

CHEMICAL THERMODYNAMICS

**Hot iron nail
exposed to
oxygen
releases lots
of heat
energy.**



The Nature of Energy

I. Types of energy:

- A. Kinetic Energy – energy of motion
- B. Potential Energy – energy due to condition, position, or composition
- C. Internal energy
- D. Heat energy, electricity, light

II. Units for energy:

- A. calorie – (cal) quantity of heat required to change the temperature of one gram of water by one degree Celsius
- B. Joule (J) – SI unit for heat $1 \text{ cal} = 4.184 \text{ J}$

THERMODYMANICS

Thermodynamics is the study of the motion of heat energy as it is transferred from the system to the surrounding or from the surrounding to the system.

System – the portion of the universe selected for thermodynamic study

Surroundings – the portion of the universe with which a system interacts

The transfer of heat could be due to a physical change or a chemical change.

There are three laws of chemical thermodynamics.



CHEMICAL THERMODYNAMICS

The first law of thermodynamics:

Energy and matter can be neither created nor destroyed; only transformed from one form to another. The energy and matter of the universe is constant.

The second law of thermodynamics:

In any spontaneous process there is always an increase in the entropy of the universe. The entropy is increasing.

The third law of thermodynamics:

**The entropy of a perfect crystal at 0 K is zero.
There is no molecular motion at absolute 0 K.**

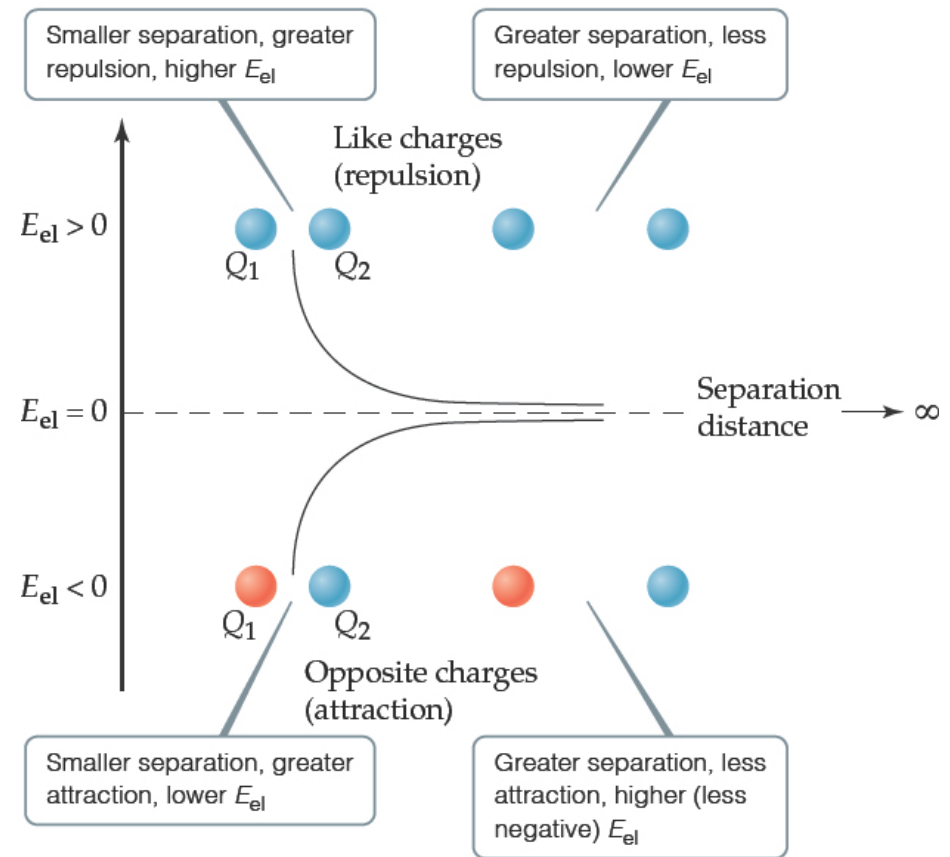
Chemical Energy Is Mainly Potential Energy

- The most important form of potential energy in molecules is electrostatic potential energy, E_{el} :

$$E_{el} = \frac{kQ_1Q_2}{d}$$

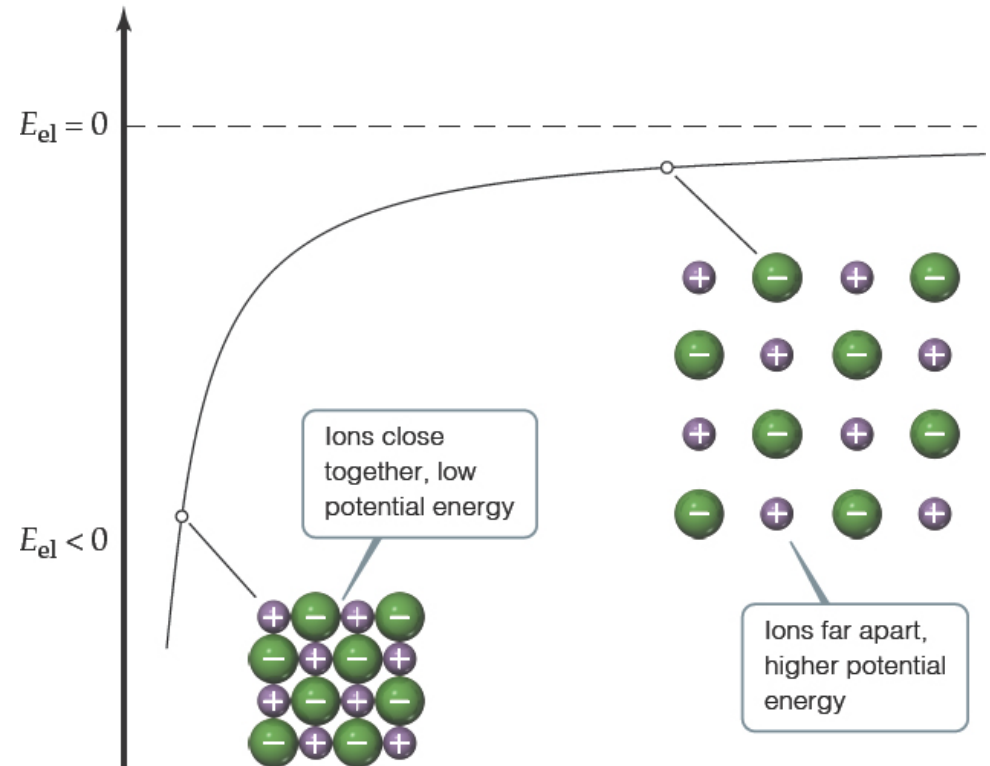
- Reminder: the unit of energy commonly used is the Joule:

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



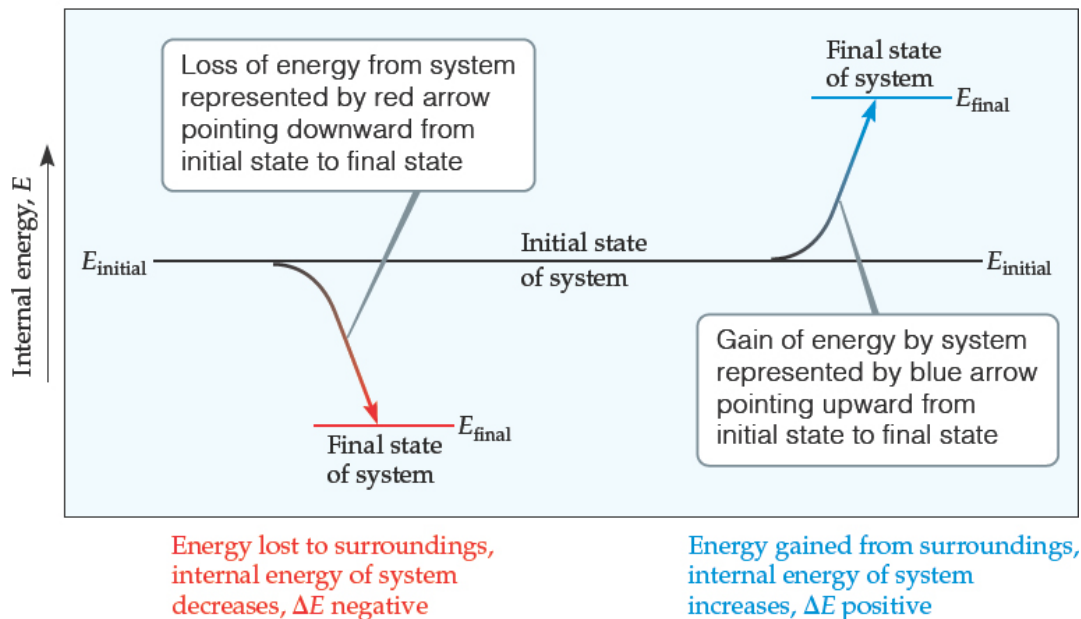
Attraction Between Ions

- Electrostatic attraction is seen between oppositely charged ions.
- Energy is released when chemical bonds are formed; energy is consumed when chemical bonds are broken.



Internal Energy (1 of 2)

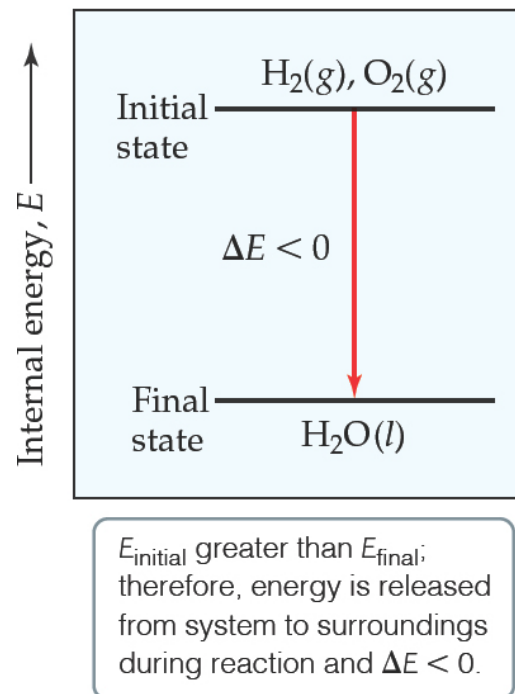
- The **internal energy** of a system is the sum of all kinetic and potential energies of all components of the system; we use **E** to represent it.
- We generally don't know E, only how it **changes** (ΔE)



Internal Energy (2 of 2)

By definition, the change in internal energy, ΔE , is the final energy of the system minus the initial energy of the system:

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



UNITS for HEAT ENERGY

Heat energy is usually measured in either Joules, given by the unit (J), and kilojoules (kJ) or in calories, written shorthand as (cal), and kilocalories (kcal).

$$1 \text{ cal} = 4.184 \text{ J}$$

NOTE: This conversion correlates to the specific heat of water which is 1 cal/g °C or 4.184 J/g °C.

Units of Energy

- **joule (J)** is the amount of energy needed to move a 1 kg mass a distance of 1 meter
 - $1 \text{ J} = 1 \text{ N}\cdot\text{m} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$
- **calorie (cal)** is the amount of energy needed to raise one gram of water by 1°C
 - kcal = energy needed to raise 1000 g of water 1°C
 - food Calories = kcals

Energy Conversion Factors

1 calorie (cal)	=	4.184 joules (J) (exact)
1 Calorie (Cal)	=	1000 calories (cal)
1 kilowatt-hour (kWh)	=	3.60×10^6 joules (J)

HEAT

The energy that flows into or out of a system because of a difference in temperature between the thermodynamic system and its surrounding.

Symbolized by " q ".

- ⇒ When heat is evolved by a system, energy is lost and " q " is negative (-).**
- ⇒ When heat is absorbed by the system, the energy is added and " q " is positive (+).**

HEAT FLOW

Heat can flow in one of two directions:

Exothermic

To give off heat; energy is lost from the
system: $(-q)$

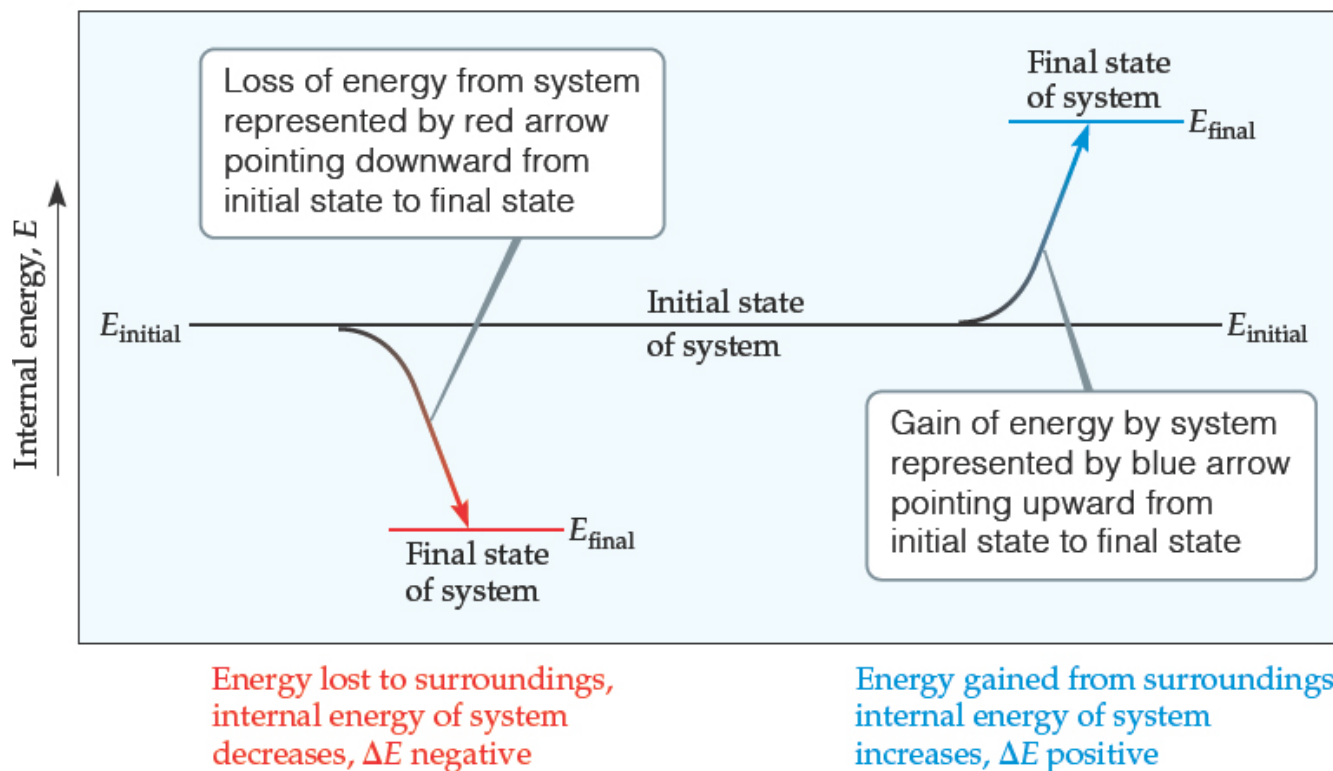
Endothermic

To absorb heat; energy is added to the
system: $(+q)$

Changes in Internal Energy (1 of 2)

IF: $\Delta E > 0$, $E_{\text{final}} > E_{\text{initial}}$

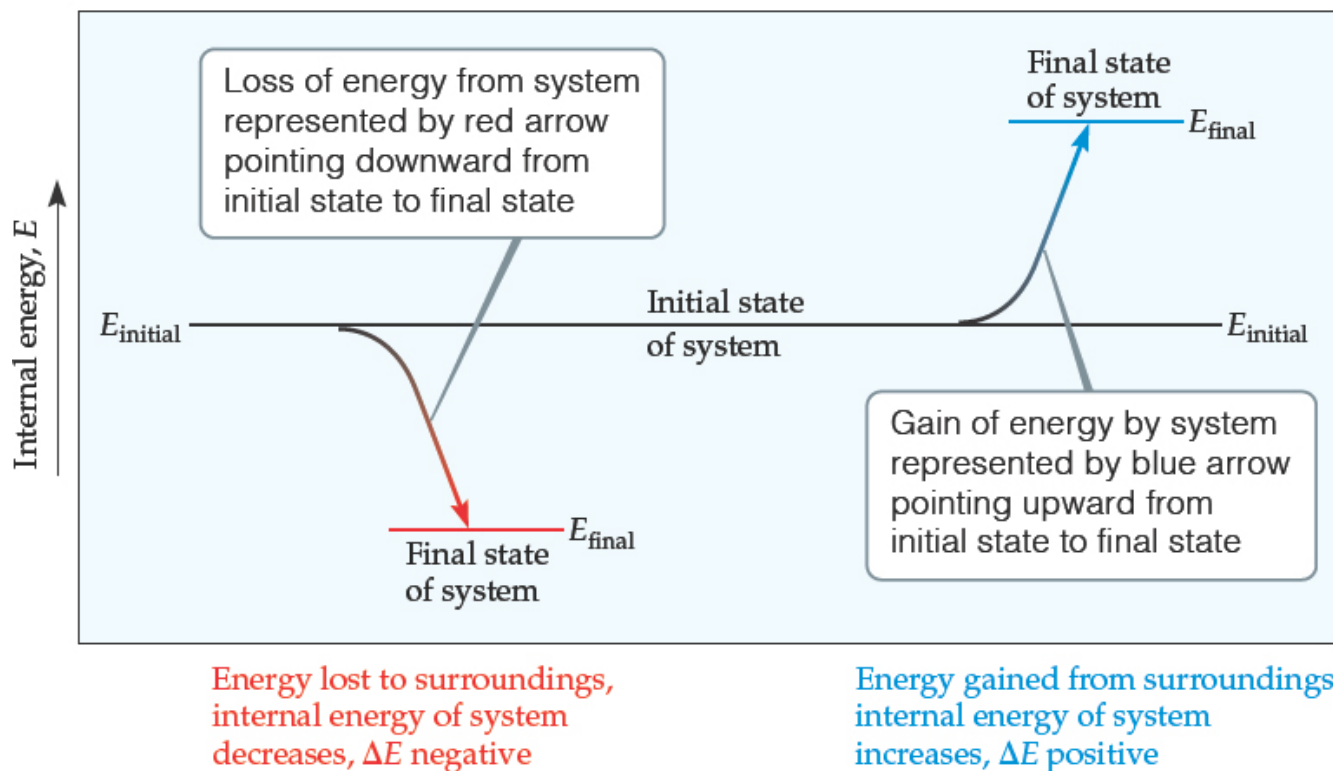
the system **absorbed** energy from the surroundings.



Changes in Internal Energy (2 of 2)

IF: $\Delta E < 0$, $E_{\text{final}} < E_{\text{initial}}$

the system **released** energy to the surroundings.



The First Law of Thermodynamics- A closer look
“The internal energy (ΔE) of an isolated system is constant.”

Internal Energy: the sum of all the kinetic/potential energy of a system.

$$\Delta E = E_{\text{final}} - E_{\text{initial}} \quad \& \quad \Delta E = q + w$$

NOTE:

q = heat added to or liberated from the system

Heat (q) = the energy transferred from a hotter object to a colder one

w = work done on or by the system.

Work (w) = the energy used to cause one object to move against a force

Sign Convention for q	Sign Convention for w
$q > 0$: Heat is transferred from the surroundings to the system	$w > 0$: Work is done by the surroundings on the system
$q < 0$: Heat is transferred from the system to the surroundings	$w < 0$: Work is done by the system on the surroundings

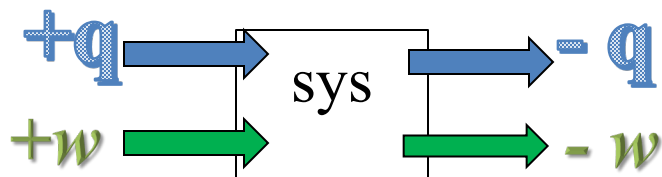
When heat is transferred from the surroundings to the system, q has a positive value. Likewise, when work is done on the system by the surroundings, w has a positive value.

Both heat added to the system and the work done on the system **INCREASE** its internal energy.

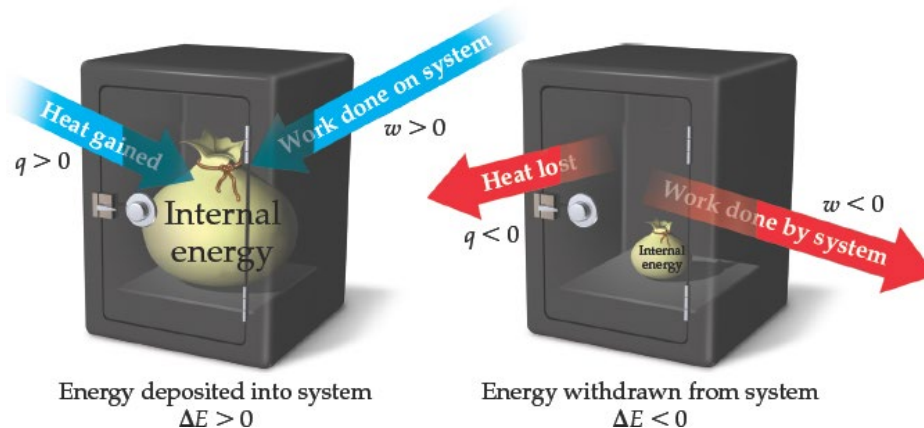
A **POSITIVE** value of ΔE indicates that the system has gained energy from its surroundings; a **NEGATIVE** value of ΔE indicates that the system has lost energy to its surroundings.

Changes in Internal Energy

- When energy is exchanged between the system and the surroundings, it is exchanged as either heat (q) or work (w).
- That is, $\Delta E = q + w$.



System is interior of vault



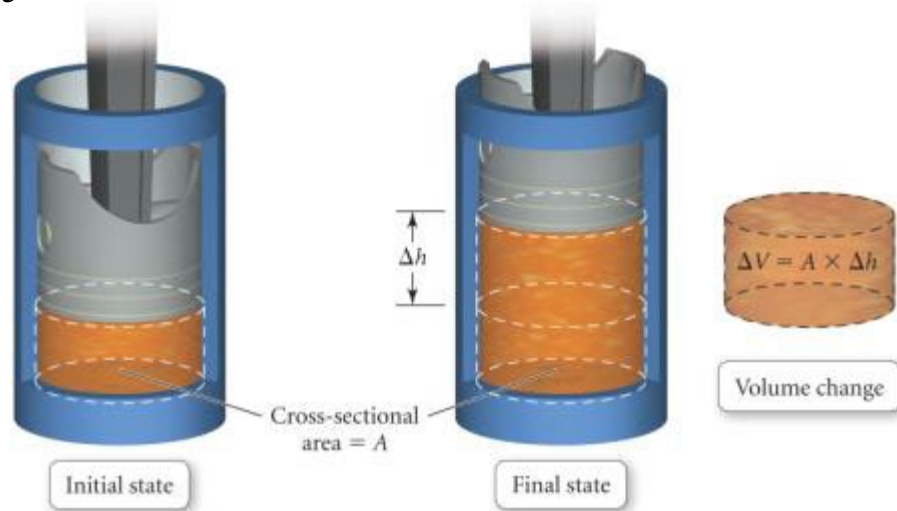
Pressure -Volume Work

- PV work is work that is the result of a volume change against an external pressure
- when gases expand, ΔV is +, but the system is doing work on the surroundings so w is —
- as long as the external pressure is kept constant

— ***Work* = External Pressure x Change in Volume**

$$w = -P\Delta V$$

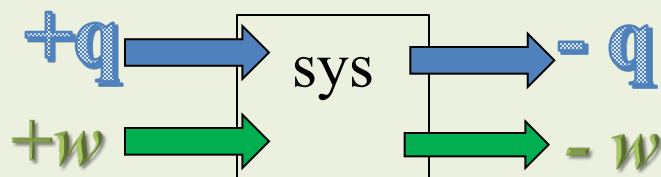
- to convert the units to joules use $101.3 \text{ J} = 1 \text{ atm}\cdot\text{L}$



Example– If a balloon is inflated from 0.100 L to 1.85 L against an external pressure of 1.00 atm, how much work is done?

Given:	$V_1=0.100 \text{ L}, V_2=1.85 \text{ L}, P=1.00 \text{ atm}$		
Find:	$w, \text{ J}$		
Concept Plan:	<div style="text-align: center;"> $\boxed{P, \Delta V} \Rightarrow \boxed{w}$ $w = -P \bullet \Delta V$ </div>		
Relationships:	$101.3 \text{ J} = 1 \text{ atm L}$		
Solution:	<div style="display: flex; justify-content: space-between;"> <div style="width: 30%;"> $\Delta V = V_2 - V_1$ $\Delta V = 1.85 \text{ L} - 0.100 \text{ L}$ $= 1.75 \text{ L}$ </div> <div style="width: 30%;"> $w = -P \bullet \Delta V$ $= -(1.00 \text{ atm}) \bullet (1.75 \text{ L})$ $= -1.75 \text{ atm} \bullet \text{L}$ </div> <div style="width: 30%;"> $-1.75 \cancel{\text{atm} \bullet \text{L}} \times \frac{101.3 \text{ J}}{1 \cancel{\text{atm} \bullet \text{L}}}$ $= -177 \text{ J}$ </div> </div>		
Check:	the unit and sign are correct		

Lecture Questions on the first law of thermodynamics.



so work was done by the system

520 kJ of work and loses
the change in internal

y system so -520 kJ
st by system -220kJ

exothermic

Q #2: A system was heated by **Absorb so endothermic** yet it
was found that its internal energy decreased by 150 J.
Was work done on the system or did the system do work?

$$\Delta E = q + w$$

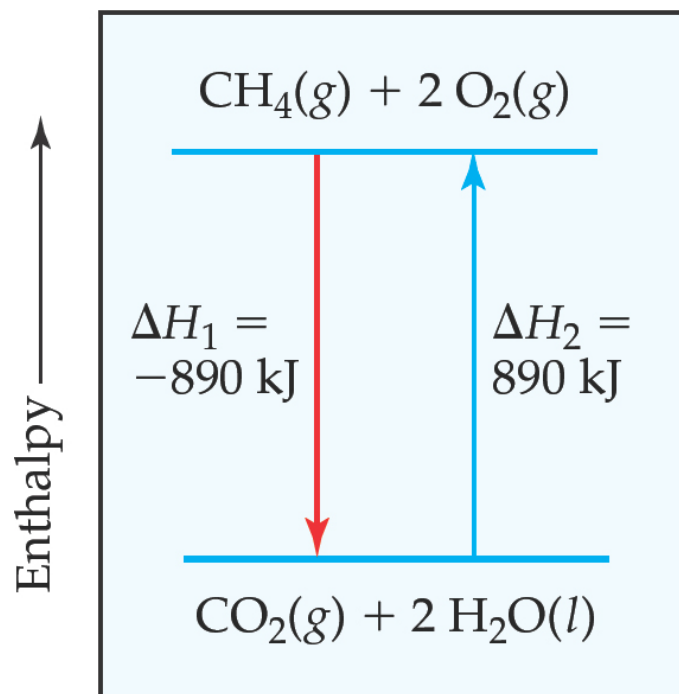
$$-150 = 300 + w$$

$$w = -450$$

Enthalpy of Reaction (1 of 2)

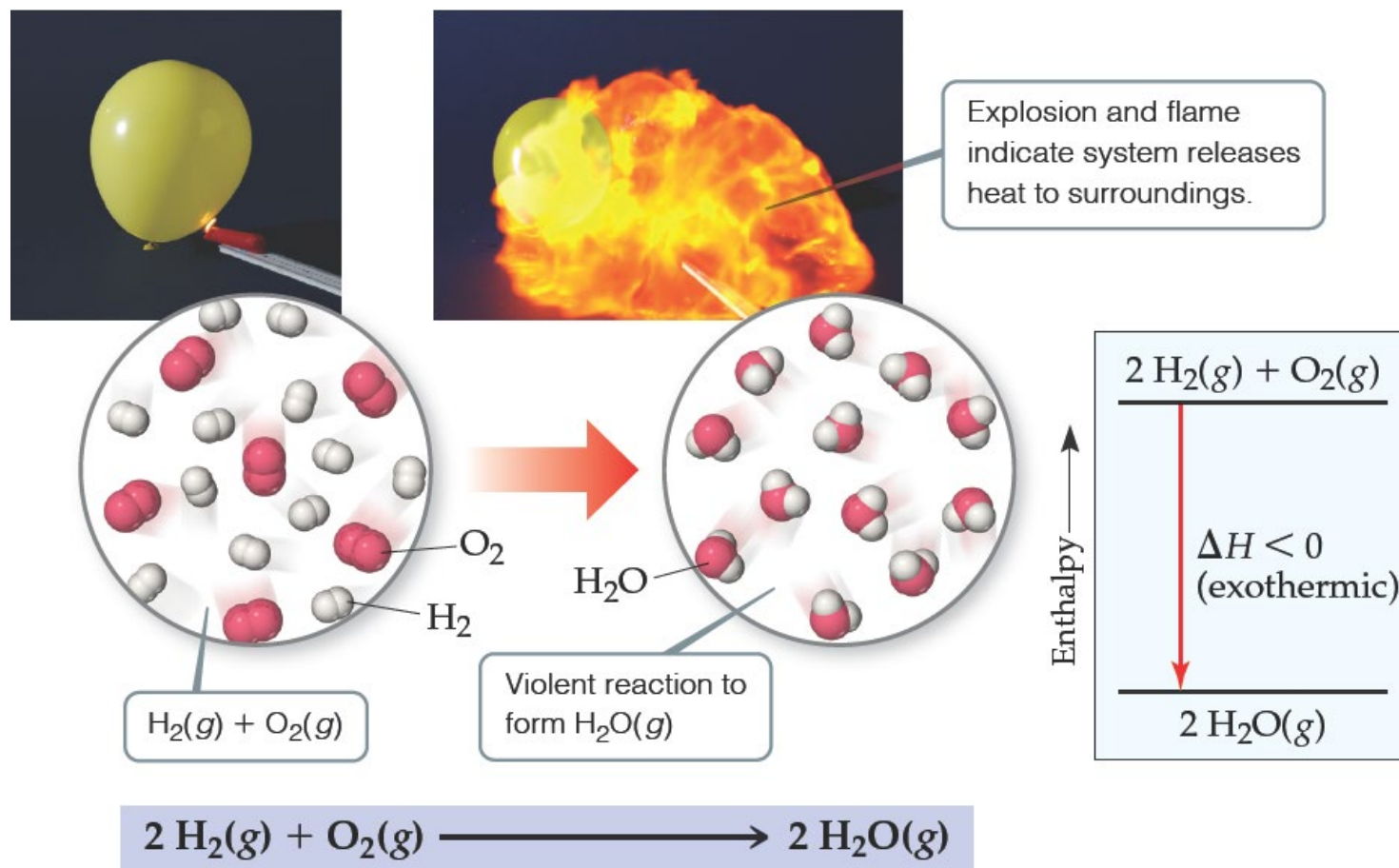
The **change** in enthalpy ΔH , is the enthalpy of the products minus the enthalpy of the reactants:

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



Enthalpy of Reaction (2 of 2)

This quantity, ΔH_{rxn} , is called the **enthalpy of reaction**, or the **heat of reaction**.



If the heat transfer involves a chemical reaction then q is called:

HEAT OF REACTION

The heat energy (ΔH ; enthalpy) required to return a system to the given temperature at the completion of the reaction.

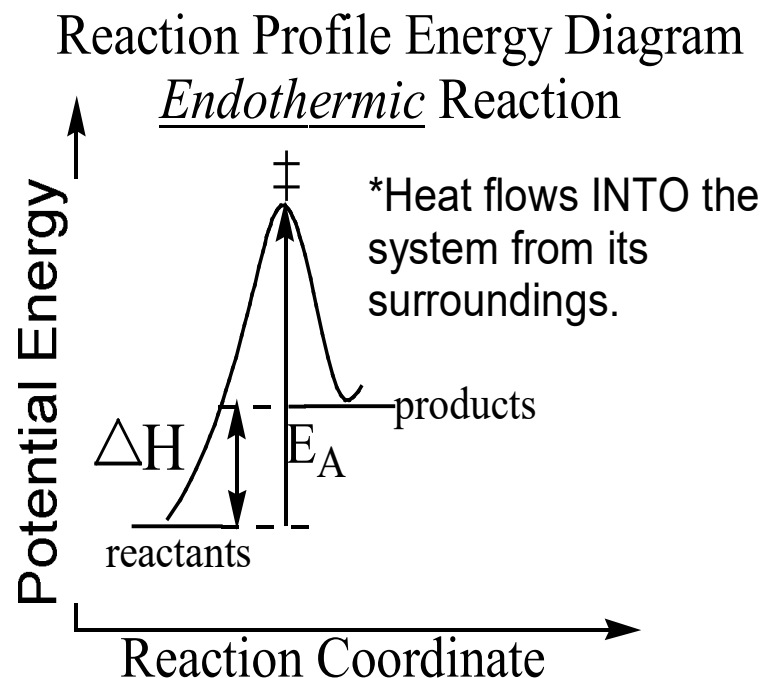
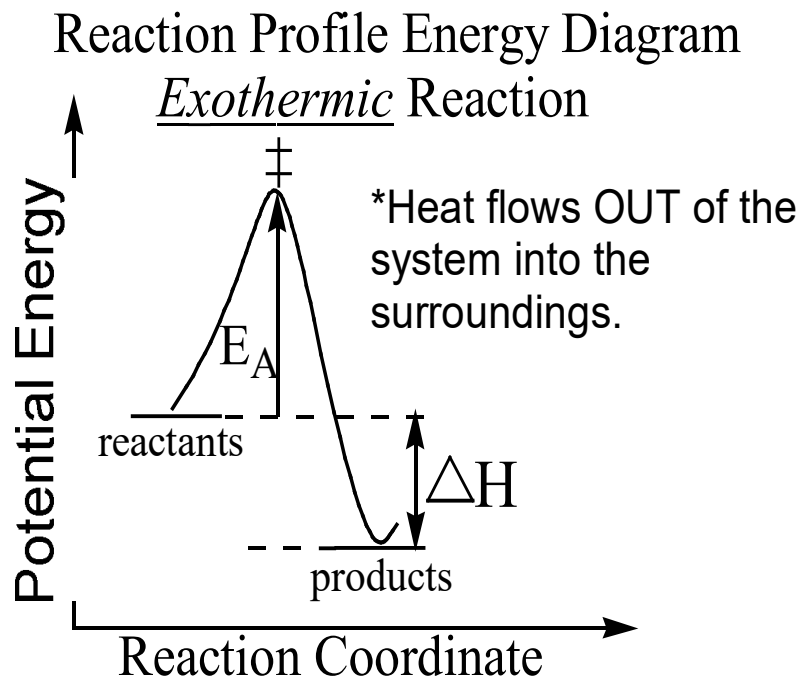
$$q = \Delta H \text{ at constant pressure}$$

The heat of reaction can be specific to a reaction like:

HEAT OF COMBUSTION

The quantity of heat energy given off when a specified amount of substance burns in oxygen.

UNITS: kJ/mol (kilojoules per mole) or kcal/mol (kilocalories per mole)



where: ΔH = heat (or enthalpy)

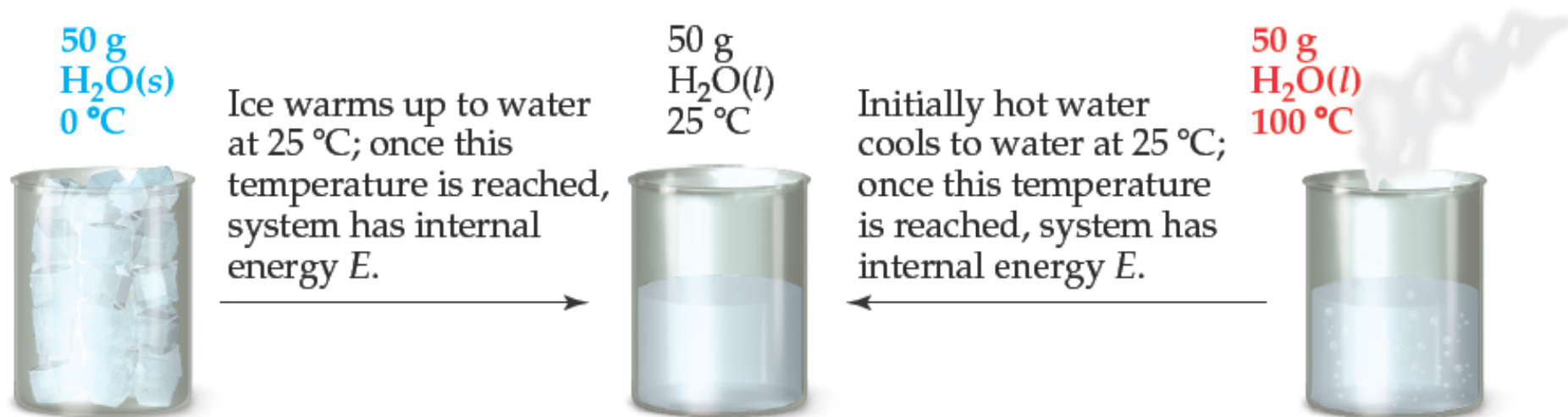
E_A = Activation Energy

‡ = Transition State (or activated complex)

State Function – a property with a value that depends only on the current state of the system and is independent of the manner in which the state was prepared.

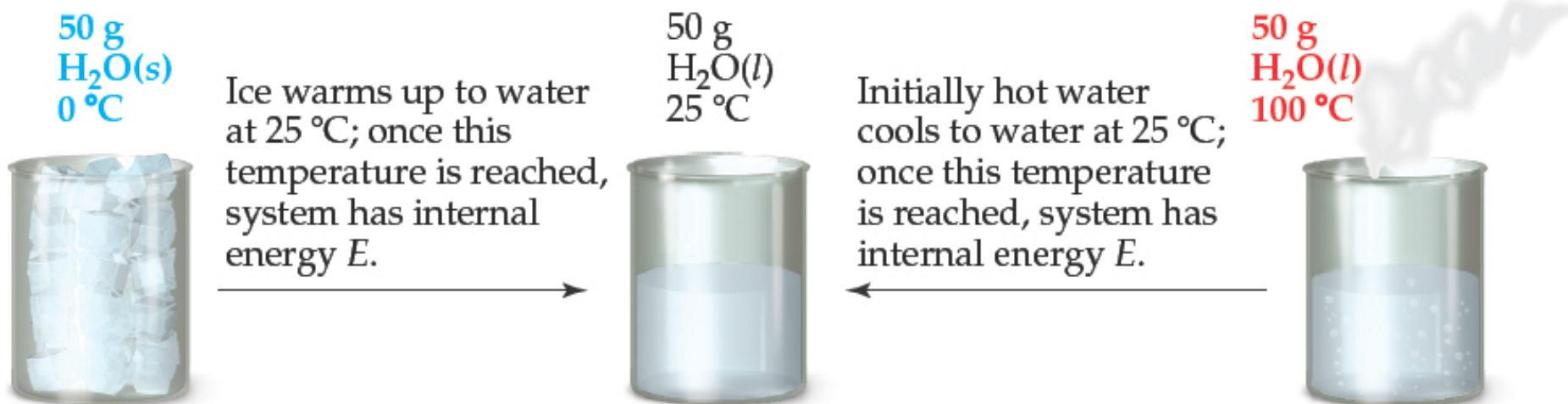
State Functions (1 of 3)

- Usually we have no way of knowing the internal energy of a system; finding that value is simply too complex a problem.
- However, we do know that the internal energy of a system is independent of the path by which the system achieved that state.
 - In the system below, the water could have reached room temperature from either direction.



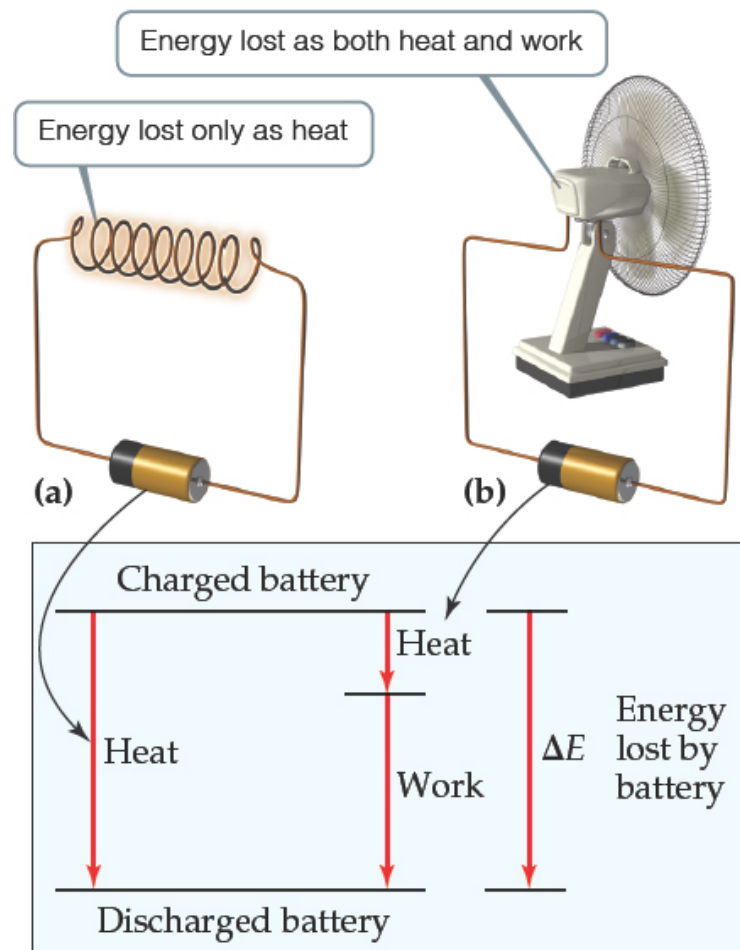
State Functions (2 of 3)

- Therefore, internal energy is a state function.
- It depends only on the present state of the system, not on the path by which the system arrived at that state.
- And so, ΔE depends only on E_{initial} and E_{final} .



State Functions (3 of 3)

- However, q and w are **not** state functions.
- Whether the battery is shorted out or is discharged by running the fan, its ΔE is the same, but q and w are **different** in the two cases.



Enthalpy

Enthalpy is the internal energy plus the product of pressure and volume:

$$H = E + PV$$

When the system changes at constant pressure, the change in enthalpy becomes,

$$\Delta H = \Delta (E + PV) \quad \text{or} \quad \Delta H = \Delta E + P\Delta V$$

$$\Delta E = q + w \quad \text{and} \quad w = -P\Delta V,$$

BUT!

which we can substitute these into the enthalpy expression:

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

$$\Delta H = (q + w) - w$$

$$\Delta H = q$$

- So, at constant pressure, the change in enthalpy **is** the heat gained or lost.

Enthalpy

The change in enthalpy, ΔH , equals the heat gained or lost by the system when the process occurs under constant pressure (q_p).

i. $\Delta H = H_{\text{final}} - H_{\text{initial}} = q_p$

ii. A positive value of ΔH indicates that the system has gained heat from the surroundings.

iii. A negative value of ΔH indicates that the system has released heat to the surroundings.

iv. Enthalpy is a state function.

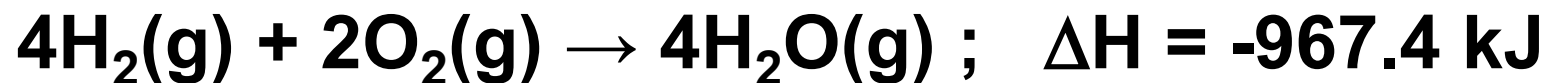
Enthalpy Thermodynamic Equations

Rules:

i. ΔH value is dependent on the phase of the substance.



ii. When a thermodynamic equation is multiplied by a factor, the ΔH is also multiplied by the same factor.



iii. ΔH value is dependent on the direction of the equation.



Lecture Questions on enthalpy

1. In the presence of a Pt catalyst, NH_3 will burn in air to give NO. Consider the following gas phase reactions:



What is ΔH for:

a) $8 \text{NH}_3 + 10 \text{O}_2 \rightarrow 8 \text{NO} + 12 \text{H}_2\text{O}$

b) $\text{NO} + \frac{3}{2} \text{H}_2\text{O} \rightarrow \text{NH}_3 + \frac{5}{4} \text{O}_2$?

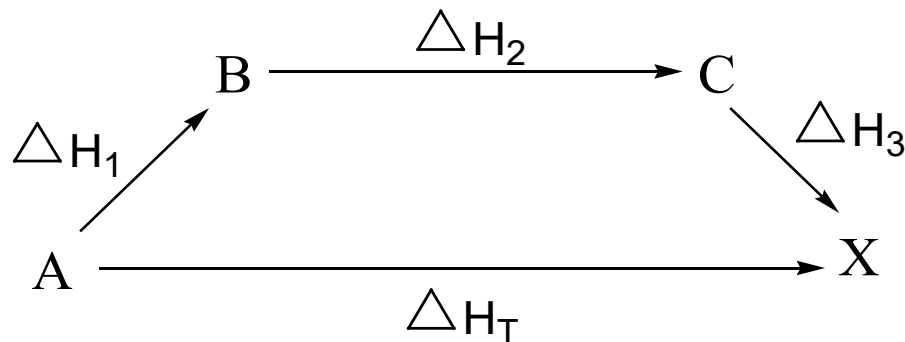
a) The original equation is doubled so $2(-906\text{kJ}) = \mathbf{-1812\text{kJ}}$

b) This is more complicated;
note the equation is reversed so switch sign
and it is divided by 4

$$\text{So } -(-906)/4 = \mathbf{+ 227 \text{ kJ}}$$

2. Consider the reaction $A \rightarrow X$. The enthalpy change for the reaction represented above is ΔH_T . This reaction can be broken down into a series of steps as shown in the following diagram:

Determine the relationship that must exist among the various enthalpy changes in the pathways shown above.

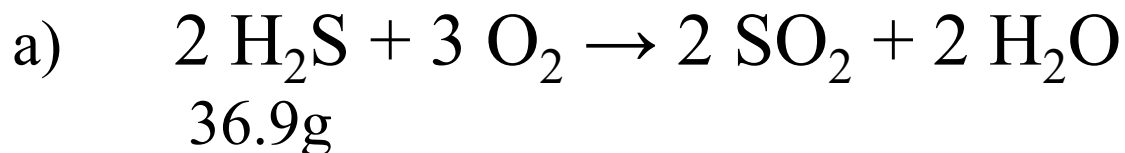


Lecture Questions on Stoichiometry & Enthalpy of Reaction

3a. Hydrogen sulfide burns in air to produce sulfur dioxide and water vapor. If the heat of reaction is -1037 kJ for this reaction, calculate the enthalpy change to burn 36.9 g of hydrogen sulfide in units of kcal?

3b. Sulfur dioxide reacts with water to form hydrogen sulfide gas. What is the enthalpy change for this reaction?

3c. Label both of the above reactions as either endothermic or exothermic.



b) + 134.5 kcal

Reaction is reversed

endothermic

$$36.9 \text{ g H}_2\text{S} \left(\frac{1 \text{ mol H}_2\text{S}}{34 \text{ g H}_2\text{S}} \right) \left(\frac{-1037 \text{ kJ}}{2 \text{ mol H}_2\text{S}} \right) \left(\frac{1 \text{ kcal}}{4.184 \text{ kJ}} \right) =$$

-562.7 kJ or -134.5 kcal

exothermic

Summary of Enthalpies of Reaction (ΔH_{rxn})

the enthalpy change that accompanies a reaction.

A. For an **ENDOTHERMIC** reaction, the reactants have *lower* enthalpies than do the products (ΔH is positive).

B. For an **EXOTHERMIC** reaction, the reactants have *higher* enthalpies than do the products (ΔH is negative).

C. Two important rules to apply:

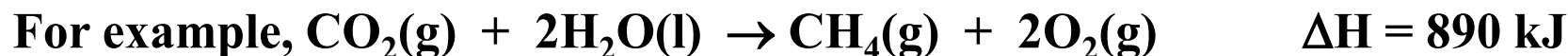
1. The magnitude of ΔH is directly proportional to the amount of reactants or products.

For example, the combustion of one mole of methane evolves 890 kJ of heat:



The combustion of **2** moles of methane produces 2(-890 kJ) or -1780 kJ of heat.

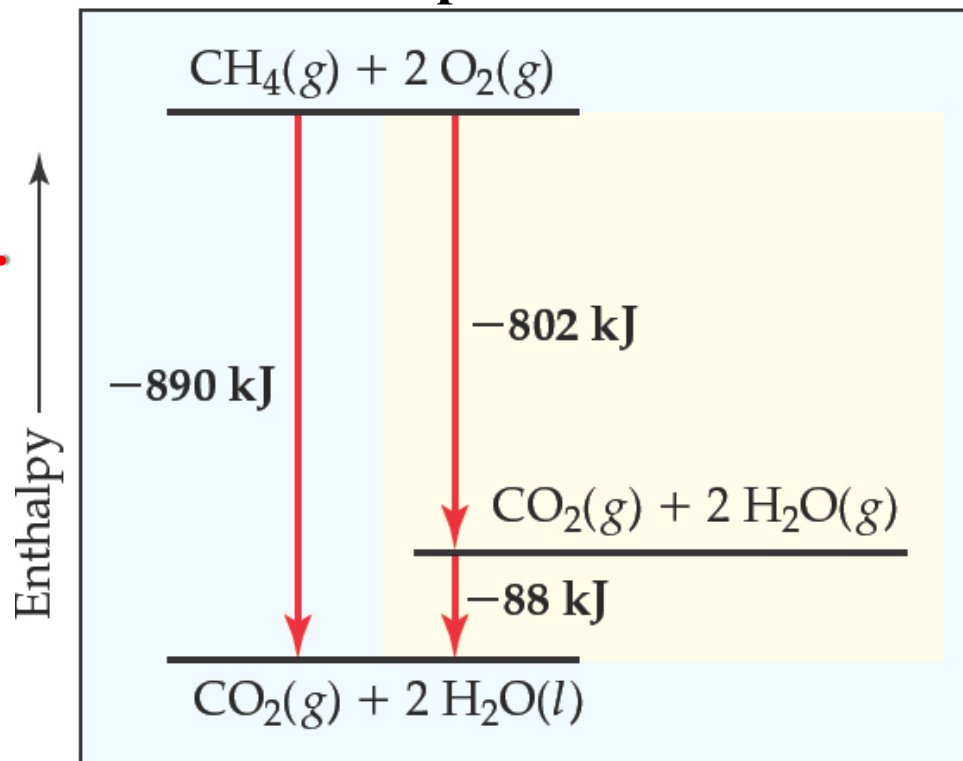
2. ΔH for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction.



Hess's Law

- Hess's law: If a reaction is carried out in a series of steps, ΔH for the overall reaction equals the sum of the enthalpy changes for the individual steps.
- Because H is a state function, for a particular set of reactants and products, ΔH is the same whether the reaction takes place in one step or in a series of steps.

CANVAS
LECTURE
VIDEO
ACTIVITY!!!



Hess's Law

If a reaction is carried out in a series of steps, ΔH for the reaction will be equal to the sum of the enthalpy changes for the individual steps.

For example, consider the reaction of tin and chlorine:

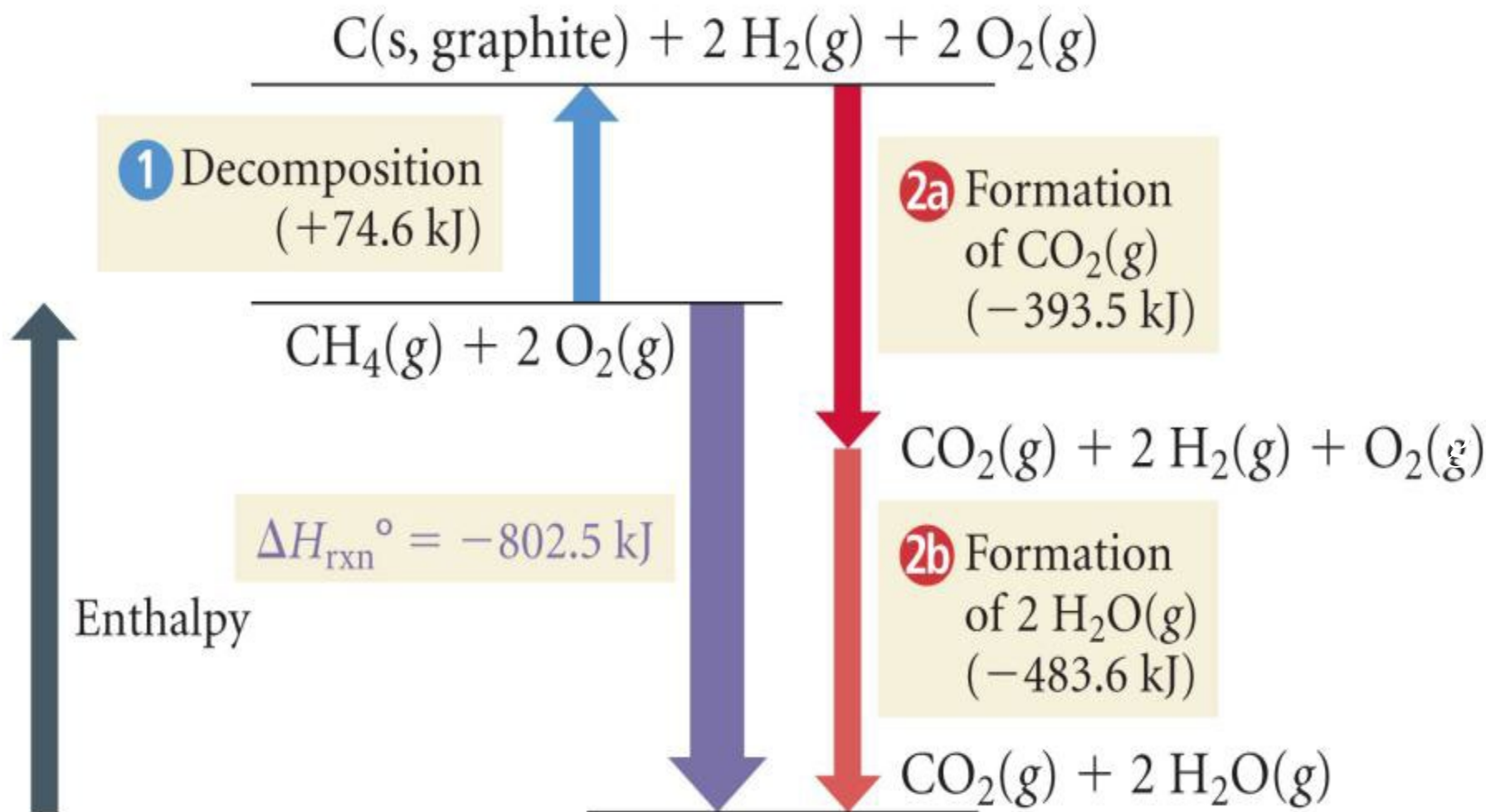


Add up both reactions to obtain:





Calculating the Enthalpy Change for the Combustion of Methane





Calculating the Enthalpy Change for the Combustion of Methane



Sample 1 - Calculate the Enthalpy Change in the Reaction from theory



1. Write formation reactions for each compound from its elements and determine the ΔH_f° for each:

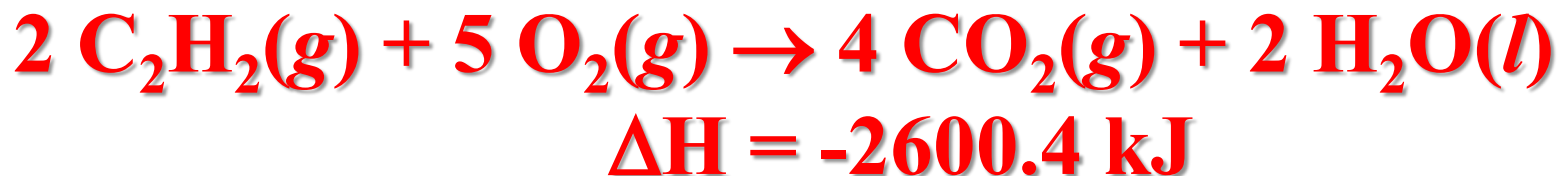
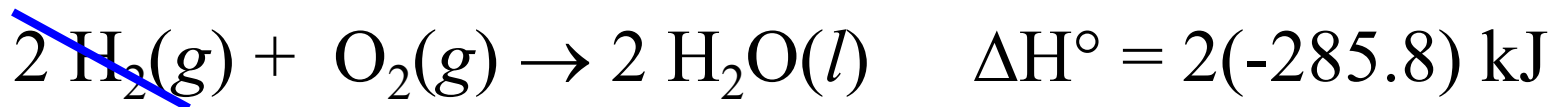
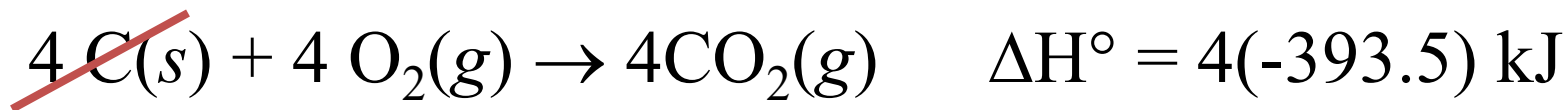
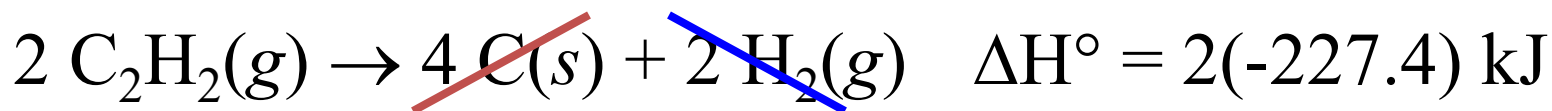


These values are the ones found in the appendix;
The equations are mutual knowledge so not written

Sample 1 - Calculate the Enthalpy Change in the Reaction from theory



2. Arrange equations so they add up to desired reaction



Lecture Questions on Hess's Law



Consider:



- 1) CO is a product so we keep the order but multiply by 2
- 2) Since that makes 2 CO_2 which must cancel out, we double eqn 2



$$\Delta H = -221 \text{ kJ}$$

1. Acetic acid is contained in vinegar.

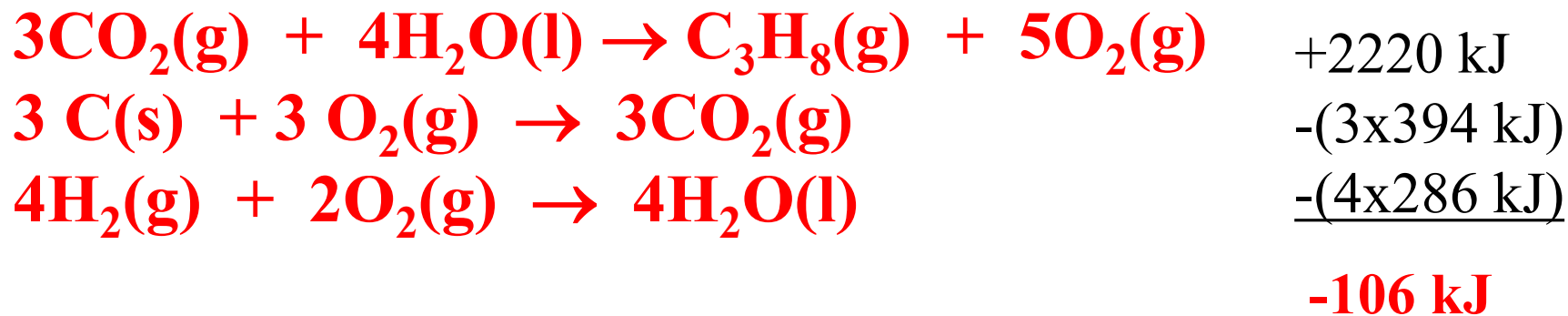
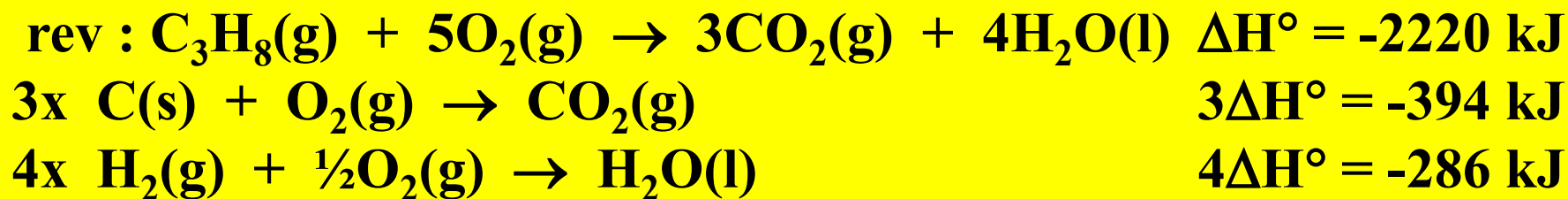
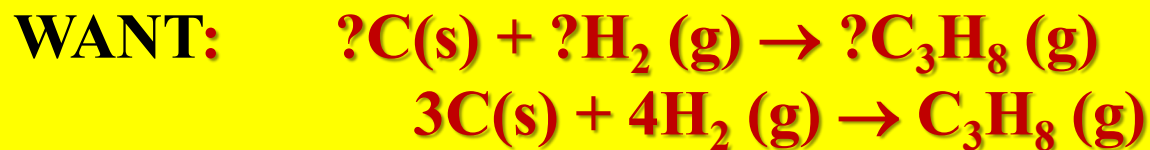
Suppose the following occurred:



Eqtn 1 must be reversed; eqnt 2 & 3 doubled; so

$$+871 + 2(-286) + 2(-394) = -489 \text{ kJ}$$

2. Consider the synthesis of propane from solid carbon and hydrogen gas. Determine the enthalpy change for 1 mol of gaseous propane given the following thermochemical data:

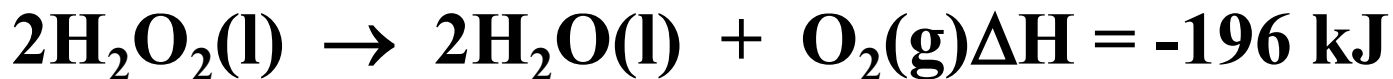


GROUP QUIZ #12 on Stoichiometry & Enthalpy of Reaction

1. How much heat is released when 4.50 g of methane gas is burned in a constant pressure system? Is this reaction endothermic or exothermic?



2. Hydrogen peroxide can decompose to water and oxygen by the reaction:



Calculate the value of q when 5.00 g of $\text{H}_2\text{O}_2(\text{l})$ decomposes at constant pressure.