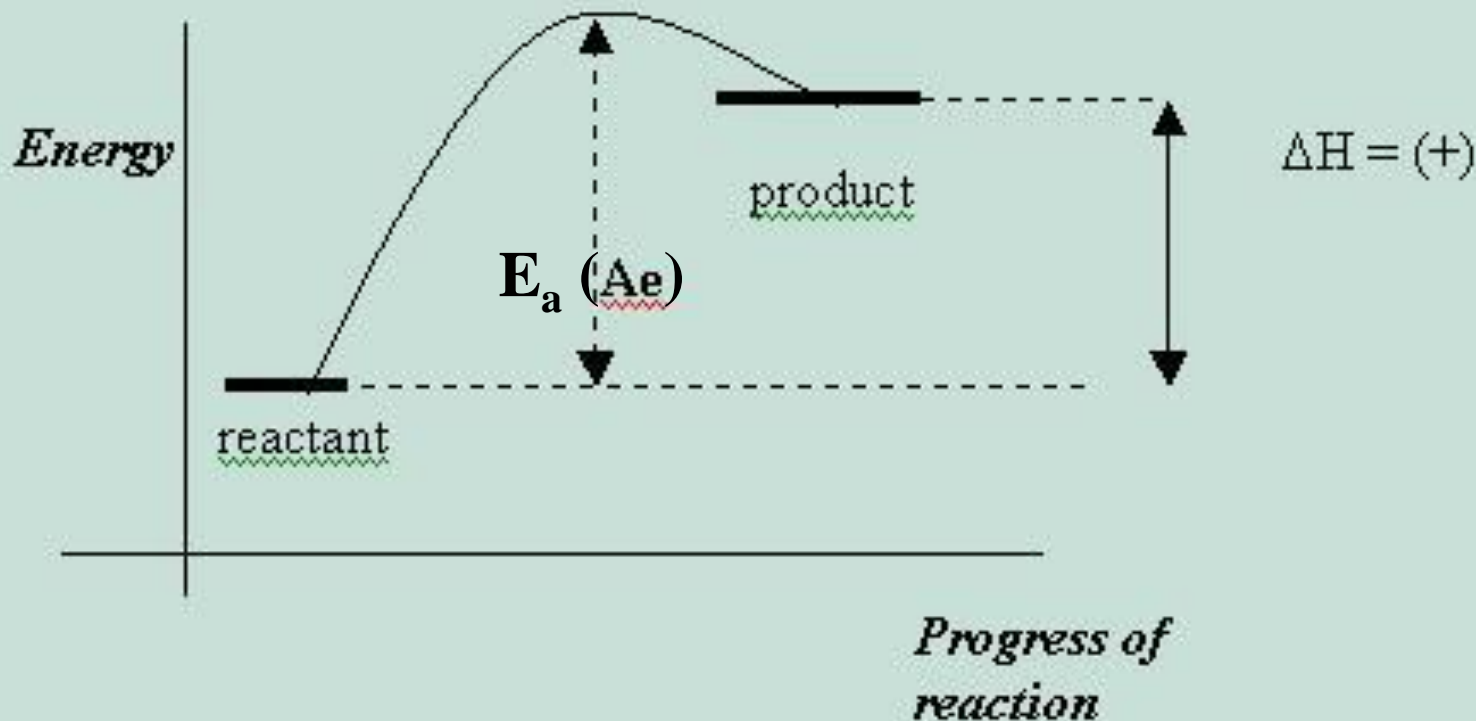
The energy in the product(s) DROPS

This energy is RELEASED (usually as heat)

The surrounding temperature goes UP

ENDOTHERMIC REACTIONS

ENDOTHERMIC
PROFILE



Reactant + Energy (heat) \Rightarrow Product

- Reactants contain less stored or potential energy than products
- The energy in the product(s) **INCREASES**
- This energy is **ABSORBED** (usually as heat)
- The surrounding temperature goes **DOWN**

Ways to show Enthalpy

1. Adding energy to the reaction



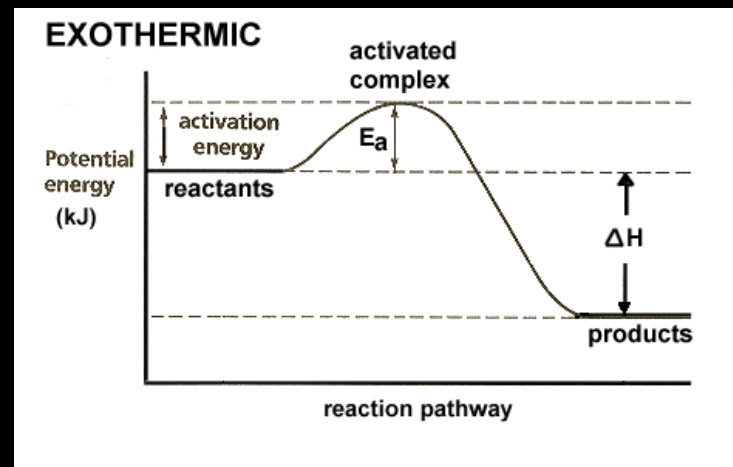
2. ΔH values for a reaction (+/-)



3. Molar Enthalpies for substances (+/-)

$$\Delta H = -393.5 \text{ kJ/mol}$$

4. Graphical Representation



Homework

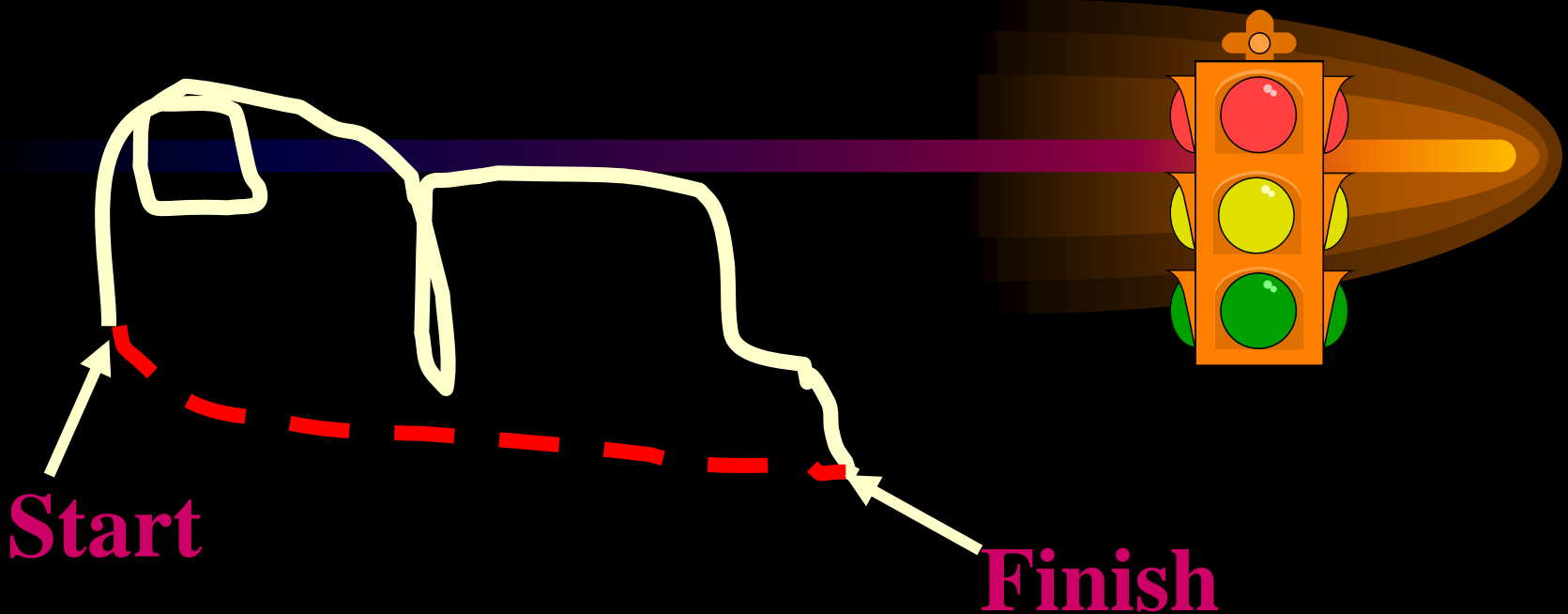


J. Finding ΔH for Reactions



1. Hess's Law (Indirect Method)
2. Using ΔH formation (Direct Method)

1. Hess's Law

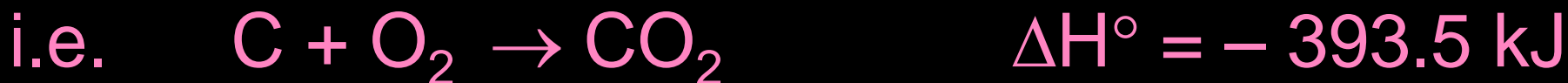
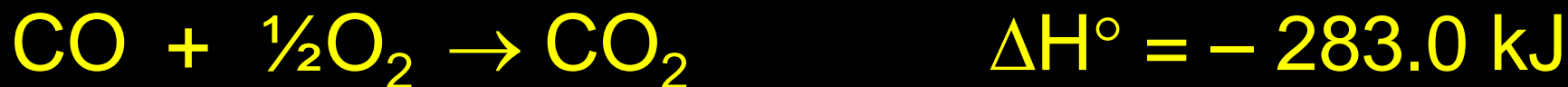
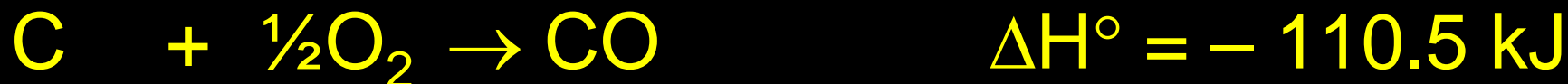


Both lines accomplished the same net result - they went from start to finish. But Hess's Law is the indirect path.

Hess's law

- Hess's Law states that the heat of a whole reaction is equivalent to the sum of its steps.
- For example: $C + O_2 \rightarrow CO_2$

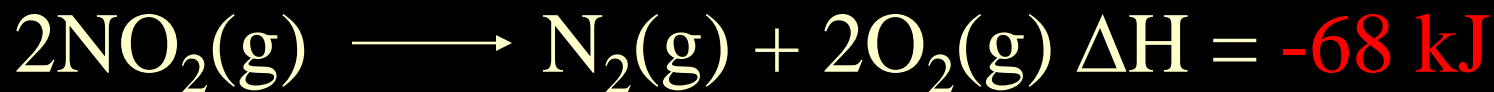
This can occur as 2 steps



- Hess's law allows us to add equations.
- We add all reactants, products, & ΔH° values.

Hess' Law: Details

- One can always reverse the direction of a reaction when making a combined reaction. When you do this, the sign of ΔH changes.



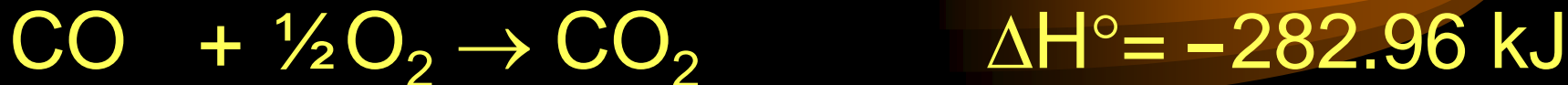
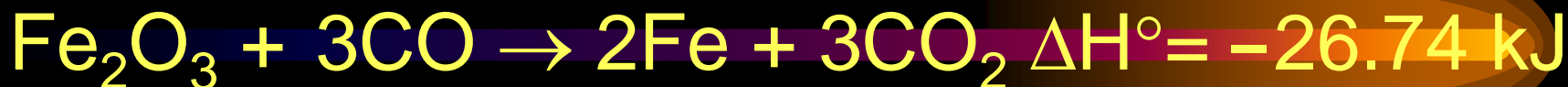
Details (cont.)

- The magnitude of ΔH is directly proportional to the quantities involved.
- As such, if the coefficients of a reaction are multiplied by a constant, the value of ΔH is also multiplied by the same integer.

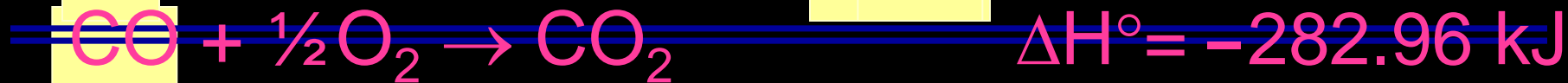
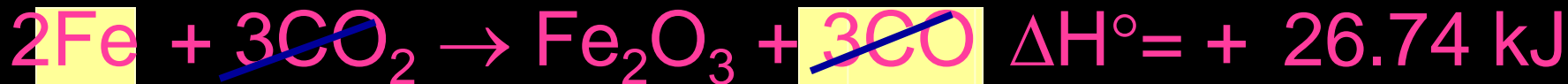


Hess's Law Example #1

We may need to manipulate equations further:



- 1: Align equations based on reactants/products.
- 2: Multiply based on final reaction.
- 3: Add equations.



Hess's Law Example #2

Determine the heat of reaction for the reaction:



Using the following sets of reactions:



Hint: The three reactions must be algebraically manipulated to sum up to the desired reaction.

and.. the ΔH values must be treated accordingly.



Using the following sets of reactions:

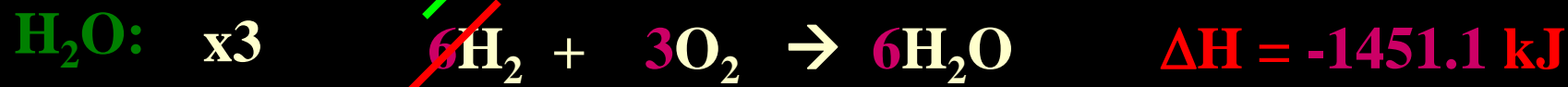


O₂: Found in more than one place, SKIP IT (its hard).

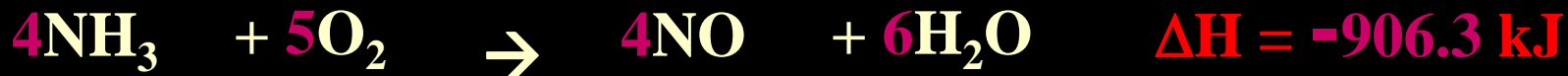




O₂: Found in more than one place, SKIP IT.



Cancel terms and take sum.



Is the reaction endothermic or exothermic?

Hess's Law Example #3

Determine the heat of reaction for the reaction:



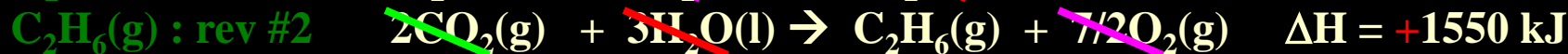
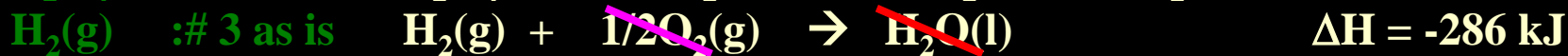
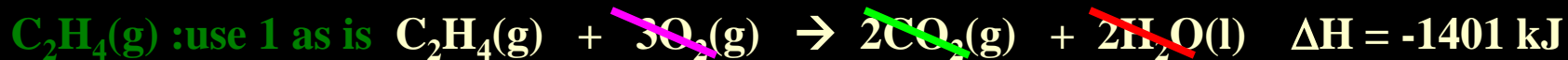
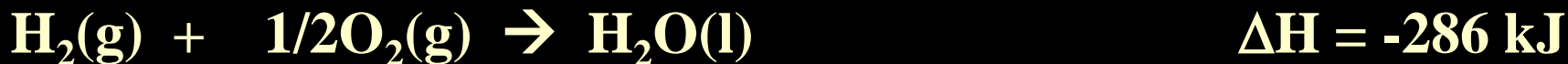
Use the following reactions:



Determine the heat of reaction for the reaction:



Use the following reactions:



Hess' Law Example #4

What is ΔH for the following reaction?

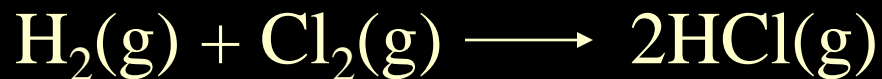


You're given the following reactions:

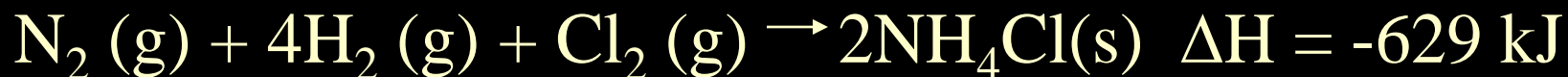


Example #5

- Calculate ΔH for the following reaction:



Given the following:



Calculating ΔH Using Heats of Formation(Direct method)

- The heat (or enthalpy) of a reaction (ΔH) can be calculated using the standard enthalpy of formation for each of the reactants and products.
- A standard enthalpy of formation is the quantity of energy released or absorbed when one mole of the substance is formed from its elements in their standard states.
- The symbol for standard enthalpy of formation is ΔH_f° .
- Elements in their standard state will have an enthalpy of formation equal to zero.
- The heat of a reaction is the change in enthalpy and therefore, is calculated by determining the difference in enthalpy between the products and reactants:

$$\Delta H_R = \sum \Delta H_f^\circ \text{ PRODUCTS} - \sum \Delta H_f^\circ \text{ REACTANTS}$$

- When adding the ΔH_f° values, they must be multiplied first by the coefficients in the **BALANCED** chemical equation.
- **BEWARE OF THE STATES** - they must match!
- See back of text or handout for the table of ΔH_f° values.

Sample Problem:

Using heats of formation, calculate the ΔH for the combustion of ethane reaction. Assume that the products are both gases. Express the answer in kJ/mol of ethane.



Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. How much heat is released per mole of benzene combusted? The standard enthalpy of formation of benzene is 49.04 kJ/mol .

-3267.44 kJ

HOMWORK

