Chapter 7

Thermochemistry

Energy

Capacity to move against a force

- can be against a force like gravity, or the force between electrical charges, etc.
  - ➢ Potential Energy

- can be against the force of inertia when accelerating an object to give it a velocity
  - ➢ Kinetic Energy

The kind of energy associated with velocity is "Kinetic Energy", E_k

$$E_k = \frac{1}{2} m v^2$$

m = mass
v = velocity

kg m^2/s^2

kg $(m/s)^2 = m^2/s^2$

We can use this equation to deduce the units for energy

kg m^2/s^2 is called a "Joule" (symbol: J)

SI unit for energy: Joule (J)

Other, traditional units for energy

calorie (cal)

- Amount of heat needed to warm 1 gram of water by 1°C
- 1 cal = 4.184 J

capitalized

Calorie (Cal)

- “food calorie” or “dietary calorie”
- The “Calories” you find on food labels
- 1000 calories (1 kcal)
- 1 Calorie = 4.184 kJ

The kind of energy associated with moving against a frictionless force is “Potential Energy”, E_p

moving a mass m against Earth’s gravity:

$$E_p = m\,g\,h$$

m = mass
g = proportionality constant (to calculate gravitational force)
h = height (by which m is moved against gravitational force)

moving a cation and an anion apart:

$$E_p = k_e \frac{Q_+ Q_-}{r}$$

Q_+ = cation charge
Q_- = anion charge
k_e = proportionality constant
r = distance between charges

Both kinetic energy and potential energy can belong to “**macroscopic**” (dust-size and up) as well as “**microscopic**” (atomic scale) objects

“Mechanical energy”

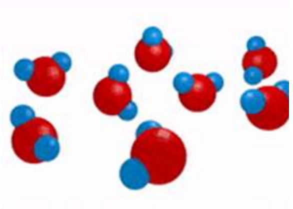
Energy (kinetic or potential) of a macroscopic movement

- ➢ Movement of a microbe
- ➢ Bouncing on a trampoline

“Thermal energy”

Energy (kinetic or potential) randomly distributed to microscopic objects

- ➢ Kinetic energy of atoms moving randomly
- ➢ Potential energy in stretched and bent bonds



Transfer of Energy

Work:

Transfer of **mechanical energy**

-- by a <u>macroscopic force</u> acting over a distance

Heat:

Transfer of **thermal energy**

-- due to a temperature difference

- ➢from hot object to cold object

Energy is a **state function**

work and **heat** are **not**

State Function:

- a property that does <u>not</u> depend on the system's <u>past</u>

- only depends on the *present* state

➢ It's like your bank account. Its balance is what it is.

➢ You might arrive at the same account balance by winning the lottery and then spending it all, or never winning it and never spending the extra money.

A very important aspect of a state function:

<u>**Change**</u> in a state function depends only on the **beginning state** and the **end state**.

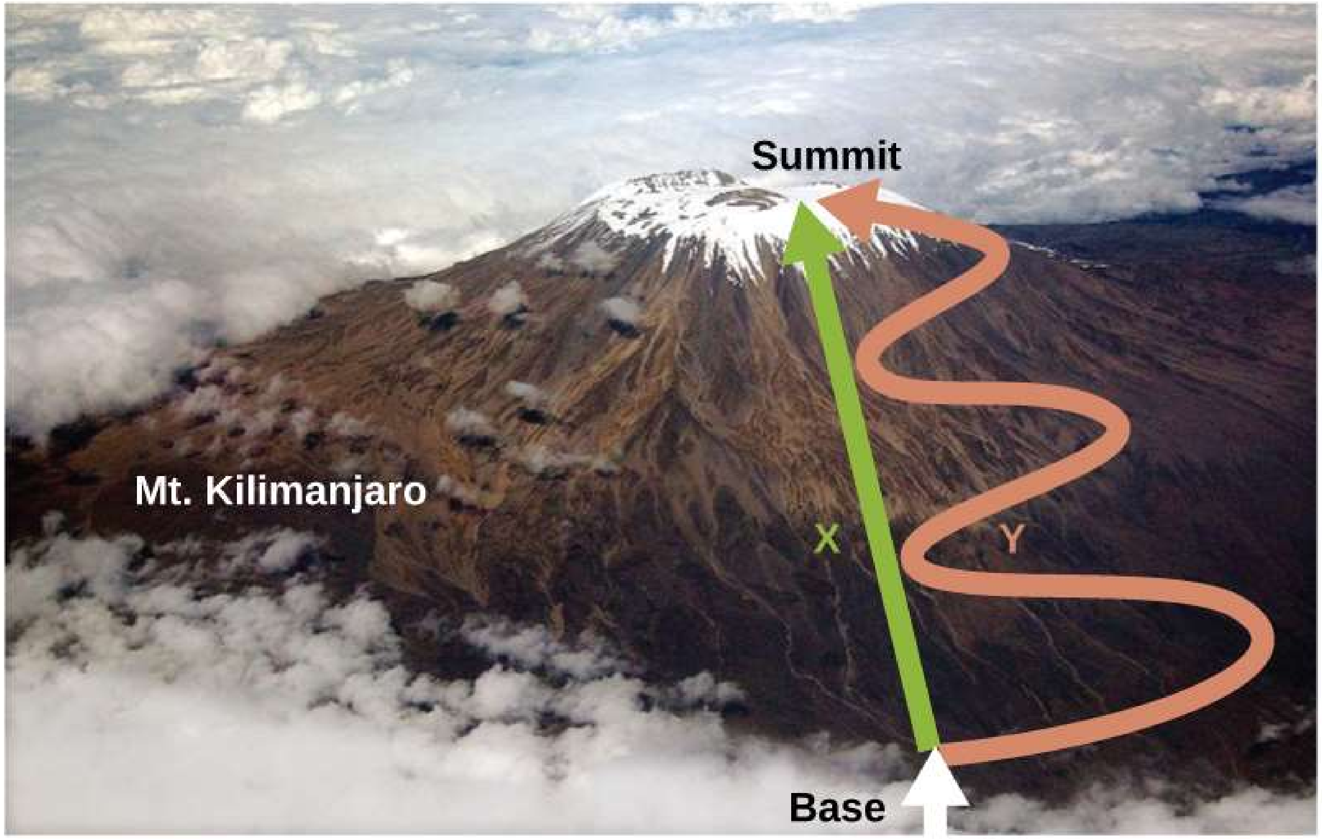
-- does **not** depend on the **path** between

Height is a state function

- So is the gravitational potential energy gained by climbing that height

Distance traveled to gain that height is **not**

- It can be very circuitous, or direct



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Law of conservation of energy

The total energy of the universe is constant.

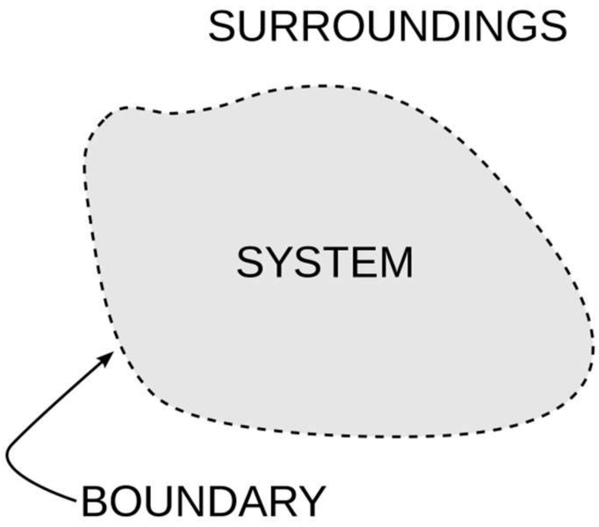
Energy can be converted from one form to another but cannot be created nor destroyed.

Potential Energy ⟷ Kinetic Energy

Mechanical Energy ⟷ Thermal Energy

System: part of the universe on which we focus on

Surroundings: everything else in the universe



Universe = System + Surroundings

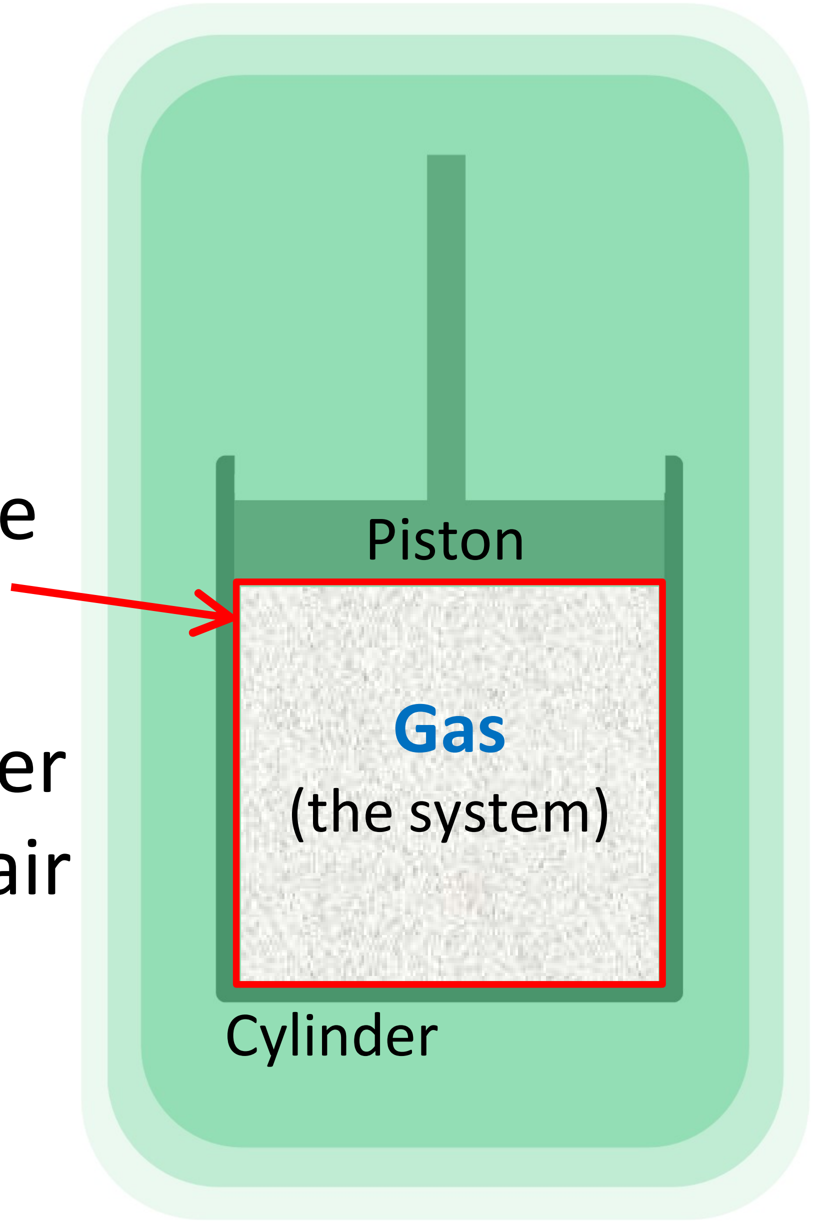
- The total energy of the universe is constant.
- The energy of the system or the surroundings need not be.

A tangible system and surroundings: Gas in a cylinder with a piston

Gas is the system

Boundary is at the inner surface of the cylinder and the piston

Surroundings is everything other than the gas (cylinder, piston, air around the whole contraption, etc.)

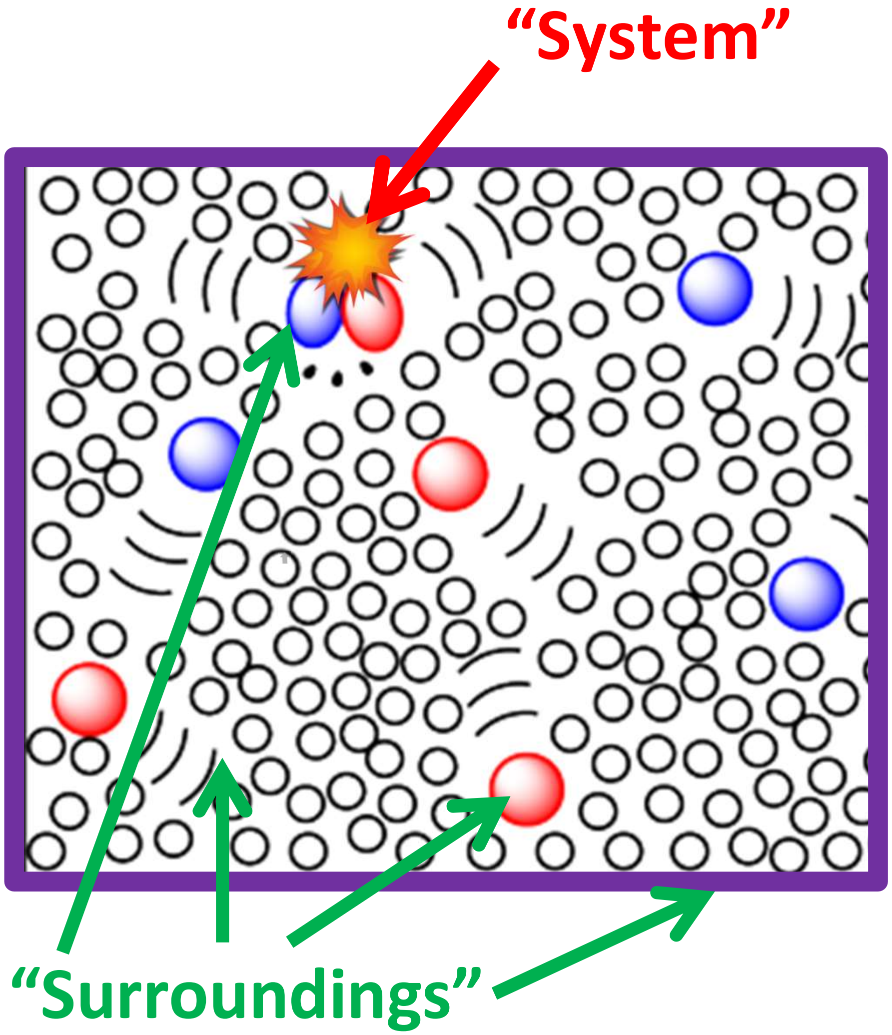


The “system” and its boundary is a bit abstract in the case of reactions

System: The reaction process itself. No atoms!

- Actually just the electrons in atoms rearranging in some way

Surroundings: All the matter around (even the atoms involved in the reaction), excluding the electrons that are involved in bond making and breaking.



Boundary: Exists only conceptually.

The surroundings and the system share the same space.

Direction of Heat Flow

Endothermic Process:

- **Heat** flows **into** the system.

  System **absorbs** heat from the surroundings

  - in the case of a reaction, the reactants absorb heat

Thermal Energy **gained** by the **system** = Thermal Energy **lost** by the **surroundings**

Direction of Heat Flow

Exothermic Process:

- **Heat** flows **out of** the system.

  System **releases** heat to the surroundings

  - in the case of a reaction, the reactants release heat

Thermal Energy **lost** by the **system** = Thermal Energy **gained** by the **surroundings**

Concept Practice

Is the freezing of water an endothermic or exothermic process? Explain.

It is exothermic.

We need to remove heat from water to freeze it.

Concept Practice

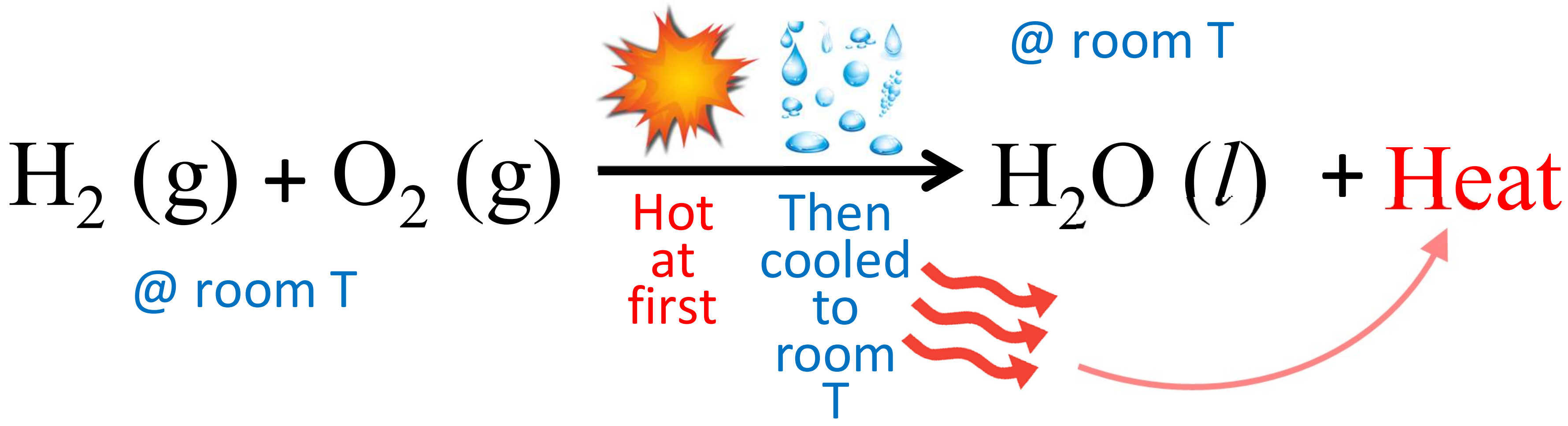
Classify each process as exothermic or endothermic. Explain. The system is underlined in each example.

- Your hand gets cold when you touch ice.
  “gets cold”: “loses heat” ⇒ exothermic
- The ice gets warmer when you touch it.
  “gets warm”: “gains heat” ⇒ endothermic
- Water is being heated in a kettle on a stove.
  “being heated”: “gains heat” ⇒ endothermic
- Water vapor condenses on a cold pipe.
  condensing it requires removing heat ⇒ exothermic
- Ice cream melts.
  To melt, it needs to absorb heat ⇒ endothermic

Concept Practice

Hydrogen gas and oxygen gas at room temperature and 1 atm pressure react violently to from water, which is then condensed to liquid water by returning the conditions to the starting temperature and pressure.

- Which is lower in energy?
  - ➢a mixture of hydrogen and oxygen gases?
  - ➢or water?
- Is this an exothermic or endothermic reaction? Explain.



$$H_2\,(g) + O_2\,(g) \xrightarrow[\text{Hot at first} \quad \text{Then cooled to room T}]{} H_2O\,(l) + \text{Heat}$$

@ room T

Hot at first

Then cooled to room T

@ room T

- The formed H-O bonds are lower in energy than the broken H-H and O-O bonds. So, at the same temperature, water is lower in energy than the H_2 and O_2 mixture. But in hot water, the energy lost from the bonds is contained as thermal energy in the produced water molecules.

- The thermal energy is **removed as heat** when the water condenses. Therefore it is an **exothermic** process.

Normally, when we talk about a **reaction** being **exothermic** or **endothermic**, we assume that the reactants we start with and the products we end up with are all **at the same temperature**, typically 25°C.

Even if the temperature can (and does) change during the reaction, we measure the energy released or absorbed when the products are ultimately at the same temperature as the reactants.

Internal Energy (E)

The sum of the kinetic and potential energies* of all the particles in the system.

- Kinetic Energy:
  - Due to the random speeds of all the particles
- Potential Energy:
  - Gained against the forces they apply on one another
  - Molecules against other molecules, atoms stretching and bending chemical bonds, electron-nucleus attractions

* Doesn't include chemically irrelevant energies such as the gravitational potential energy, the kinetic energy due to the planetary motions (which the system is a part of), etc.

Change* in Internal Energy (ΔE)

There are two ways to change internal energy *E:*

“heat” = **q**

“work” = **w**

$$\Delta E = q + w$$

* “Change” (for any quantity, not just E) is represented by the capital Greek letter “delta” (**Δ**).

It is always “final minus initial”:

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

When the quantity **increases**, the “change” is **positive**.

When the quantity **decreases**, the “change” is **negative**.

Values of thermodynamic quantities

Thermodynamic quantities consist of two parts:

Number: magnitude (size)

Sign: **+** or **–**

- Direction of the flow (for q and w)
- Direction of the change for any "state function"

-- Such as internal energy E

-- P, V, T, n we saw earlier (also state functions)

-- Other quantities derived from state functions

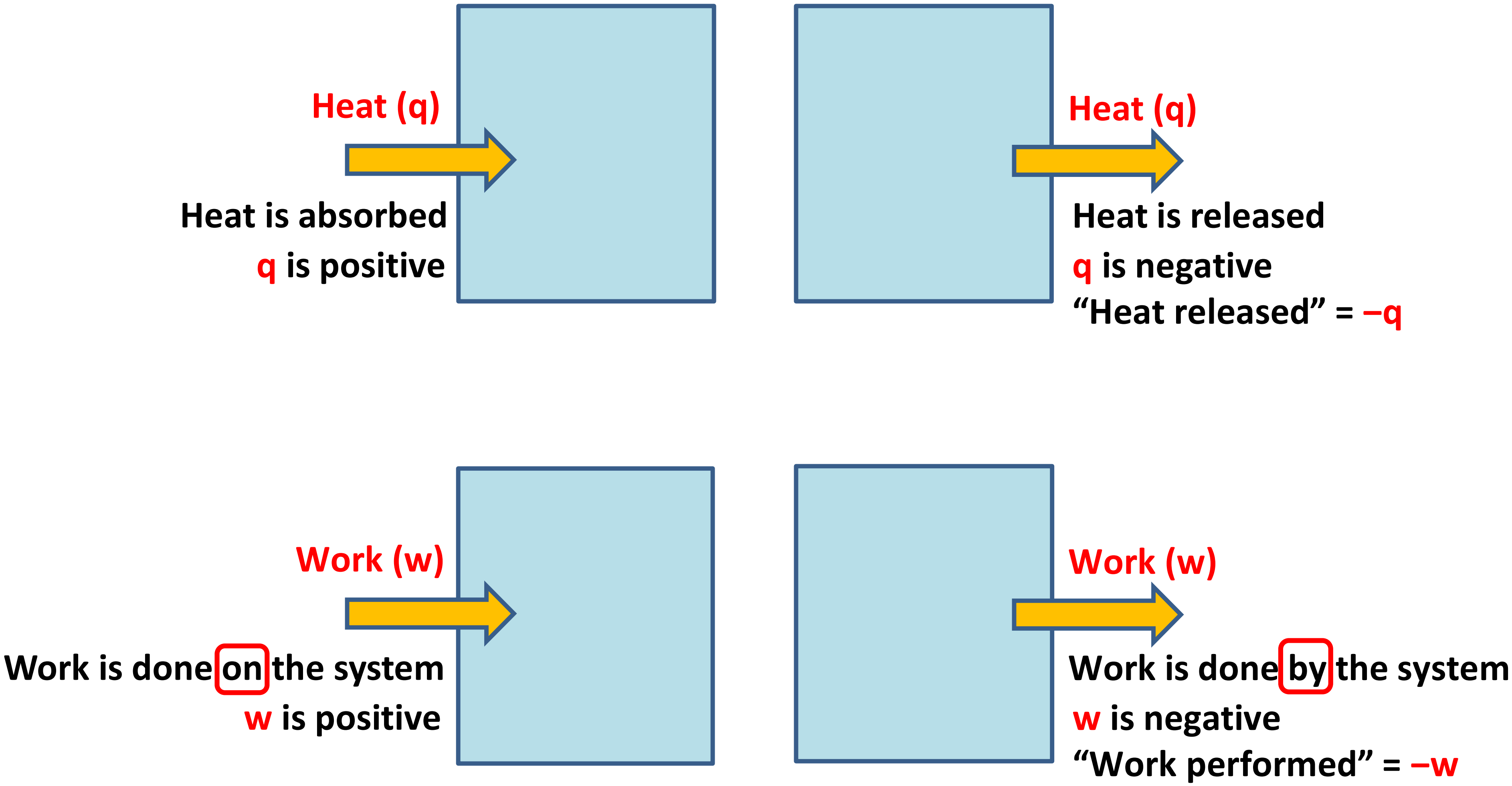
On the signs of thermodynamic quantities

The sign of the change or the flow reflects the <u>system's</u> point of view*

$\Delta E = 15$ kJ	the system **gained** 15 kJ of energy
$\Delta E = -56$ kJ	the system **lost** 56 kJ of energy
$q = 13$ kJ	the system **gained** 13 kJ of "heat" (more correctly: thermal energy)
$q = -13$ kJ	the system **lost** 13 kJ of "heat"
$w = 55$ kJ	55 kJ of work done **on** the system (**gained** energy)
$w = -55$ kJ	the system **performed** 55 kJ of work (**lost** energy)

*Unless the quantity is specified to be for the surroundings, in which case we are focusing on the surroundings as the relevant "system" at that moment

From the system’s point of view:



Heat (q)

Heat is absorbed

q is positive

Heat (q)

Heat is released

q is negative

“Heat released” = −q

Work (w)

Work is done on the system

w is positive

Work (w)

Work is done by the system

w is negative

“Work performed” = −w

Implications of the +/– sign conventions for q and w

The sign convention implies:

“heat” (q) means “heat absorbed by the system”

q = “heat absorbed by the system”

–q = “heat released by the system”

i.e. we report –q when asked “heat released”

[if heat was actually released, q is negative, and “heat released” (–q) would be a positive number]

“work” (w) means “work done on the system”

w = “work done **on** the system”

–w = “work done **by** the system”

i.e. we report –w when asked “work done by the system”

"Work" in chemistry

We defined work as "Transfer of mechanical energy by a macroscopic force acting over a distance".

Except for electrical work involved in electrochemistry, "work" in chemistry involves **volume change against a pressure** (equivalent to moving a distance against a force).

When a system's volume expands, it does so against an external pressure.

- The system performs work

$$w = -P\Delta V$$

makes work negative when the system expands (ΔV is +)

Volume change

against an external pressure

Practice

Which of the following performs more work?

a) A gas expanding against a pressure of 2 atm from 1.0 L to 4.0 L.

b) A gas expanding against a pressure of 3 atm from 1.0 L to 3.0 L.

a) $w = –P\Delta V = –(2\text{ atm})(4.0\text{L} – 1.0\text{L}) = –6\text{ L·atm}$

work performed = –w = –(–6) = **6 L·atm**

b) $w = –P\Delta V = –(3\text{ atm})(3.0\text{L} – 1.0\text{L}) = – 6\text{ L·atm}$

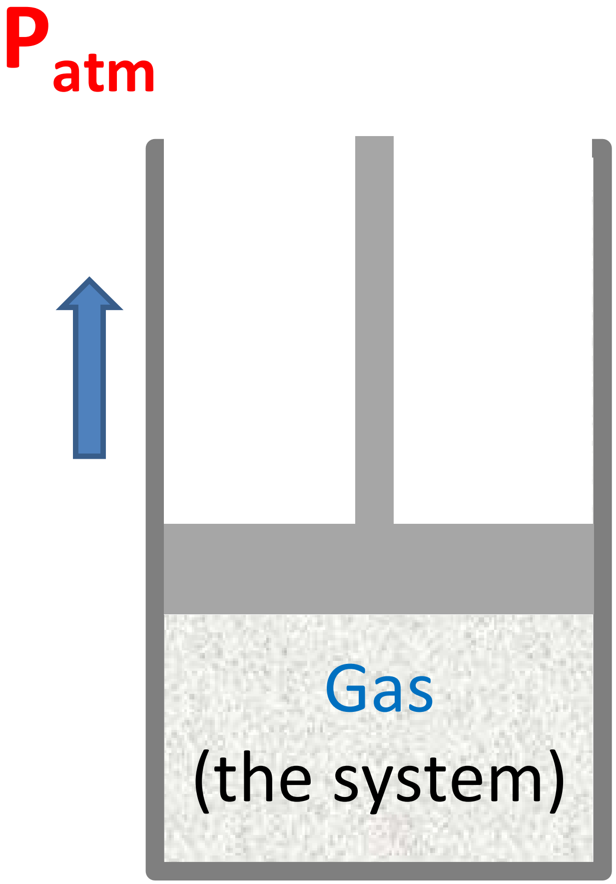
work performed = –w = –(–6) = **6 L·atm**

They perform the same amount of work

$$w = -P\Delta V$$

Pressure against which movement is made

- Not necessarily the pressure of the system!



When the system is expanding:

$w = -P_{external}\,\Delta V$

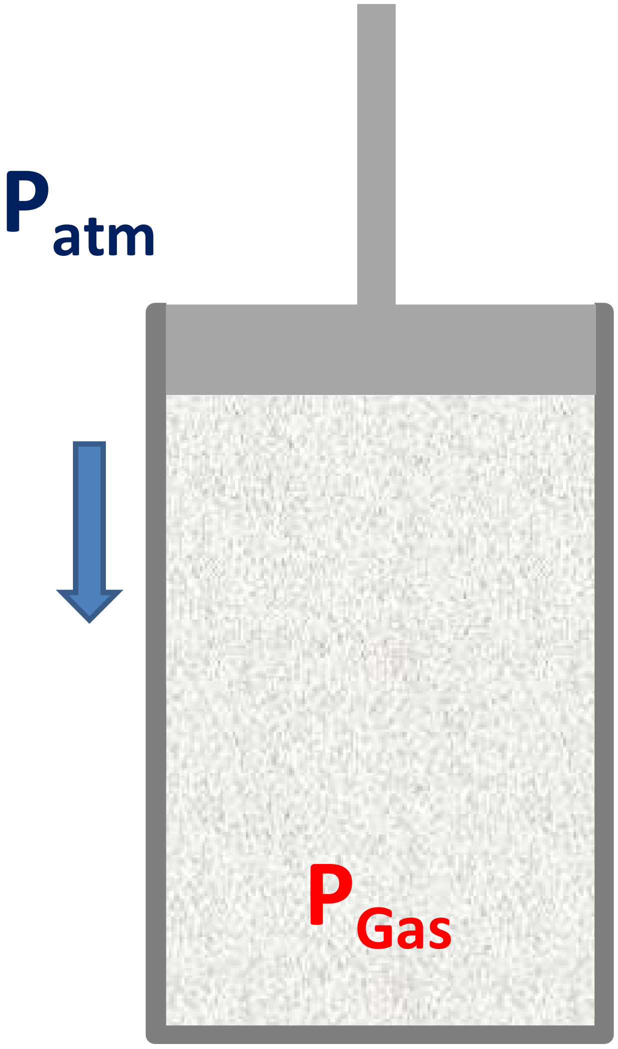
$$w = -P_{atm}\,\Delta V$$

When the system is being compressed:

$w = -P_{system}\,\Delta V$

$\uparrow$

Now the system pressure **is** the pressure against which movement is made



$$w = -P_{Gas}\,\Delta V$$

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Practice

Water can exist as gas or liquid at 100°C and 1 atm (both numbers are exact). Under these conditions, 157 L of steam is condensed into liquid water. We can ignore the volume of liquid water. Calculate the work involved. Was work performed by the system or on the system?

Liquid water volume ≈0
All the steam volume is lost.
The system volume decreased.
$w = -P\Delta V = -(1\ \text{atm})(0\ \text{L} - 157\ \text{L}) = 157\ \text{L·atm}$

w is positive

work was performed **on** the system

Practice

Zinc is more active than H_2(g), and replaces H^+ (aq) from an acid solution. What is the work involved when 1.0 mol Zn(s) reacts with HCl(aq) and produce hydrogen gas at standard temperature and pressure? Was work performed by the reacting substances or on them? Volume of solids and liquids can be neglected. Hydrogen gas can be regarded as an ideal gas.

$$Zn(s) + 2\ HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

- Only the volume of hydrogen gas will be considered.
- 1 mol of Zn produces 1 mol of H_2(g) according to the reaction equation.
- 1 mol of ideal gas occupies 22.42 L volume

$$w = -P\Delta V = -(1\ \text{atm})(22.42\ \text{L} - 0\ \text{L}) = -22.42\ \text{L}\cdot\text{atm}$$

w is negative; therefore work was performed by the system

Enthalpy: A more convenient kind of energy

- We would like to be able to measure energy changes quickly and conveniently.
- Measuring heat is easier than measuring work.
- Change in internal energy **E** involves both.
- If we define a different kind of energy content whose change didn't involve work, it would be pretty convenient.

Enthalpy

Enthalpy (H) is a composite energy defined as:

$$H = E + PV$$

We can interpret it as:

Internal energy of the system plus the work required to make room for it (to create its **volume** starting from zero) against a pressure (such as the atmospheric pressure against which the volume would have to be created).

Change in Enthalpy, ΔH

Ironically, Enthalpy's inclusion of the work required to create the system's volume makes **ΔH immune to the work involved** in processes.

$\Delta H = \Delta E + \Delta(PV)$

$\Delta H = \Delta E + P\Delta V$ @ constant P (it acts as just a constant)

Since $\Delta E = q + w$, and $w = -P\Delta V$, we have

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

⇨ $\Delta H = q$ @const. P

We can use **q** at constant P to measure **ΔH**

Change in Enthalpy, ΔH

- Enthalpy is derived from state functions (E, P, V)
- Therefore it is a state function
- Change in its value (ΔH) is determined by the initial and final state only
- Therefore, in the case of a reaction, ΔH is determined by the enthalpy of the reactants and products only

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

Thermochemical reaction equations

The reaction equation with a matching ΔH

For example:

$$\mathrm{C_3H_8}(g) + \mathbf{5}\mathrm{O_2}(g) \rightarrow \mathbf{3}\mathrm{CO_2}(g) + \mathbf{4}\mathrm{H_2O}(l) \qquad \Delta H = -2221\ \mathrm{kJ}$$

implied **1**

In a thermochemical equation, the coefficients are more than for stoichiometric mole ratios.

The coefficients are also the actual moles of substances **corresponding to the ΔH** listed with the reaction.

Thermochemical reaction equations

$C_3H_8(g) + \mathbf{5}O_2(g) \rightarrow \mathbf{3}CO_2(g) + \mathbf{4}H_2O(l) \quad \Delta H = \mathbf{-2221\ kJ}$

implied **1**

The thermochemical equation above indicates:

When **1 mol** of C_3H_8(g) combusts with **5 mol** O_2(g), enthalpy change (or **heat**, at constant P) is **-2221 kJ**

Practice

Consider, again, the combustion of propane, C_3H_8:

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H = -2221\text{ kJ}$$

Calculate ΔH in which 5.00 g of propane is burned in excess oxygen at constant pressure.

We apply stoichiometry to ΔH just as we would apply to moles of product

$$5.00\text{ g } C_3H_8 \times \frac{1\text{ mol } C_3H_8}{44.0\text{ g } C_3H_8} \times \frac{-2221\text{ kJ}}{1\text{ mol } C_3H_8} = -252\text{ kJ}$$

Measuring Heat: Calorimetry

- Heat flows from the hot material to the cold one
- The material gaining heat gets warmer
- The material losing heat gets colder
- Given time, the two materials (or objects) equilibrate at **the same, final temperature T_{final}**

We measure heat by measuring temperature changes:

$$\Delta T = T_{final} - T_{initial}$$

units of ΔT : **°C**

Kelvins (K) would be equivalent. Why?

But every material needs a different amount of heat to warm up by 1°C, even if they have the same mass.

But the amount of heat also depends on the amount and kind of material we have.

Amount of heat needed to change the temperature of an object (or a material) by one degree is called "**heat capacity**": **C**

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

units of **C**: **J / °C**

or **cal/ °C** **etc.**

The "heat capacity" defined above is the **total heat capacity** of an object.

- Takes into account kind and amount of material

It refers to a whole object, or a whole sample.
We don't need to know the object's mass as long as we know its total "heat capacity".

How much heat is needed to warm up the world's oceans by 0.50°C?
Given: The (total) heat capacity of the oceans is 1.386×10^{24} cal/°C

$$q = C\,\Delta T$$

$$= (1.386 \times 10^{24}\ \text{cal/°C})\ (0.50\ \text{°C}) = 6.9 \times 10^{23}\ \text{cal}$$

For a specific material, the amount of heat needed to **warm 1 gram** of it **by 1°C** is a characteristic property specific to that material, and is called "**specific heat capacity**", or "**specific heat**": **c**

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

mass

units of c: **J / °C·g**

or **cal/ °C·g** **etc.**

Beware:

- Confusingly, in many places, just "heat capacity" is used to mean "specific heat capacity". Watch the context!

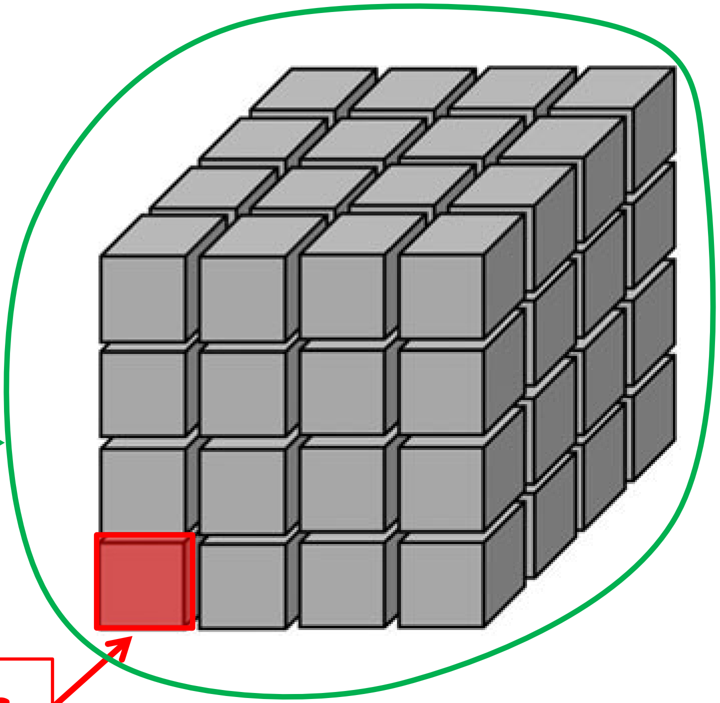
Heat capacity and specific heat capacity for a given material

For a specific material, the total "heat capacity" C and "specific heat capacity" s are simply related: **C** = m · **c**

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

$$q = C\ \Delta T$$

q needed to increase T of entire object (with mass **m**) by 1°C
= C = **m** · **c**



q needed to increase T of 1 gram by 1°C = **c**

Measuring heat for a single material

For a specific material:

It makes sense to use specific heat capacity **c**

instead of total heat capacity **C**

- We just look up its specific heat capacity **c**
- Weighing the material (to get **m**) is much easier than measuring its total heat capacity.

$$q = m\,c\,\Delta T$$

Measuring heat for a complex object made of many materials

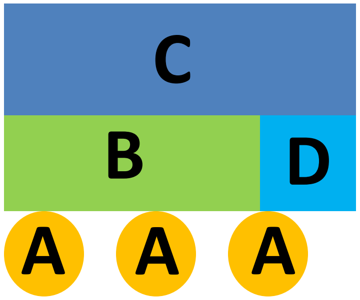
For a complex object:

It makes sense to use the total “heat capacity” **C**

- perform one experiment to determine its heat capacity **C**, and use that with ΔT forever after!

$$q = \underset{\uparrow}{C}\,\Delta T$$

$$\boxed{\overset{?}{m_A\, c_A} + \overset{?}{m_B\, c_B} + \overset{?}{m_C\, c_C} + \overset{?}{\ldots}}$$

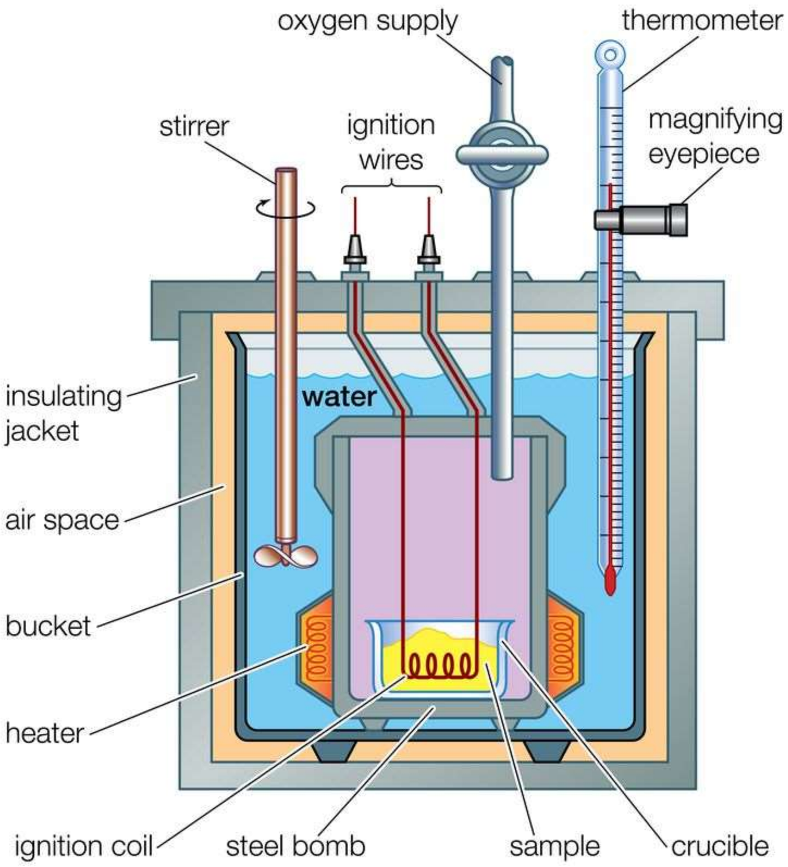


It’s hard to find the **mass** and specific heat capacity of each and every component of a complex object! For example, your phone!

Bomb calorimeters are complex objects

So they come with their measured “heat capacity”, also called “Calorimeter constant”

$$q_{calorimeter} = C_{calorimeter}\,\Delta T$$



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Measuring Heat: Calorimetry

For any material, or object:

$$\boxed{\begin{array}{l} \mathbf{q = C\,\Delta T} \\ \\ \mathbf{q = m\,c\,\Delta T} \end{array}}$$

means

$$\boxed{\begin{array}{lcl} \Delta T > 0 & \Longrightarrow & q > 0 \\ \Delta T < 0 & \Longrightarrow & q < 0 \end{array}}$$

If the “surroundings” gets warmer, then

$q_{\text{surroundings}}$ is positive

and

q_{system} is negative (with equal magnitude)

because $\boxed{\mathbf{q_{system} = -q_{surroundings}}}$

Measuring Heat: Calorimetry

- A calorimeter provides "surroundings" for the "system" we want to study
- Measuring the ΔT of the "surroundings" and using the known heat capacity of the surroundings, we can measure the heat for the "system"
- The "system" can be a piece of material we want to measure the specific heat of
- Or it can be a reaction we want to measure the "heat of reaction" of

$$q_{system} = -q_{calorimeter}$$

Measuring Heat: Bomb Calorimeter

A “bomb calorimeter” is used to measure heat at **constant volume** (ΔV=0)

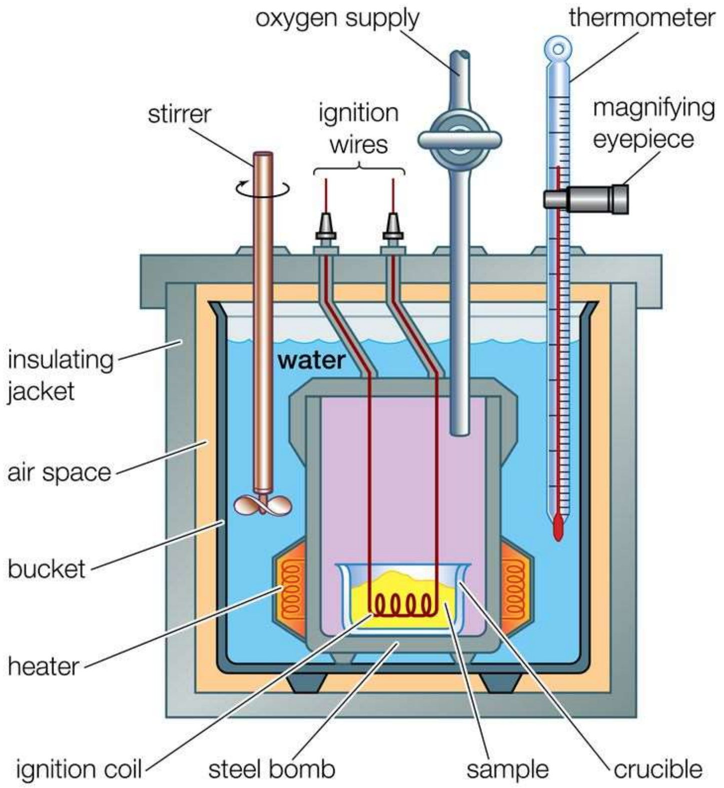
$$w = -P\,\overset{0}{\cancel{\Delta V}} = 0$$

$$\Delta E = q + \overset{0}{\cancel{w}} = q$$

So **q = ΔE** $\longleftarrow \Delta E_{system}$

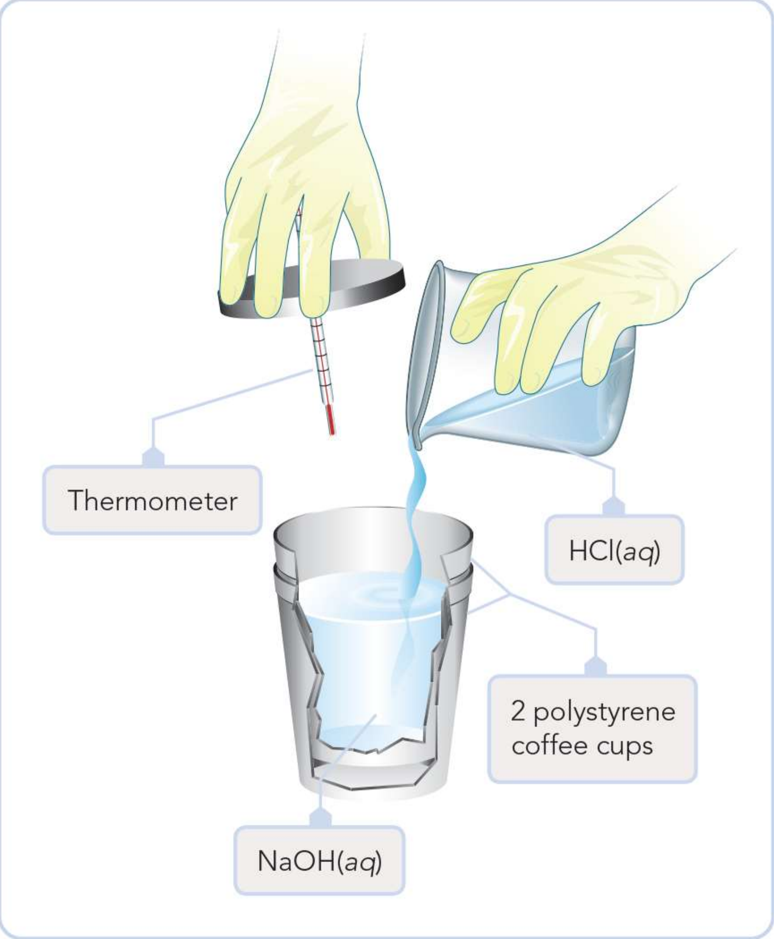
$$\Delta E_{system} = q_{system} = -q_{calorimeter}$$

“bomb calorimeter” measures ΔE



Measuring Heat: “Coffee-cup” Calorimeter

A “coffee-cup calorimeter” is a simple calorimeter used to measure heat at **constant pressure** ($\Delta P=0$, and in general $\Delta V \neq 0$)



$$\Delta H = \Delta E + P\,\Delta V = q + w - w = q$$

So $q = \Delta H$

$$\Delta H_{\text{system}} = q_{\text{system}} = -q_{\text{calorimeter}}$$

“coffee-cup calorimeter” measures ΔH

Practice

0.453 g iron reacts with 27 g of solution containing excess HCl according to the following equation

$$\mathrm{Fe(s) + 2\ HCl(aq) \longrightarrow FeCl_2(aq) + H_2(g)}$$

in a coffee-cup calorimeter. The temperature of the reactants was 25.0°C before the reaction, and rises to 31.4°C after the reaction. The specific heat capacity of the solution is 4.18 J/(g °C). What is ΔH (in kJ) for the reaction as written above?

Reaction = system **solution = surroundings**

$(\Delta H_{rxn}$ for 0.453 g Fe$) = q_{rxn}$

Coefficient of Fe is 1, so we calculate ΔH **for 1 mol Fe**

$$\Delta T = 31.4\ ^\circ\mathrm{C} - 25.0\ ^\circ\mathrm{C} = 6.4\ ^\circ\mathrm{C}$$

$$q_{rxn} = -q_{sol'n} = -m\ c\ \Delta T = -(27\ \mathrm{g})\ [4.18\ \mathrm{J/(g\ ^\circ C)}]\ (6.4\ ^\circ\mathrm{C}) = -7\underline{2}2\ \mathrm{J}$$

$$\Delta H = 1\ \mathrm{mol\ Fe} \times \frac{55.85\ \mathrm{g\ Fe}}{1\ \mathrm{mol\ Fe}} \times \frac{-7\underline{2}2\ \mathrm{J}}{0.453\ \mathrm{g\ Fe}} \times \frac{1\ \mathrm{kJ}}{10^3\ \mathrm{J}} = -89\ \mathrm{kJ}$$

ΔH normally refers to products being at the same T as the reactants we started with, typically 25°C.

Then how come we measure ΔT in a calorimeter? Clearly a change in temperature!

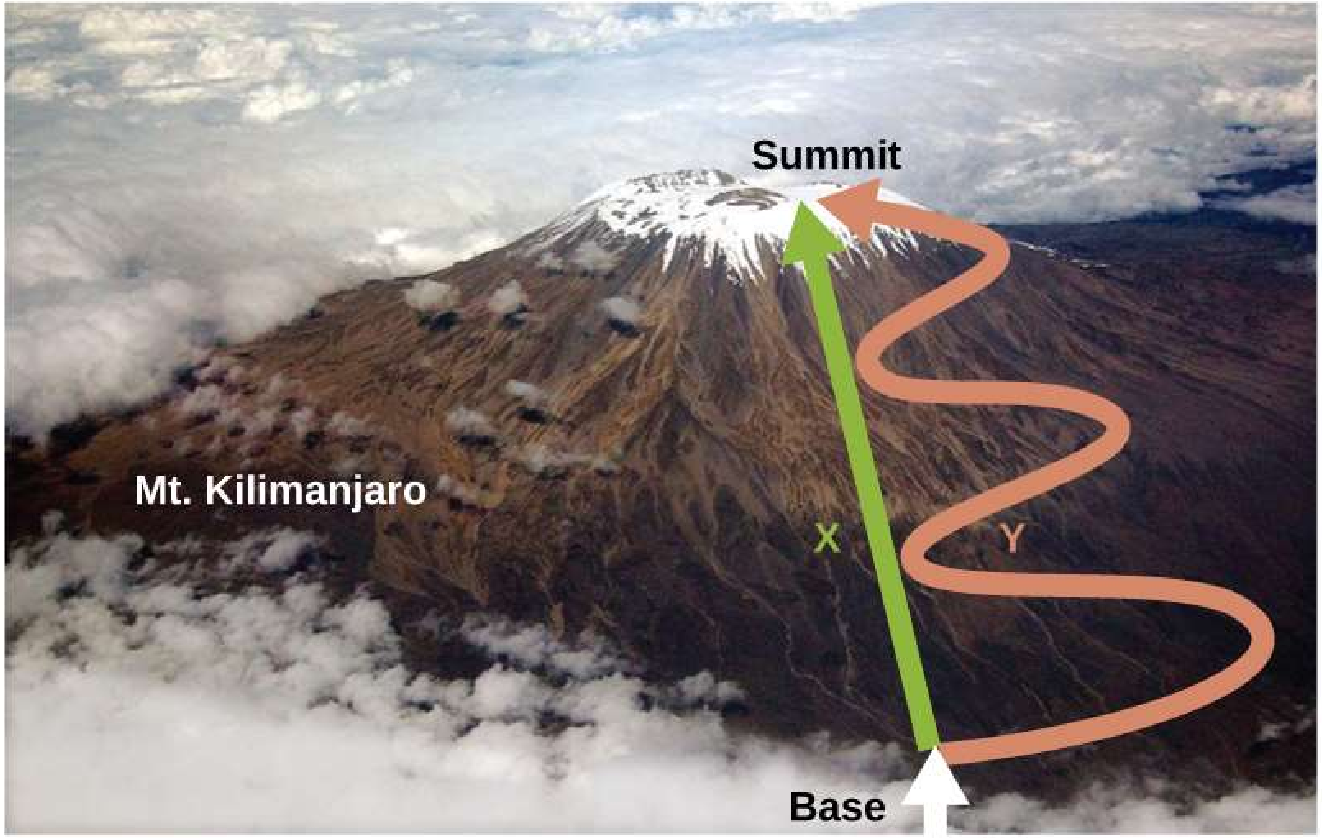
The “system” is the reaction (i.e. the electrons that rearrange, but have no heat capacity themselves)

Everything else, including the atoms that underwent the reaction, form the “surroundings”. We can measure their ΔT to calculate the q for the reaction.

Measuring ΔT relative to 25°C actually gives the q corresponding to the reaction happening at 25°C!

Hess's Law

In going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.



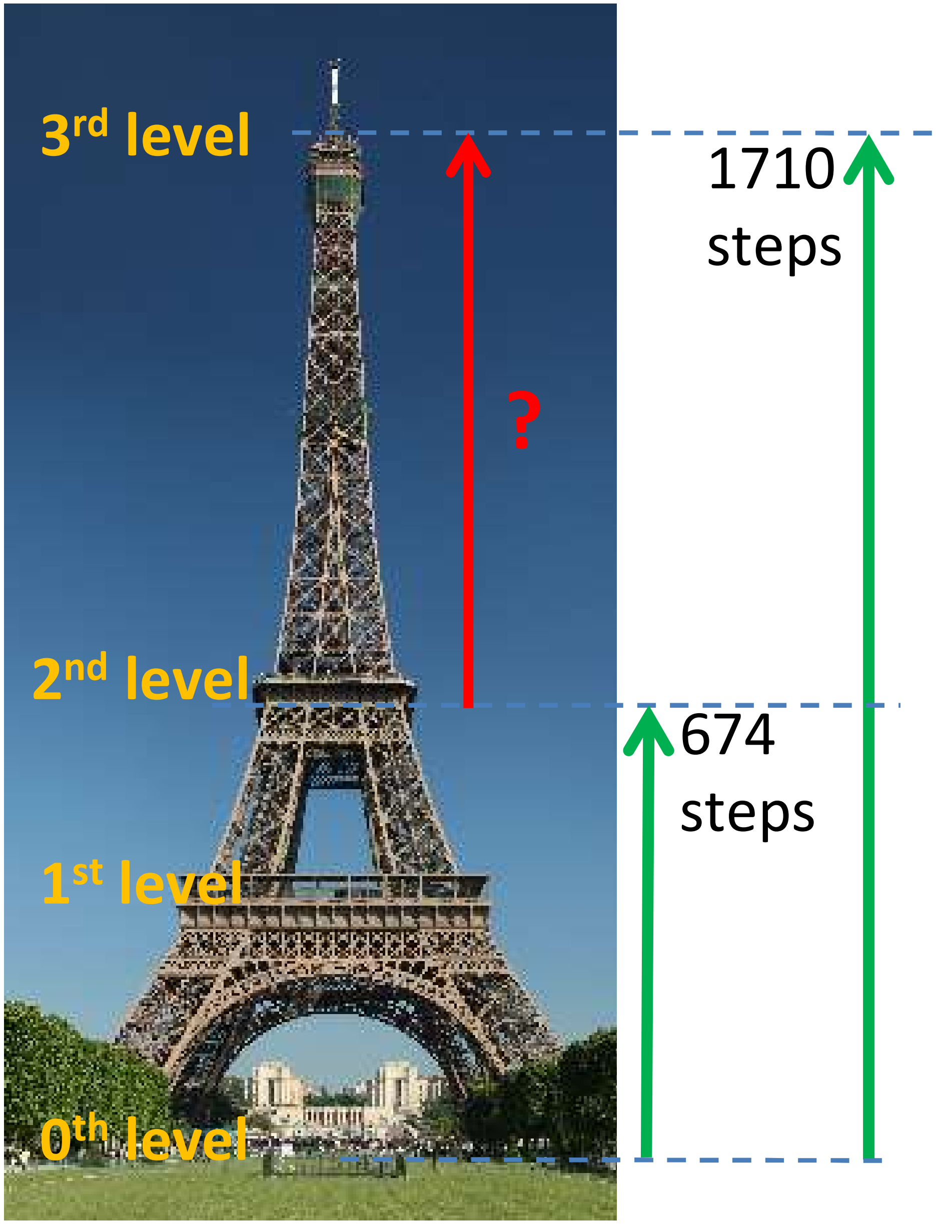
Because enthalpy is a state function

Sometimes it is useful to create a roundabout path for a net reaction. Because:

- We may know the ΔH for the many individual steps, but not the net reaction. By adding up the steps with known ΔH values, we can get the ΔH for the net reaction.

- We may know the ΔH for the net reaction, but by representing with a clever set of steps, we can calculate the ΔH for one of those steps without doing the experiment, if we know the ΔH for all the other steps.

How many stair-steps between 2nd & 3rd level?

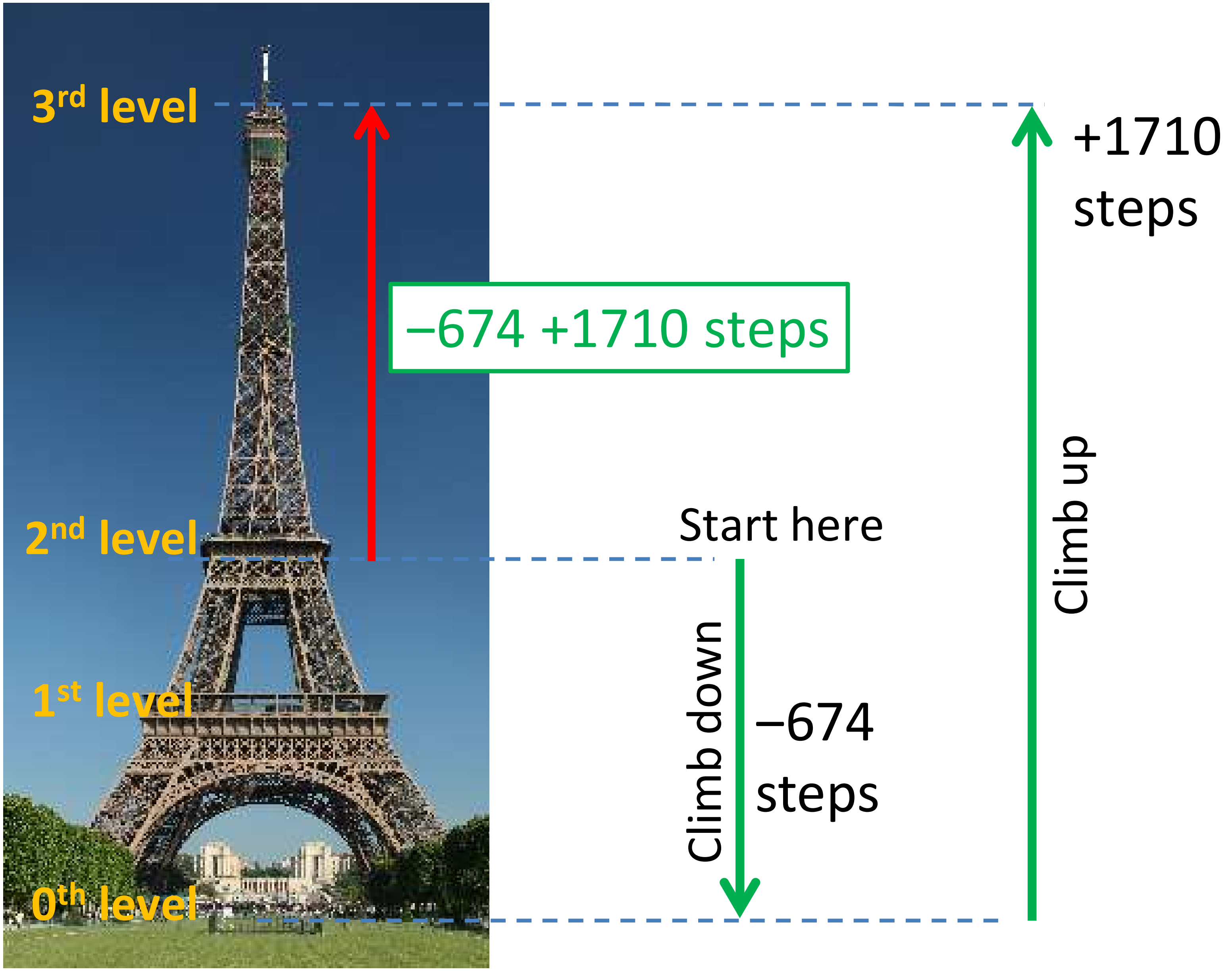


- I am not allowed to climb it.
- I’m told the total number of stair-steps from 0th level to 3rd level, and
- I am allowed to count the number of stair-steps by climbing from 0th to 2nd level

Yes, the answer is 1710 – 674

But we will put it in the form of stepwise processes.

Hess’s Law



−674 +1710 steps

+1710 steps

Climb up

Start here

Climb down

−674 steps

Hess's Law allows us to obtain ΔH of processes otherwise inaccessible to us

- The process or reaction may be difficult or impossible to conduct experimentally
- Or we might simply lack the information at the moment
- By cleverly constructing a series of stepwise processes, we can solve for the unknown ΔH.
- It can also be applied to any other state function, such as ΔE

Applying Hess’s Law

- We look for each reactant and the product in the net reaction.
- We reverse any step that has the substance on the “wrong” side.
- If the substance has a coefficient in the step different from that in the net reaction, we multiply the step by an appropriate factor to make them the same.
- We add the steps, along with their ΔH values.
- Any substances that don’t appear in the net formula will appear on both sides and cancel.

Note that:

- If a reaction is reversed, the sign of Δ*H* is also reversed.

$$A + B \longrightarrow C \qquad \Delta H = X\ \text{kJ}$$

$$C \longrightarrow A + B \qquad \Delta H = -X\ \text{kJ}$$

- The magnitude of Δ*H* is directly proportional to the quantities of reactants and products in a reaction.
  - ➢ If the coefficients in a reaction are multiplied by a factor, the value of Δ*H* is multiplied by the same factor.

$$A + B \longrightarrow C \qquad \Delta H = X\ \text{kJ}$$

$$2A + 2B \longrightarrow 2C \qquad \Delta H = 2X\ \text{kJ}$$

Example

Consider the following data:

Rxn. 1: $NH_3(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$ $\Delta H = 46$ kJ

Rxn. 2: $2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(g)$ $\Delta H = -484$ kJ

and calculate ΔH for the reaction

Net rxn: $2\ N_2(g) + 6\ H_2O(g) \longrightarrow 3\ O_2(g) + 4\ NH_3(g)$

N_2 needs to be on the left (but is on the right in rxn 1)

Reverse rxn. 1 (also puts NH_3 on the right side; good)

H_2O needs to be on the left (but is on the right in rxn 2)

Reverse rxn. 2 (also puts O_2 on the right side; good)

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$ $\Delta H = -46$ kJ

$2H_2O(g) \longrightarrow 2H_2(g) + O_2(g)$ $\Delta H = +484$ kJ

Example (cont.)

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g) \qquad \Delta H = -46\ kJ\ ]$

$2H_2O(g) \longrightarrow 2H_2(g) + O_2(g) \qquad \Delta H = +484\ kJ\ ]$

$2\ N_2(g) + 6\ H_2O(g) \longrightarrow 3\ O_2(g) + 4\ NH_3(g)$ (net reaction)

We have a coefficient of ½ for $N_2(g)$, but we need it to be 2

We have a coefficient of 2 for $H_2O(g)$, but we need it to be 6

4 x ½ gives 2 for $N_2(g)$

3 x 2 gives 6 for $H_2O\ (g)$

4 x [$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g) \qquad \Delta H = -46\ kJ$ **]**

3 x [$2H_2O(g) \longrightarrow 2H_2(g) + O_2(g) \qquad \Delta H = +484\ kJ$ **]**

Example (cont.)

Adding up the properly rearranged reaction equations:

$$\begin{array}{lll} & 2\,\mathrm{N_2(g)} + \cancel{6\,\mathrm{H_2(g)}} \longrightarrow 4\,\mathrm{NH_3(g)} & \Delta H = -184\text{ kJ} \\ + & 6\,\mathrm{H_2O(g)} \longrightarrow \cancel{6\,\mathrm{H_2(g)}} + 3\,\mathrm{O_2(g)} & \Delta H = +1452\text{ kJ} \\ \hline & \mathbf{2\,N_2(g) + 6\,H_2O(g) \longrightarrow 3\,O_2(g) + 4\,NH_3(g)} & \boxed{\Delta H = \mathbf{+1268\text{ kJ}}} \end{array}$$

A practical approach to applying Hess's Law in simpler cases:

One at a time, find each substance in the desired reaction in one of the proposed steps. If the the substance occurs in more than one step, skip that substance.

If the substance occurs on the wrong side of the step (it's a reactant in the step while the net reaction needs it to be a product, or vice versa), reverse the sign of the ΔH for that step. If not, keep the current sign.

Multiply the step's ΔH by a factor that would make the coefficient of the substance considered equal to its coefficient in the net reaction: (coeff. in net rxn)/(coeff. in the step rxn)

Repeat for all substances in the net reaction.

Add the ΔH values obtained from steps to get ΔH for the desired reaction.

We can break any reaction into standard steps

Every substance is made of elements.

A **"formation reaction"** can be defined for every substance, going from elements to the substance.

- ➢ Also the reverse reaction

<u>We now break down the reaction into those steps:</u>

- Each reactant decomposes to its elements
  - ➢ reversed formation reactions
- The elements combine to form the products
  - ➢ formation reactions

For example:

Formation reaction of water

$$H_2(g) + \frac{1}{2}\,O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -286\ \text{kJ}$$

Used as a step if $H_2O(l)$ is one of the **products** in the reaction considered

- ➢ Because it appears as the product

Reverse of the formation reaction of water

$$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}\,O_2(g) \qquad \Delta H = \ \ 286\ \text{kJ}$$

Used as a step if $H_2O(l)$ is one of the **reactants** in the reaction considered

- ➢ Because it appears as the reactant

For the idea to be useful, we need access to extensive tables that give data on most chemicals. So we need to use the Standard Enthalpy of Formation, ΔH_f°, that goes with an unambiguously defined “formation reaction” using elements at their “standard states”.

$$\Delta H_f^{\circ} \xleftarrow{\qquad\qquad} \text{“standard”}$$

We will look at the proper definition of “formation reaction”, and “standard state” after we apply the concept first.

Using ΔH_f° values to calculate ΔH° for a reaction

The reaction $6\ NO(g) + 4\ NH_3(g) \longrightarrow 5\ N_2(g) + 6\ H_2O(l)$

Can be split up into a bunch of **formation reactions**:

- In the normal, forward direction for products
- In the reverse direction for reactants

$$6\ NO(g) + 4\ NH_3(g) \longrightarrow 5\ N_2(g) + 6\ H_2O(l)$$

$$\left(N_2(g) \longrightarrow N_2(g)\right) \qquad \Delta H^\circ = \Delta H_{f}^\circ{}_{,N_2(g)} \Big) \times 5$$

$$\left(H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)\right) \qquad \Delta H^\circ = \Delta H_{f}^\circ{}_{,H_2O(g)} \Big) \times 6$$

$$\left(NO(g) \longrightarrow \tfrac{1}{2}O_2 + N_2(g)\right) \qquad \Delta H^\circ = -\Delta H_{f}^\circ{}_{,NO(g)} \Big) \times 6$$

$$\left(NH_3(g) \longrightarrow \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2(g)\right) \qquad \Delta H^\circ = -\Delta H_{f}^\circ{}_{,NH_3(g)} \Big) \times 4$$

Add up the ΔH° for the steps ΔH°_{rxn}

$$\Delta H^\circ_{rxn} = 5\Delta H_{f}^\circ{}_{,N_2(g)} + 6\Delta H_{f}^\circ{}_{,H_2O(l)} - 6\Delta H_{f}^\circ{}_{,NO(g)} - 4\Delta H_{f}^\circ{}_{,NH_3(g)}$$

Using ΔH_f° values to calculate ΔH° for a reaction

Here is the more familiar setup for Hess’s Law, in case the previous slide was too unfamiliar.

$$6\ NO(g) + 4\ NH_3(g) \longrightarrow 5\ N_2(g) + 6\ H_2O(l)$$

$$N_2(g) \longrightarrow N_2(g) \qquad \Delta H^\circ = \Delta H^\circ_{f\ ,N_2(g)} \qquad \times 5$$

$$H_2(g) + \tfrac{1}{2}\,O_2 \longrightarrow H_2O(l) \qquad \Delta H^\circ = \Delta H^\circ_{f\ ,H_2O(g)} \qquad \times 6$$

$$NO(g) \longrightarrow \tfrac{1}{2}\,O_2 + N_2(g) \qquad \Delta H^\circ = -\Delta H^\circ_{f\ ,NO(g)} \qquad \times 6$$

$$NH_3(g) \longrightarrow \tfrac{1}{2}\,N_2 + \tfrac{3}{2}\,H_2(g) \qquad \Delta H^\circ = -\Delta H^\circ_{f\ ,NH_3(g)} \qquad \times 4$$

$$6\ NO(g) + 4\ NH_3(g) \longrightarrow 5\ N_2(g) + 6\ H_2O(l) \qquad \Delta H^\circ_{rxn}$$

(Add up the ΔH° for the steps)

$$\Delta H^\circ_{rxn} = 5\Delta H^\circ_{f\ ,N_2(g)} + 6\Delta H^\circ_{f\ ,H_2O(l)} - 6\Delta H^\circ_{f\ ,NO(g)} - 4\Delta H^\circ_{f\ ,NH_3(g)}$$

Hess's Law

$$\Delta H^\circ_{rxn} = 5\Delta H^\circ_{f,N_2(g)} + 6\Delta H^\circ_{f,H_2O(l)} - 6\Delta H^\circ_{f,NO(g)} - 4\Delta H^\circ_{f,NH_3(g)}$$

Factor out the negative sign:

$$\Delta H^\circ_{rxn} = \underbrace{[5\Delta H^\circ_{f,N_2(g)} + 6\Delta H^\circ_{f,H_2O(l)}]}_{\boxed{\begin{array}{l}\text{Sum of } \Delta H_f^\circ \text{ values}\\ \text{multiplied by coefficients;}\\ \text{for } \underline{\text{products}}\end{array}}} - \underbrace{[6\Delta H^\circ_{f,NO(g)} + 4\Delta H^\circ_{f,NH_3(g)}]}_{\boxed{\begin{array}{l}\text{Sum of } \Delta H_f^\circ \text{ values}\\ \text{multiplied by coefficients;}\\ \text{for } \underline{\text{reactants}}\end{array}}}$$

The general formula to find ΔH°_{rxn} from enthalpies of formation:

$$\boxed{\Delta H^\circ_{rxn} = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants})}$$

$\sum$ means "summation"

n_p : coefficient of each product

n_r : coefficient of each reactant

Practice

Calculate ΔH° for the following reaction:

$$2\ \mathrm{Na}(s) + 2\ \mathrm{H_2O}(l) \longrightarrow 2\ \mathrm{NaOH}(aq) + \mathrm{H_2}(g)$$

Given the following information:

	ΔH_f° (kJ/mol)
$\mathrm{Na}(s)$	0
$\mathrm{H_2O}(l)$	–286
$\mathrm{NaOH}(aq)$	–470
$\mathrm{H_2}(g)$	0

$$\Delta H^\circ = [(2)\Delta H_f^\circ{}_{,\mathrm{NaOH(aq)}} + (1)\Delta H_f^\circ{}_{,\mathrm{H_2(g)}}] - [(2)\Delta H_f^\circ{}_{,\mathrm{Na(s)}} + (2)\Delta H_f^\circ{}_{,\mathrm{H_2O\ (l)}}]$$

$$= \mathbf{-368\ kJ}$$

What exactly is a “formation reaction”?

- The only reactants are elements
- The only product is the substance formed
- The coefficient of the product is an implied 1

Then:

ΔH of the formation reaction is ΔH_f for the substance formed

The elements on the reactant side of a "formation reaction" must be in their standard state.

For example:

Oxygen exists as a diatomic gas in its standard state, not as individual atoms.

$C(\text{graphite}) + 2O(g) \longrightarrow CO_2(g)$ Not a formation reaction

Bromine exists as Br_2 molecules in the liquid (not gas) state under the conditions of the standard state.

$Na(s) + \frac{1}{2}Br_2(\mathbf{g}) \longrightarrow NaBr(s)$ Not a formation reaction

Standard states of elements:

The form in which they exist at 1 bar and 25°C

- $H_2(g)$, $N_2(g)$, $O_2(g)$, $Cl_2(g)$, $F_2(g)$, $Br_2(l)$, $I_2(s)$, $Hg(l)$
- Most stable solid crystal for solid elements, but we usually simply write (s); the rest is implied.
- When we write C(s), it's understood that it's C(graphite) and not C(diamond)!

$C(s) + O_2(g) \longrightarrow CO_2(g)$ Formation reaction

$CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$ **Not** a formation reaction

Not an element

$\frac{1}{8} S_8(s) + O_2(g) \longrightarrow SO_2(g)$ Formation reaction

$S_8(s) + 8\,O_2(g) \longrightarrow 8\,SO_2(g)$ **Not** a formation reaction

Coefficient of product > 1

$O_2(g) + O(g) \longrightarrow O_3(g)$ **Not** a formation reaction

Element not in its standard state

ΔH_f° for an element (in its standard state) is zero

$$\text{C}(\textit{graphite}) \longrightarrow \text{C}(\textit{graphite}) \qquad \Delta H_f^\circ = 0$$

$$\text{O}_2(g) \longrightarrow \text{O}_2(g) \qquad \Delta H_f^\circ = 0$$

However, ΔH_f° of an element in a <u>non-standard state</u> would **<u>not</u>** be zero

$$\tfrac{1}{2}\text{O}_2(g) \longrightarrow \text{O}(g) \qquad \Delta H_f^\circ = 248 \text{ kJ}$$

$$\tfrac{1}{2}\text{I}_2(s) \longrightarrow \text{I}(g) \qquad \Delta H_f^\circ = 60.2 \text{ kJ}$$

A note about the proper use of units

ΔH in a thermochemical equation should have a unit of energy, rather than energy/mol

- When written next to a reaction
- When called “enthalpy of reaction”

It is proper to use energy/mol only when ΔH is listed as “Enthalpy of formation of XYZ”

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l) \quad \Delta H = -286\ \text{kJ}$

but

Enthalpy of formation of $H_2O(l) = \Delta H_f = -286\ \text{kJ/mol}$