

Lecture 11

thermodynamics

We'll be dealing with the *energy* of
chemical reactions

How do you keep track of it?
Where does it come from?



Energy

- Can come from a variety of sources:
 - Light (photochemistry)
 - Electricity (electrochemistry)
 - Heat (thermochemistry)



What is Energy?

- The ability to:
 - do work
 - transfer heat.
- Work: Energy used to cause an object that has mass to move.
- Heat: Energy used to cause the temperature of an object to rise.

Work

- Energy used to move an object over some distance.
- $w = F \cdot d$,
- w = work,
- F = force
- d = distance over which the force is exerted.

Note units:

$$F = ma, \text{ mass}(\text{distance}/\text{s}^2)$$

$$W = F(d) = \text{mass}(\text{distance}^2/\text{s}^2)$$

$$= mv^2$$



(a)



(b)

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Heat



- Energy can also be transferred as heat.
- Heat flows from warmer objects to cooler objects.

Kinetic Energy

Energy an object possesses by virtue of its motion.

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



Potential Energy

Energy an object possesses by virtue of its position or chemical composition.

More potential E

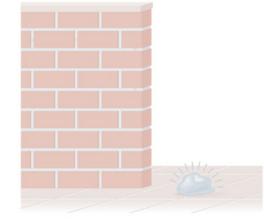
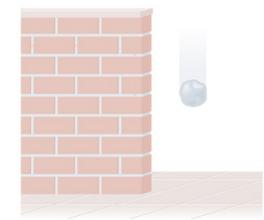
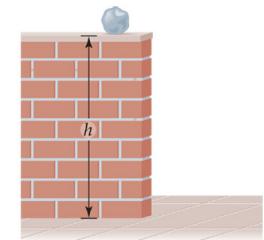


Less P.E. as bike goes down.



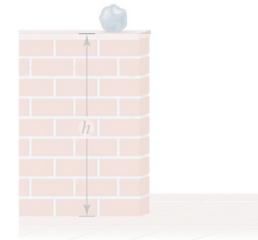
Transferal of Energy

- a) Add P.E. to a ball by lifting it to the top of the wall

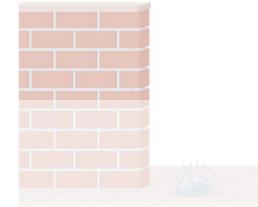
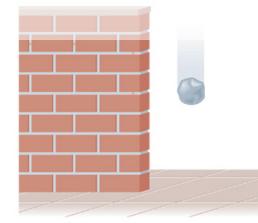


Transferal of Energy

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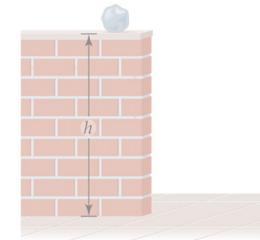


- b) As the ball falls,
P.E -----> K. E. ($1/2mv^2$)



Transferal of Energy

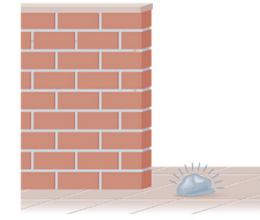
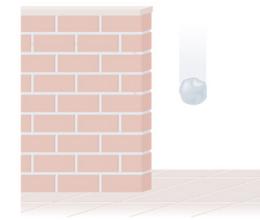
- a) Add P.E. to a ball by lifting it to the top of the wall



- b) As the ball falls,
 $P.E \rightarrow K.E. (1/2mv^2)$

Ball hits ground, K.E. =0, but E has to go somewhere. So

1. Ball gets squashed
2. Heat comes out.



Energy accounting

- We must identify where different types of energy go.
- Therefore, we must identify the *places*.

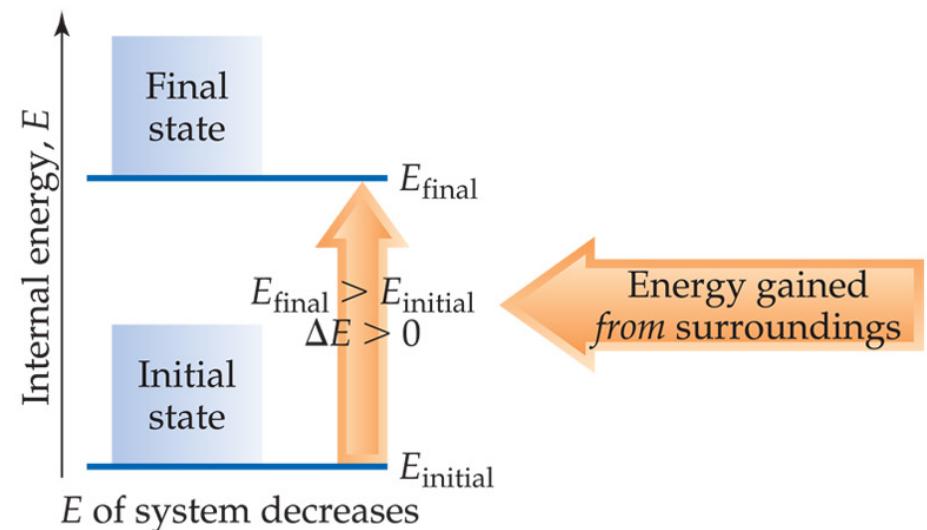
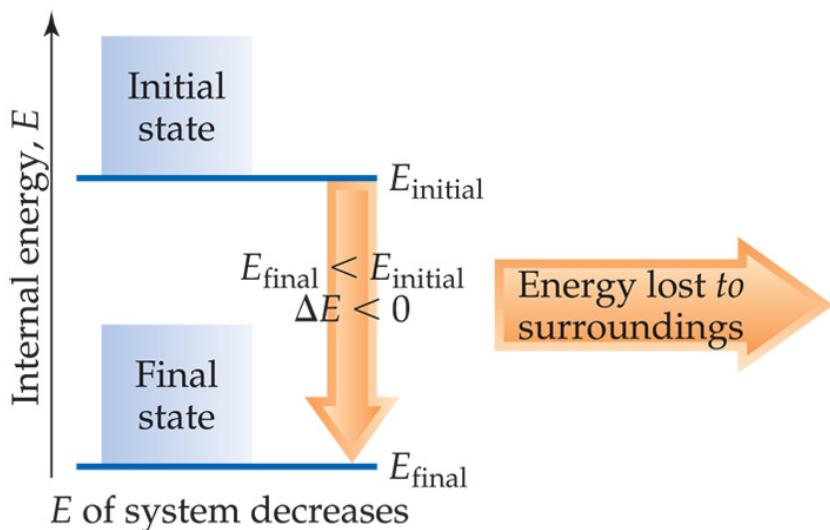
System and Surroundings



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

First Law of Thermodynamics

- Energy is conserved.
- In other words, the total energy of the universe is a constant; $\Delta E_{\text{System}} = -\Delta E_{\text{surroundings}}$



Internal Energy

The internal energy of a system is the sum of all kinetic and potential energies of all components of the system; we call it E .

$$E_{\text{internal, total}} = E_{\text{KE}} + E_{\text{PE}} + E_{\text{electrons}} + E_{\text{nuclei}} + \dots$$

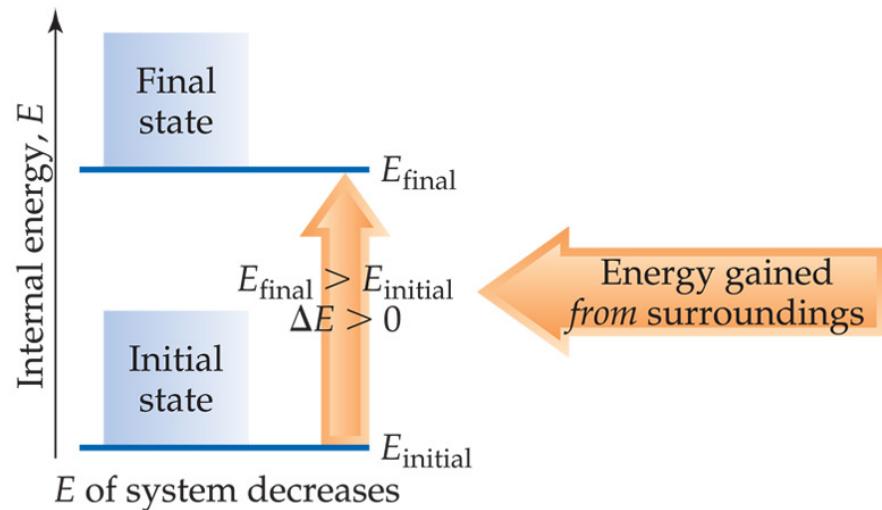
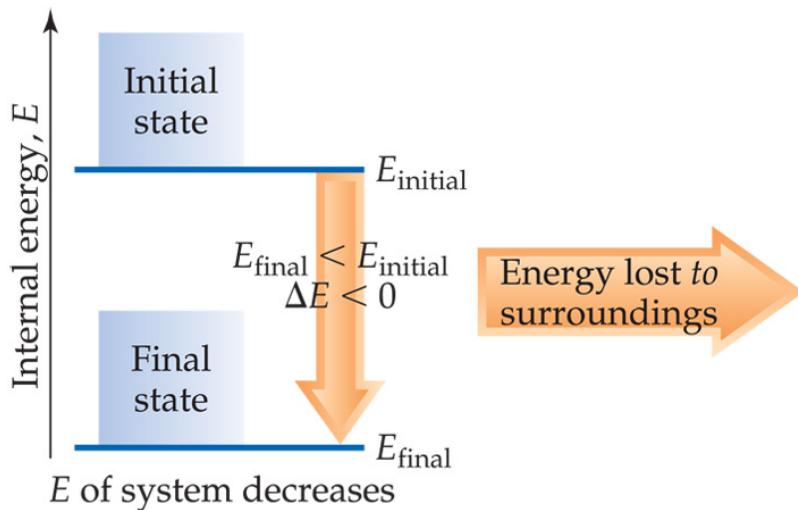
Almost impossible to calculate total internal energy

Instead we always look at the **change** in energy (ΔE).

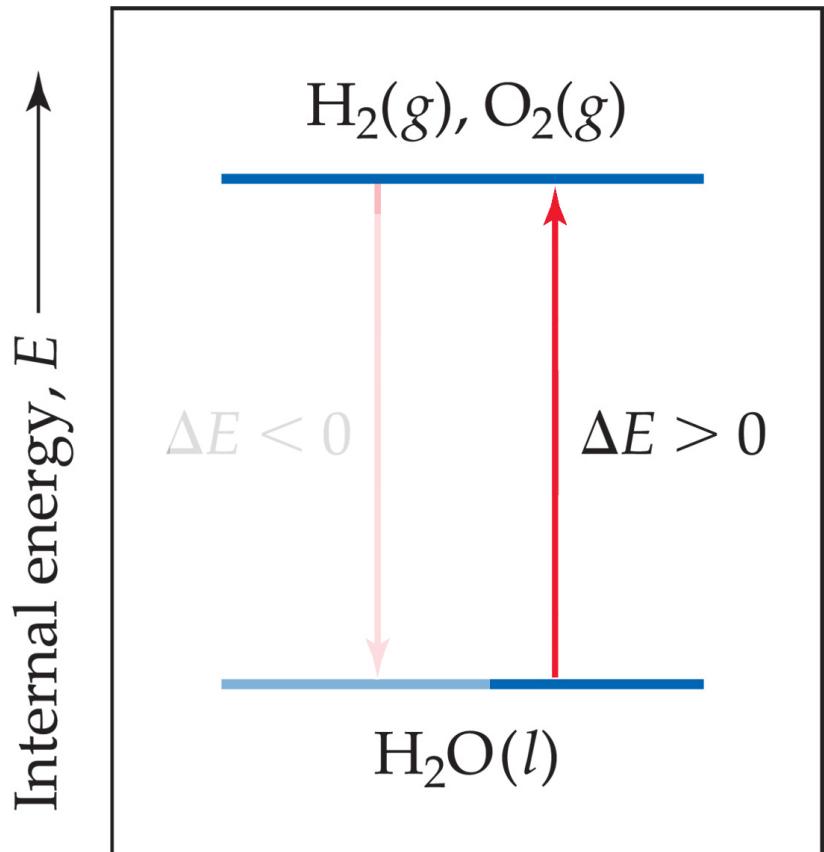
Internal Energy

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

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

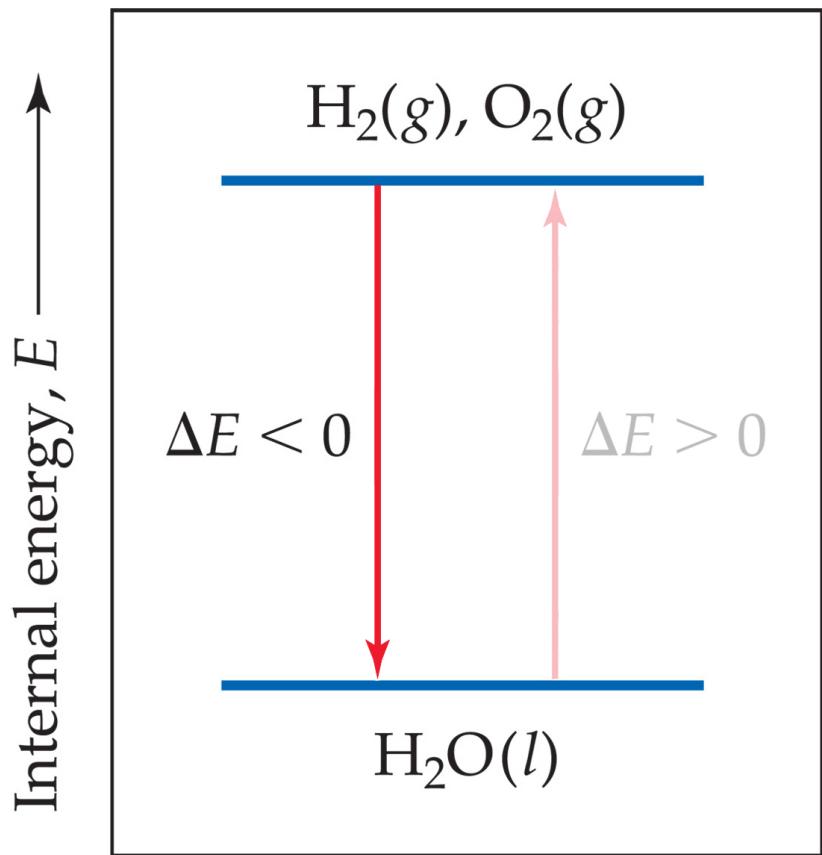


Changes in Internal Energy



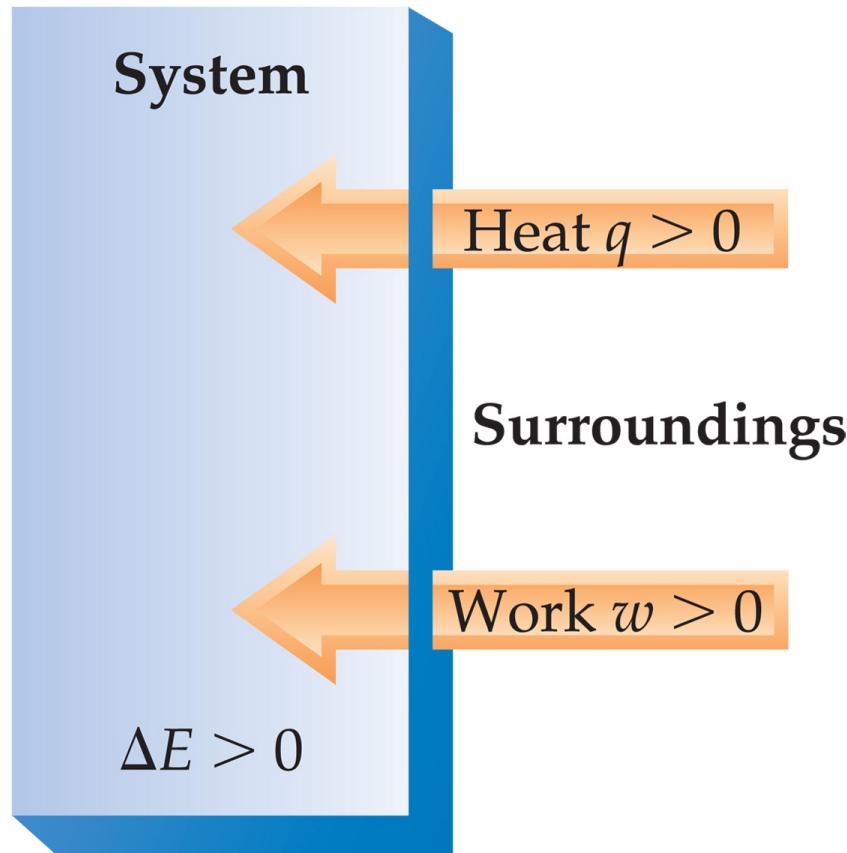
- If $\Delta E > 0$, $E_{\text{final}} > E_{\text{initial}}$
 - Therefore, the system *absorbed* energy from the surroundings.

Changes in Internal Energy



- If $\Delta E < 0$, $E_{\text{final}} < E_{\text{initial}}$
 - Therefore, the system *released* energy to the surroundings.

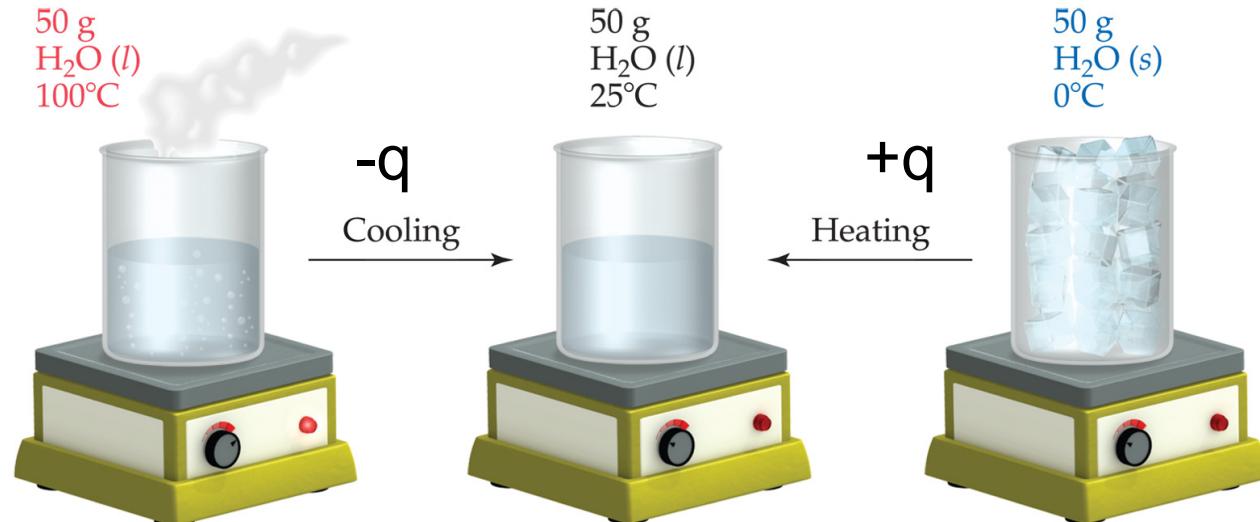
Changes in Internal Energy



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

ΔE , q , w , and Their Signs

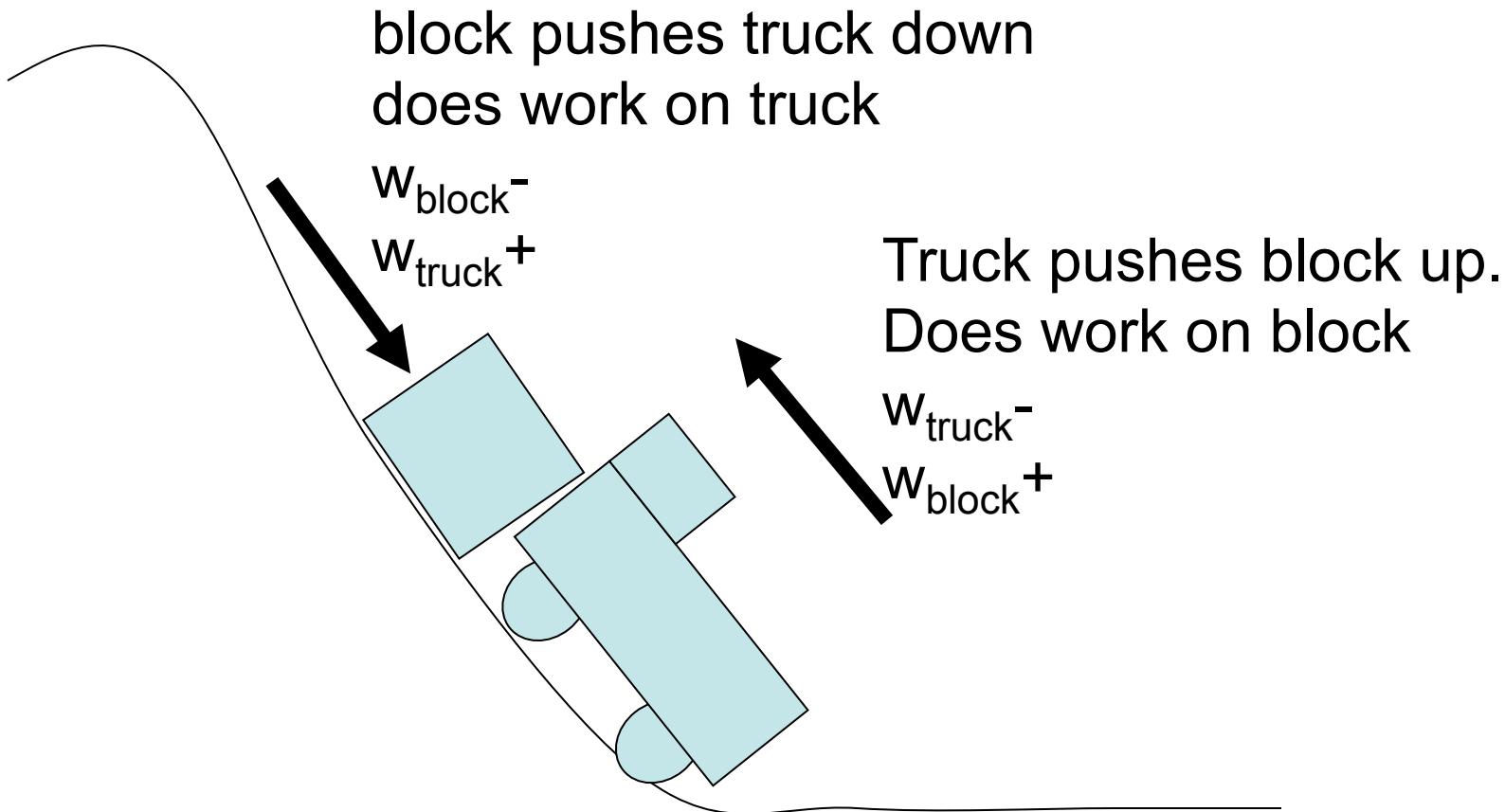
For q	+ means system <i>gains</i> heat	- means system <i>loses</i> heat
For w	+ means work done <i>on</i> system	- means work done <i>by</i> system
For ΔE	+ means <i>net gain</i> of energy by system	- means <i>net loss</i> of energy by system



Surroundings
suck heat out of
water.

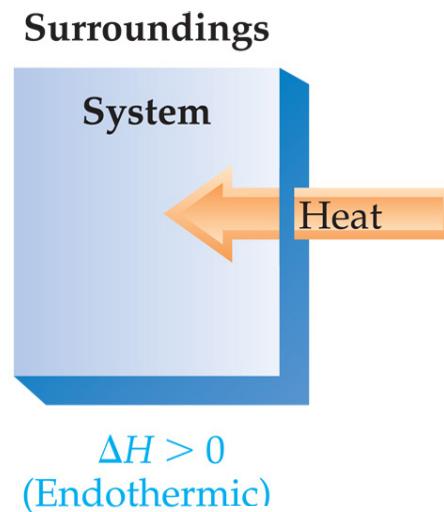
hot plate adds
heat to water

Sign of work



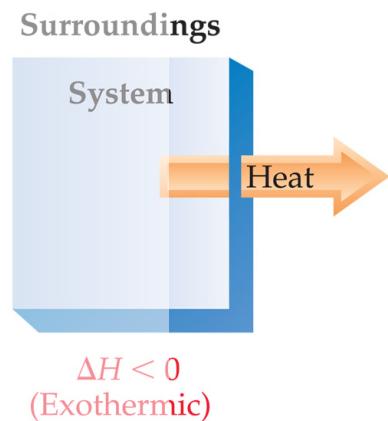
Exchange of Heat between System and Surroundings

- When heat is absorbed by the system from the surroundings, the process is **endothermic**.



Exchange of Heat between System and Surroundings

- When heat is absorbed by the system from the surroundings, the process is **endothermic**.
- When heat is released by the system to the surroundings, the process is **exothermic**.



Units of Energy

- The SI unit of energy is the joule (J).

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

- An older, non-SI unit is still in widespread use: The calorie (cal).

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

Energy has units of (mass)(velocity)²

Remember kinetic energy was $1/2mv^2$

Energy, specific heat and temperature change

Calorimetry

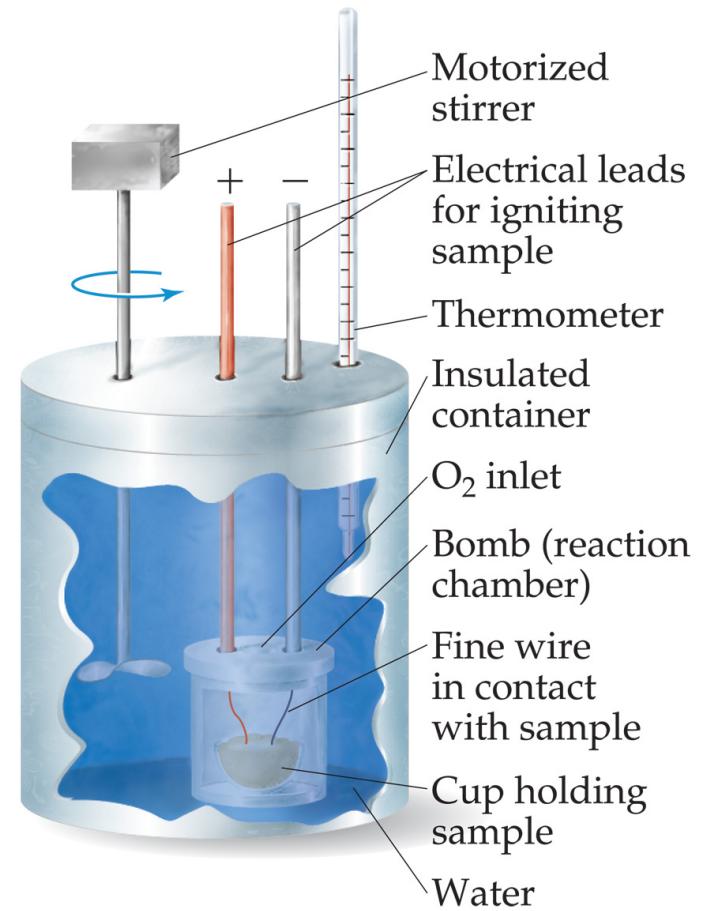
How is heat measured? Calorimetry

Color = heat

metry = measure

A calorimeter is a device for measuring heat transfer

How does this work?



Heat Capacity and Specific Heat

- Heat capacity
- The amount of energy required to raise the temperature of an object by 1 K (1°C) is its heat capacity.
- We define specific heat capacity (or simply specific heat) as the amount of energy required to raise the temperature of 1 g of a *specific substance* by 1 K.

Heat Capacity and Specific Heat

Specific heat = $\frac{\text{heat transferred}}{\text{mass} \times \text{temperature change}}$

$$s = \frac{q}{m \Delta T}$$

$$\frac{\text{Heat change}(q)}{\text{J}} = \frac{\text{specific heat}(s)}{\text{JK}^{-1}\text{g}^{-1}} * \frac{\text{mass}(m)}{\text{g}} * \frac{\text{temp. change}(T)}{\text{K}}$$

$$sm\Delta T = q$$

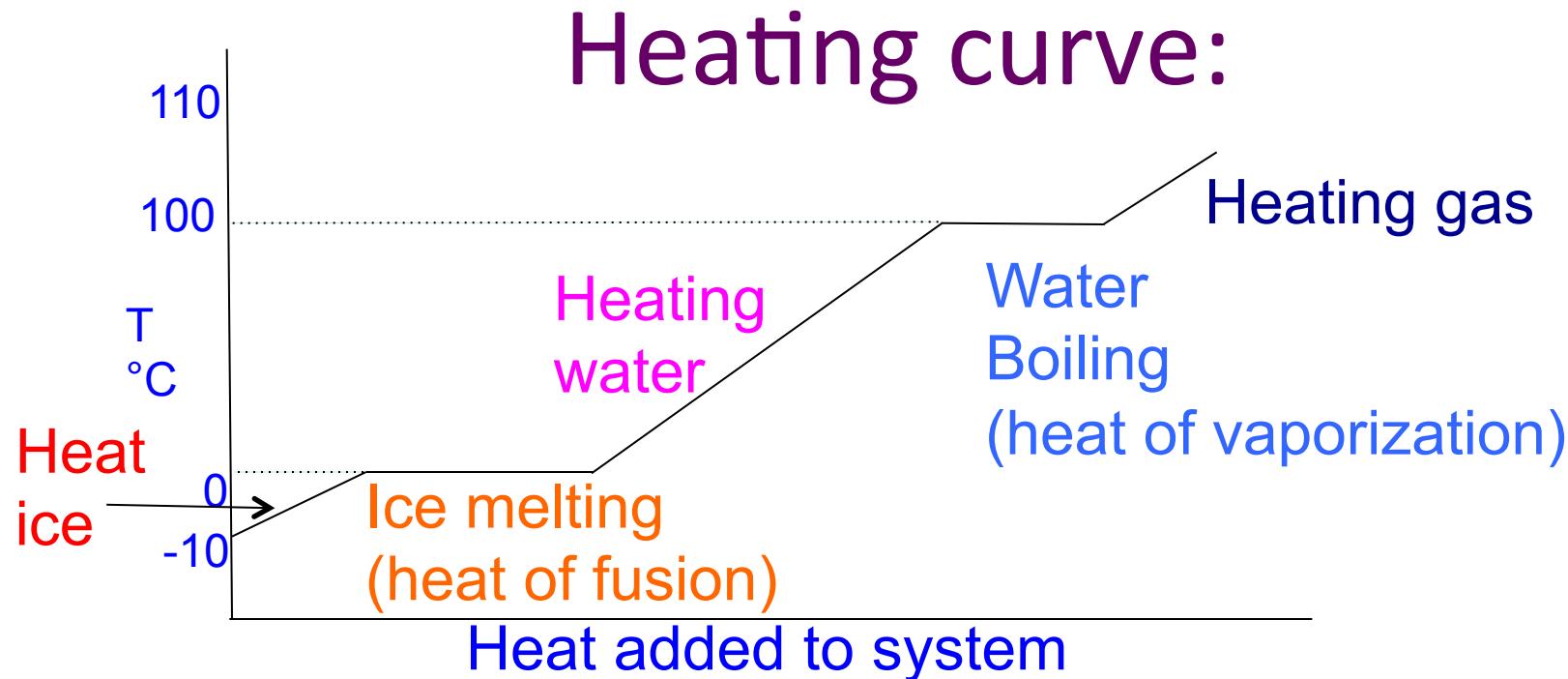
Examples

- How much heat is required to raise the temperature of 50 g of water from 20° C to 45 °C? Sp. Heat = $4.184 \text{ JK}^{-1}\text{g}^{-1}$
- $Q = sm(T_{\text{final}} - T_{\text{init}})$
- $Q = 4.184 \text{ JK}^{-1}\text{g}^{-1} * 50 \text{ g} * (45 - 20 \text{ }^{\circ}\text{C}) = 5230 \text{ J}$
- How much will the temperature rise if 1000 J of energy are used to heat a 10g block of copper ($s_{\text{Cu}}=0.385 \text{ JK}^{-1}\text{g}^{-1}$)
- $1000 \text{ J} = 0.385 \text{ JK}^{-1}\text{g}^{-1} * 10\text{g} * \Delta T$
- $\Delta T=260 \text{ }^{\circ}\text{C}$

Lecture 12

Energy and changes of state

- Change of state:
- Solid → liquid liquid → solid
- Liquid → gas gas → liquid
- A change of state will occur at a constant T.
melting ice will stay at 0°C until all the
ice is melted. You can't heat ice to higher T
than 0 °C at 1 atm.



Example calculate heat used in above (10g). Five stages:

$$\text{Heat ice: } 2.1 \text{ JK}^{-1}\text{g}^{-1} * 10\text{g} * 10^{\circ}\text{C} = 210 \text{ J} \quad (\text{sm} \Delta T, s_{\text{ice}} = 2.1 \text{ JK}^{-1}\text{g}^{-1})$$

$$\text{Melt ice: } 333 \text{ J g}^{-1} * 10\text{g} = 3330 \text{ J} \quad (\text{g(heat of fusion}_{\text{wat}}\text{)})$$

$$\text{Heat water: } 4.185 * 10\text{g} * 100^{\circ}\text{C} = 4184 \text{ J}$$

$$\text{Vaporize water: } 2260 \text{ J g}^{-1} * 10\text{g} = 22600 \text{ J} \quad (\text{g(heat of vap}_{\text{wat}}\text{)})$$

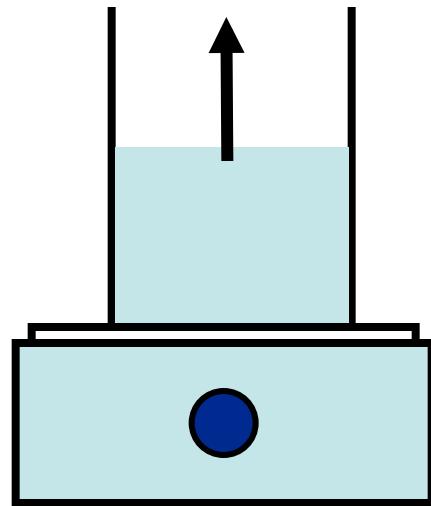
$$\text{Heat steam: } 2.0 \text{ JK}^{-1}\text{g}^{-1} * 10\text{g}(10^{\circ}\text{C}) = 200 \text{ J} \quad (s_{\text{steam}} = 2.0 \text{ JK}^{-1}\text{g}^{-1})$$



Work and heat

- 2 possibilities:
 - 1 The system does not expand. Then, there can be no force over a distance ($F \cdot D$) and no work.
 - $\Delta E = q + w = q_v$ constant volume.
 - 2. The system expands and work is done.

Work



process in an open container (chemical reaction in a beaker)

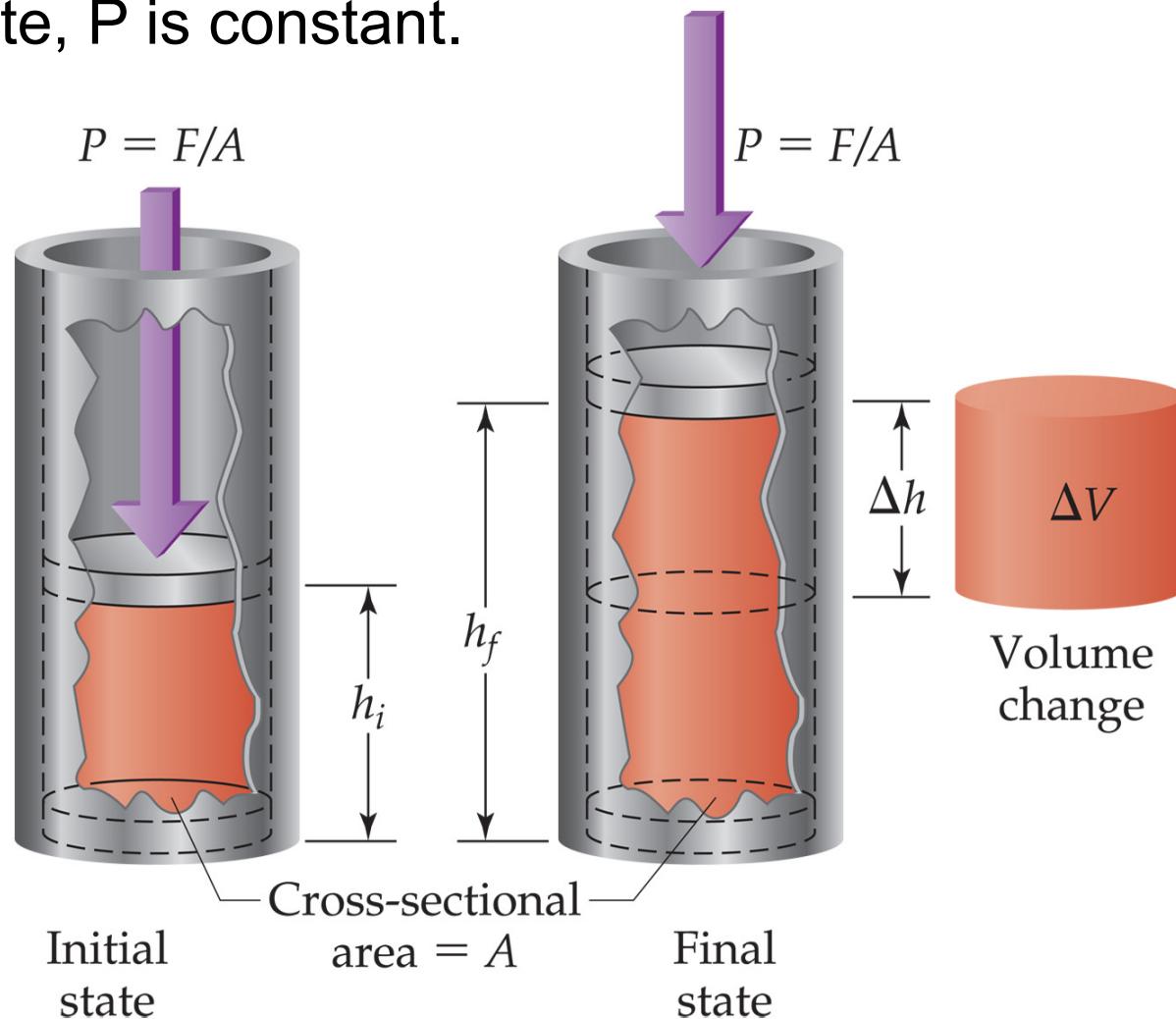
w? (can there be any work)?

Yes, evolving gases could push on the surroundings.

Thermochemistry



Catch the work, do the same process in a cylinder.
Note, P is constant.



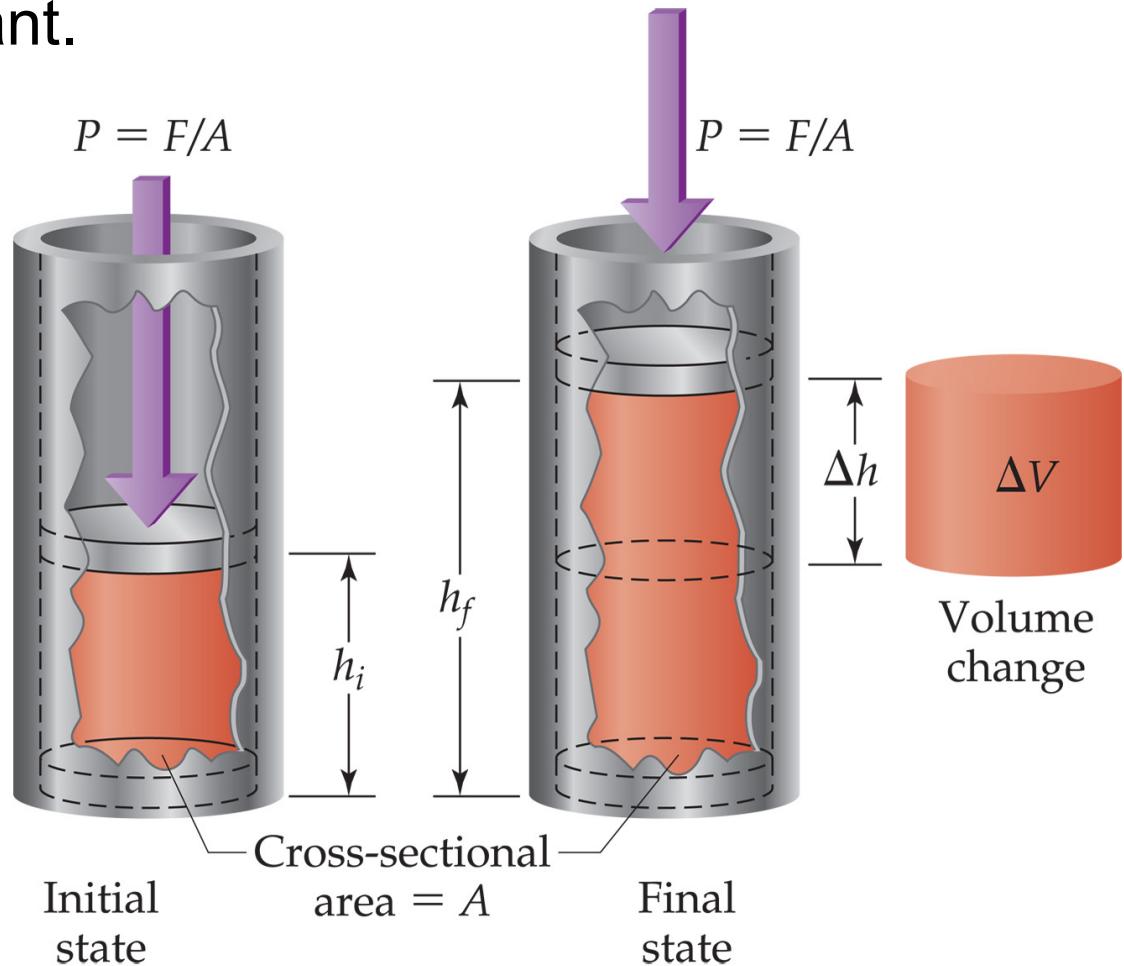
Process evolves gas, pushes on piston, work done on piston

Catch the work, do the same process in a cylinder
Note: P is constant.

$$w = F \cdot d, \quad F = P \cdot A, \quad d = \Delta h$$

$$w = -P \cdot A \Delta h = -P \Delta V$$

Negative because an **increase** in Volume means that the system is doing work on the surroundings.



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

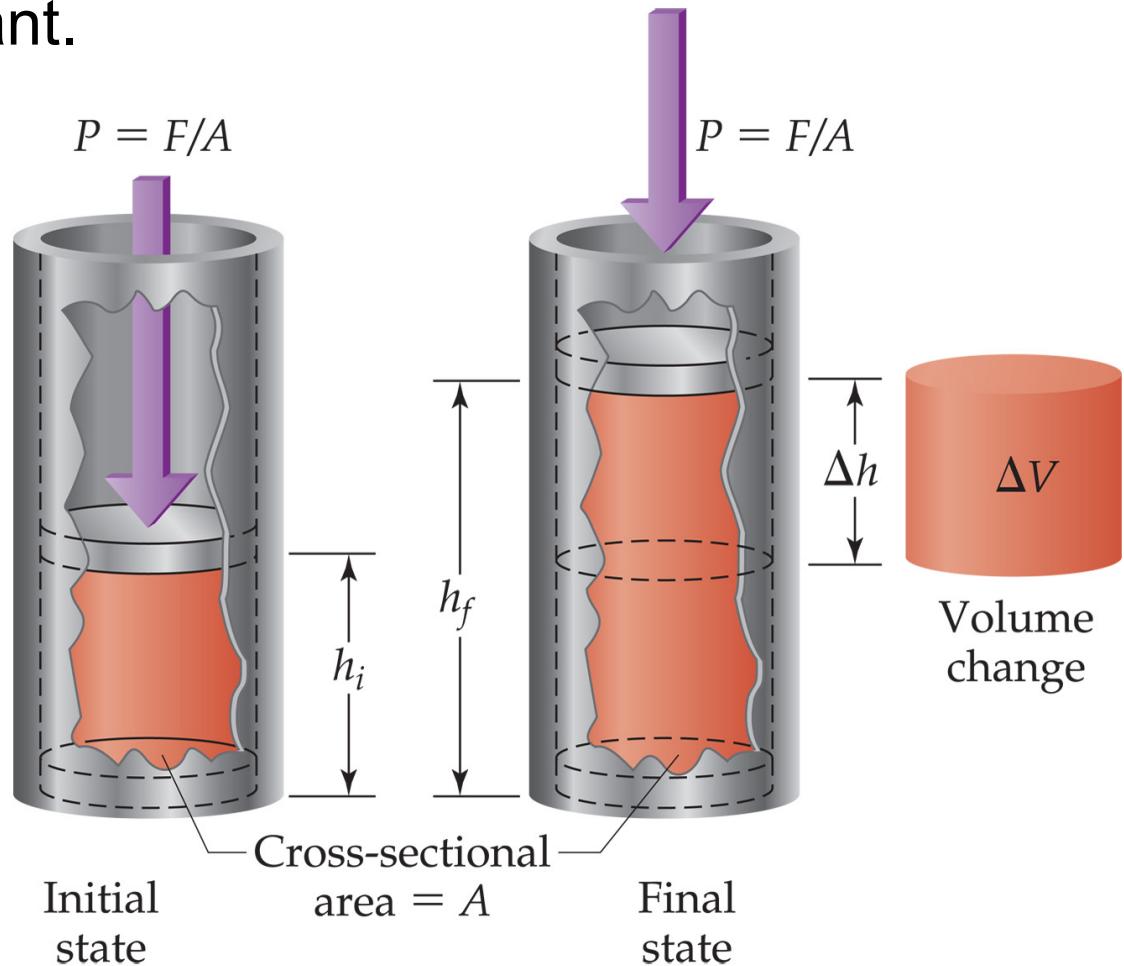
$$q_P = \Delta E + P \Delta V$$

Catch the work, do the same process in a cylinder
Note: P is constant.

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

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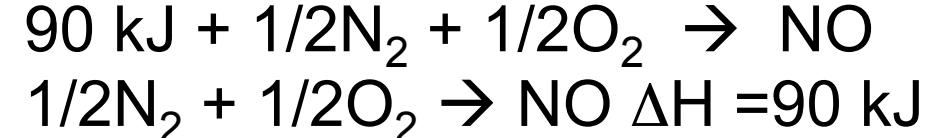
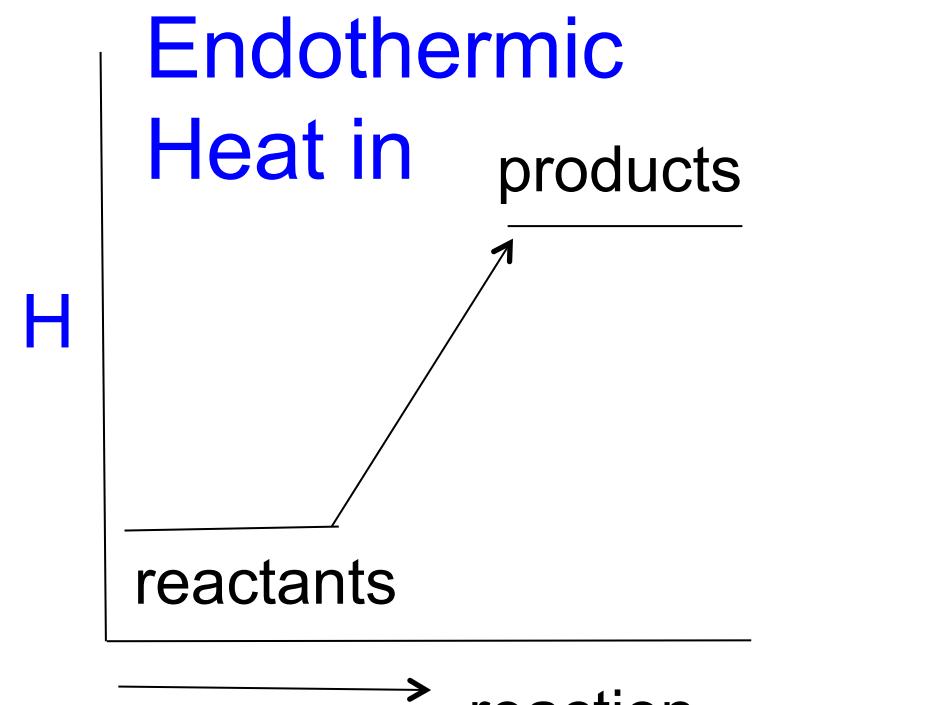
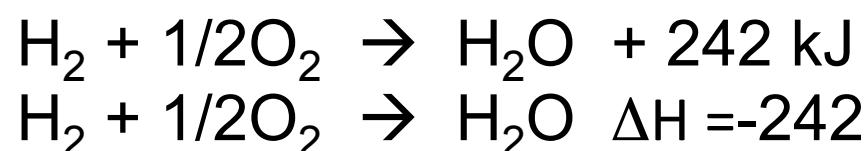
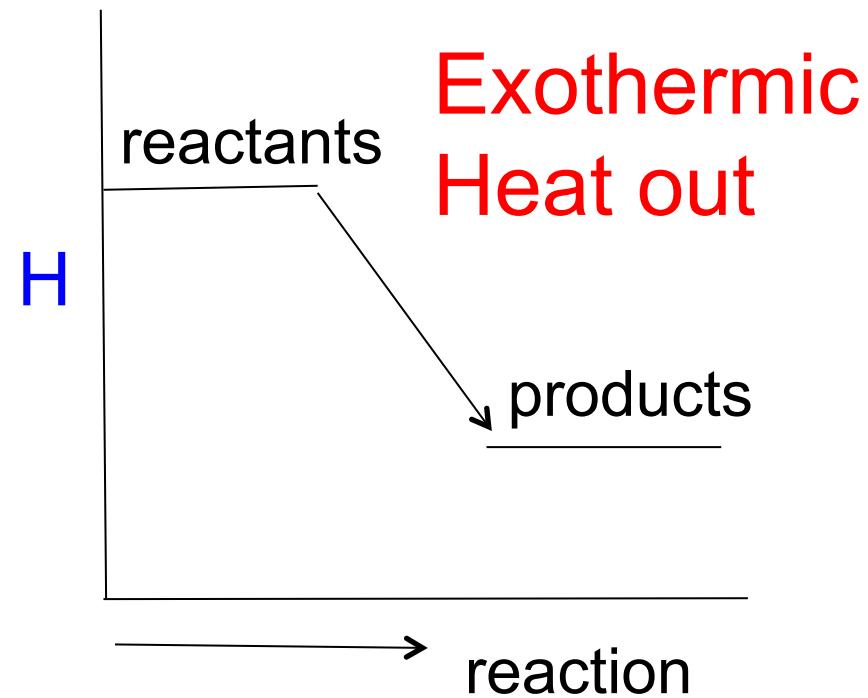
Enthalpy

- $\Delta E = q + w = q - P\Delta V$
- $q_p = \Delta E + P\Delta V$
- A new function is defined, Enthalpy (H)
- $H = E + PV$
- $\Delta H = \Delta E + P\Delta V = q_p$

Enthalpy means “heat inside” or “heat content”

Change in enthalpy is the heat gained or lost by a system *at constant pressure*. The difference between ΔH and ΔE is small for chemical reactions that do not involve a change in gas volume (solids and liquids don’t have much change in volume).

The case of chemical reactions

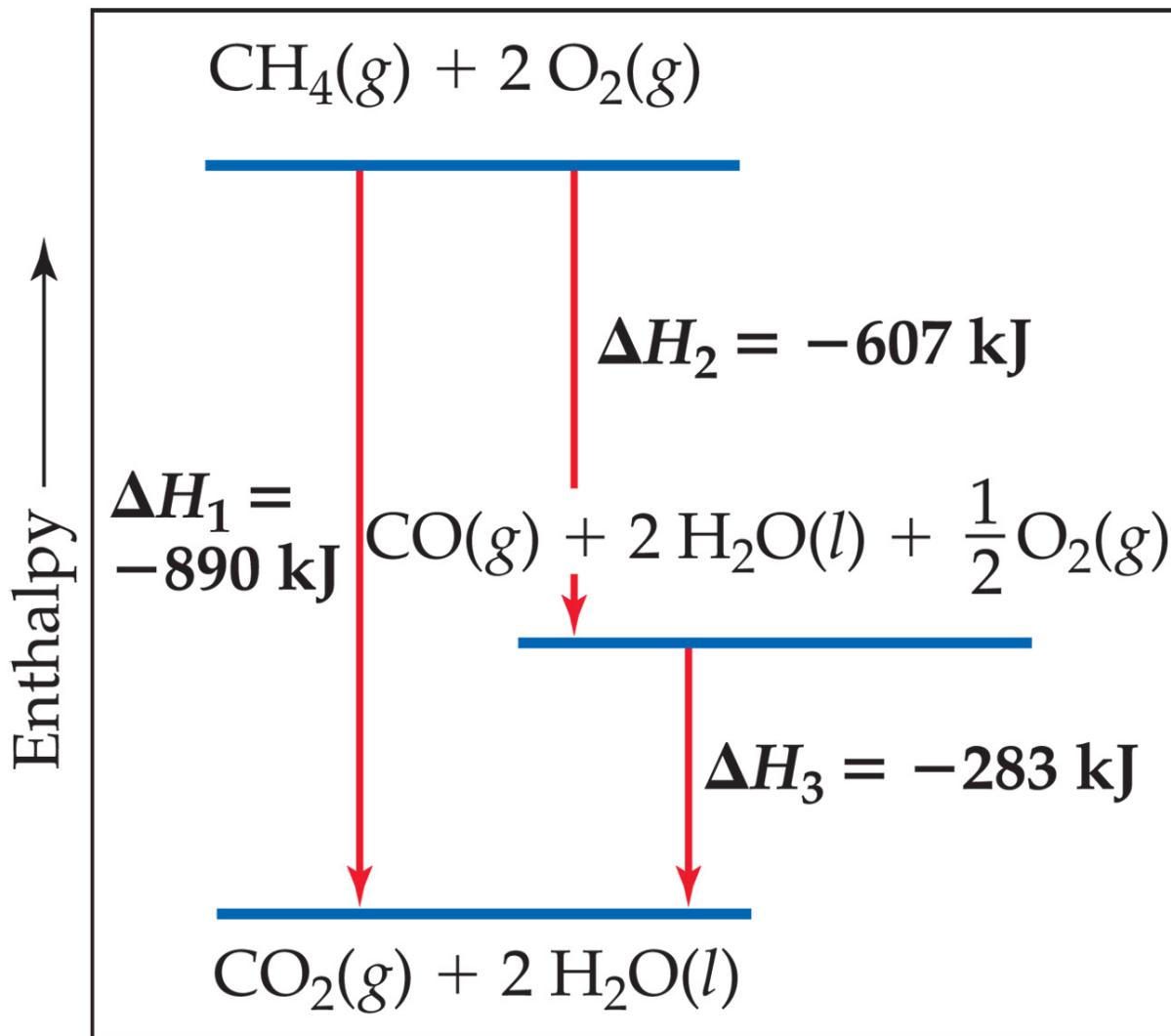


Hess's law

Hess's Law

- ΔH is known for many reactions.
- measuring ΔH can be a pain
- Can we estimate ΔH using ΔH values for other reactions?

Hess's Law

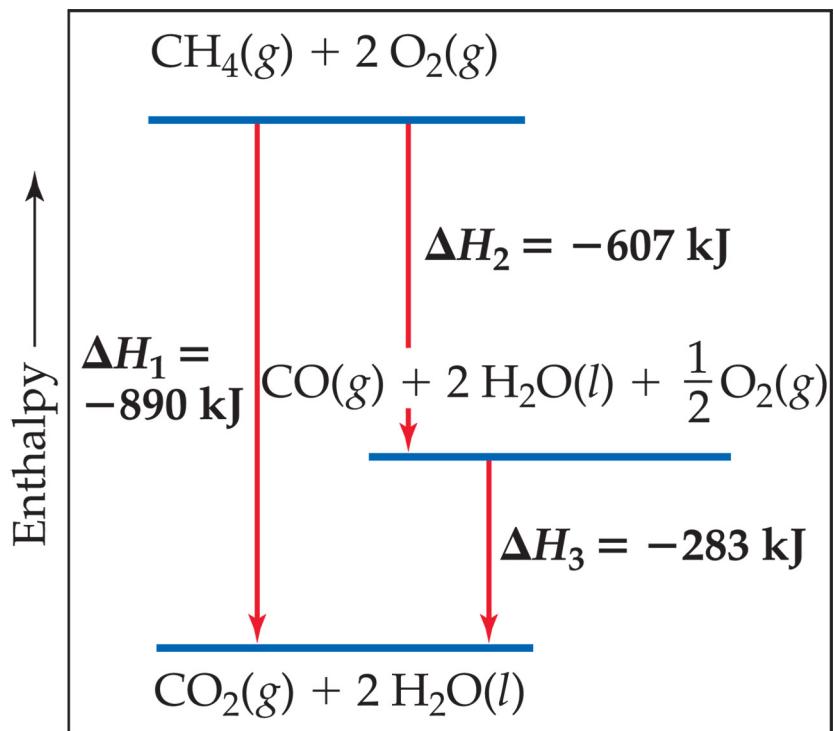


Yes!

Hess's law: states that:

ΔH for the overall reaction will be equal to the sum of the enthalpy changes for the individual steps.

Hess's Law



Why?

Because ΔH is a state function,
and is pathway independent.

Only depends on initial state of
the reactants and the final
state of the products.

Hess's law, an example

- Given the enthalpy changes for the following reactions:
- $\text{C(s)} + \text{O}_2 \rightarrow \text{CO(g)} + 1/2\text{O}_2(\text{g}) \quad \Delta H = -110 \text{ kJ}$
- $\text{C(s)} + \text{O}_2 \rightarrow \text{CO}_2(\text{g}) \quad \Delta H = -394 \text{ kJ}$
- What is ΔH for the following reaction:
- $\text{CO(g)} + 1/2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$

Hess's law, an example

- Given the enthalpy changes for the following reactions:
- $\text{C(s)} + \text{O}_2 \rightarrow \text{CO(g)} + 1/2\text{O}_2(\text{g}) \Delta H = -110 \text{ kJ}$
- $\text{C(s)} + \text{O}_2 \rightarrow \text{CO}_2(\text{g}) \Delta H = -394 \text{ kJ}$
- What is ΔH for the following reaction:
- $\text{CO(g)} + 1/2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
- 1. reverse 1st reaction to get reactants:
- $\text{CO(g)} + 1/2\text{O}_2(\text{g}) \rightarrow \text{C(s)} + \text{O}_2 \Delta H = 110 \text{ kJ}$

Hess's law, an example



What is ΔH for the following reaction:



1. reverse 1st reaction to get reactants:



2. Add 2nd reaction:



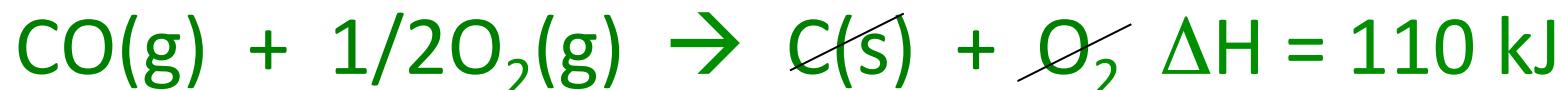
Hess's law, an example



What is ΔH for the following reaction:



1. reverse 1st reaction to get reactants:



2. Add 2nd reaction:



Hess' s law, example:

- Given:
- $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g}) \quad \Delta H = 180.7 \text{ kJ}$
- $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g}) \quad \Delta H = -113.1 \text{ kJ}$
- $2\text{N}_2\text{O}(\text{g}) \longrightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \quad \Delta H = -163.2 \text{ kJ}$
- use Hess' s law to calculate ΔH for the reaction:
- $\text{N}_2\text{O}(\text{g}) + \text{NO}_2(\text{g}) \longrightarrow 3\text{NO}(\text{g})$

Hess's law, example:

- Given:
 - $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g}) \quad \Delta H = 180.7 \text{ kJ}$
 - $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g}) \quad \Delta H = -113.1 \text{ kJ}$
 - $2\text{N}_2\text{O}(\text{g}) \longrightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \quad \Delta H = -163.2 \text{ kJ}$
- use Hess's law to calculate ΔH for the reaction:
- $\text{N}_2\text{O}(\text{g}) + \text{NO}_2(\text{g}) \longrightarrow 3\text{NO}(\text{g})$

- $\text{N}_2\text{O}(\text{g}) \longrightarrow \cancel{\text{N}_2(\text{g})} + \cancel{1/2\text{O}_2(\text{g})} \quad \Delta H = -163.2/2 = -81.6 \text{ kJ}$
- $\text{NO}_2(\text{g}) \longrightarrow \text{NO}(\text{g}) + \cancel{\text{1/2O}_2(\text{g})} \quad \Delta H = 113.1 \text{ kJ}/2 = 56.6 \text{ kJ}$
- $\cancel{\text{N}_2(\text{g})} + \cancel{\text{O}_2(\text{g})} \longrightarrow 2\text{NO}(\text{g}) \quad \Delta H = 180.7 \text{ kJ}$

- $\text{N}_2\text{O}(\text{g}) + \text{NO}_2(\text{g}) \longrightarrow 3\text{NO}(\text{g}) \quad \Delta H = 155.7 \text{ kJ}$



Enthalpies of Formation

An enthalpy of formation, ΔH_f , is defined as the ΔH for the reaction in which a compound is made from its constituent elements in their elemental forms.

That's what we did for the Thermite reaction:



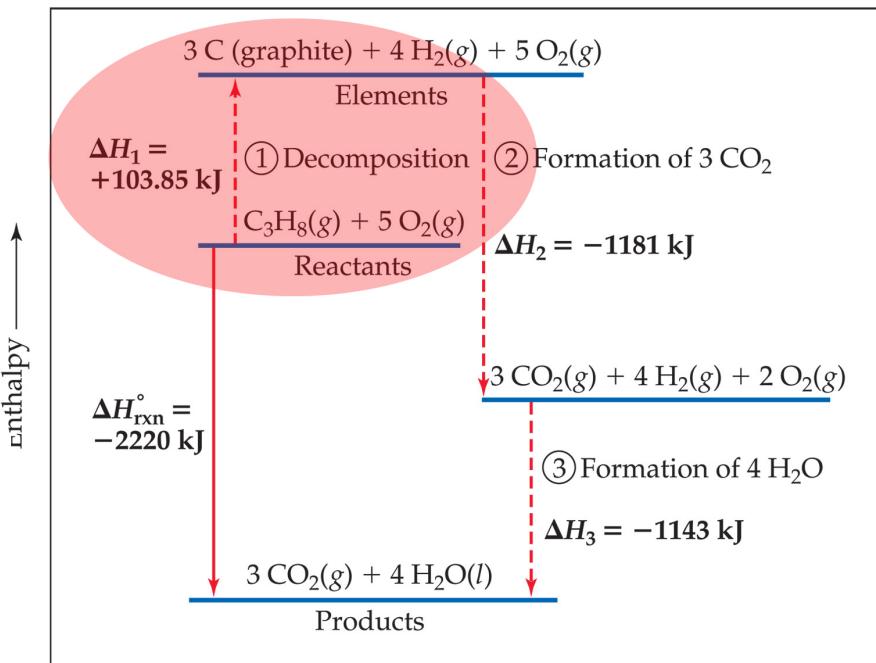
•What is the heat of reaction given:



Calculation of ΔH



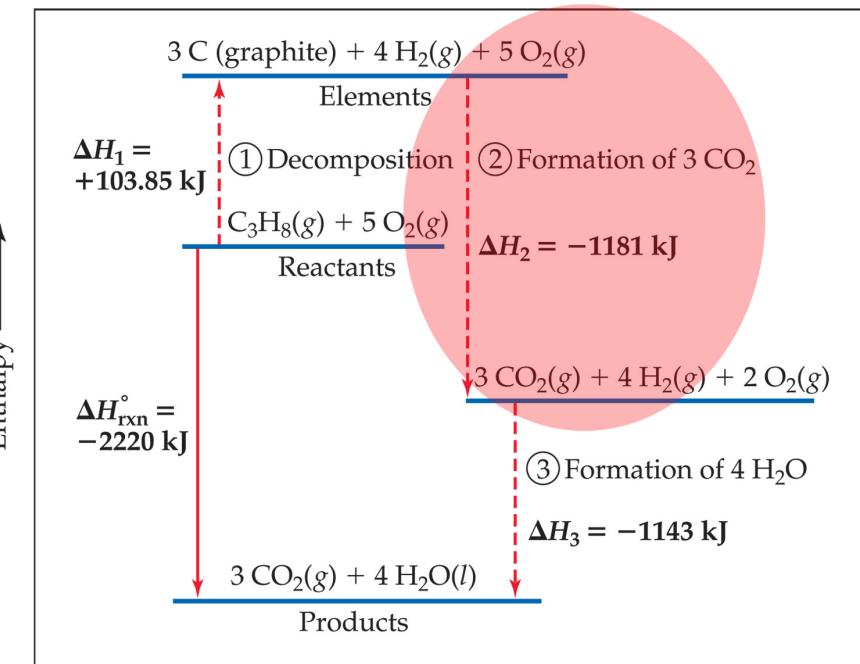
- Imagine this as occurring in 3 steps:



Calculation of ΔH



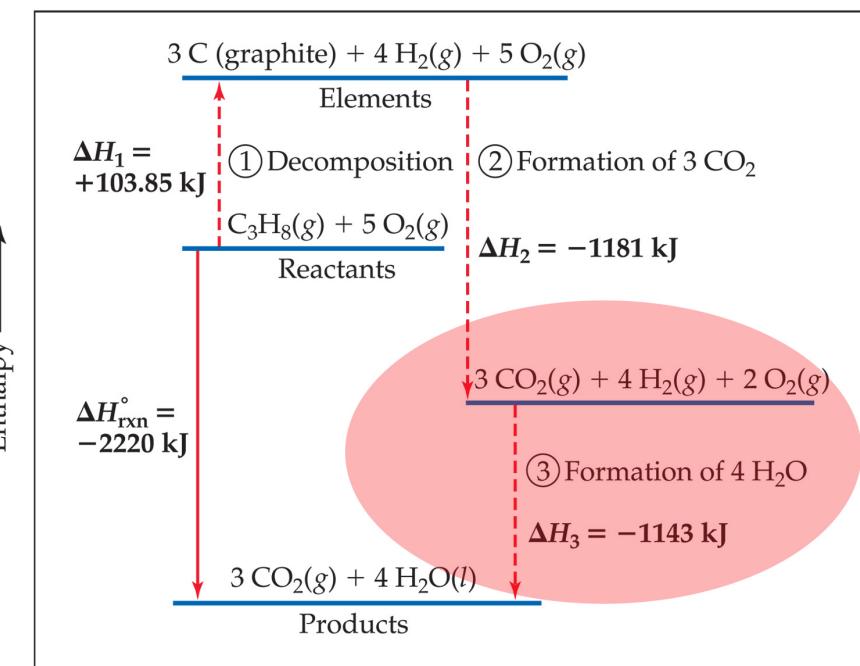
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Calculation of ΔH



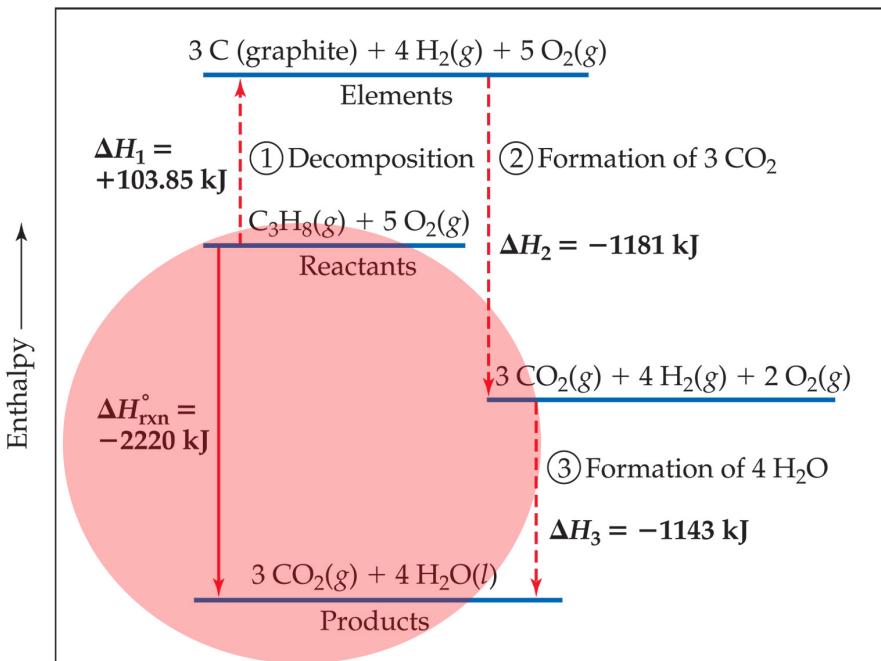
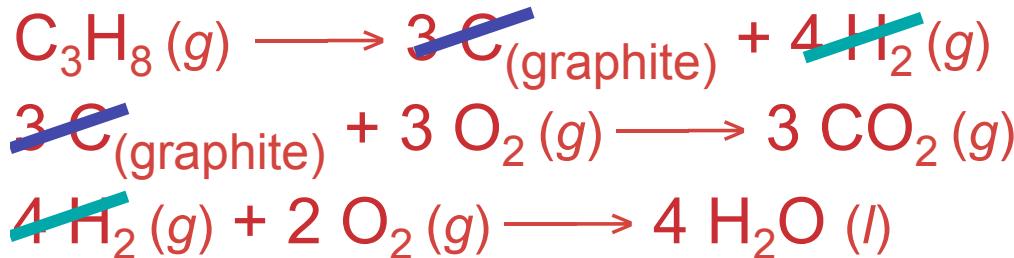
- Imagine this as occurring in 3 steps:



Calculation of ΔH



- The sum of these equations is:



Make each reactant or product from its elements
This is called the heat of formation of a compound



Calculation of ΔH

We can use Hess's law in this way:

$$\Delta H = \sum n \Delta H_f^{\circ}(\text{products}) - \sum m \Delta H_f^{\circ}(\text{reactants})$$

where n and m are the stoichiometric coefficients.

Standard Enthalpies of Formation

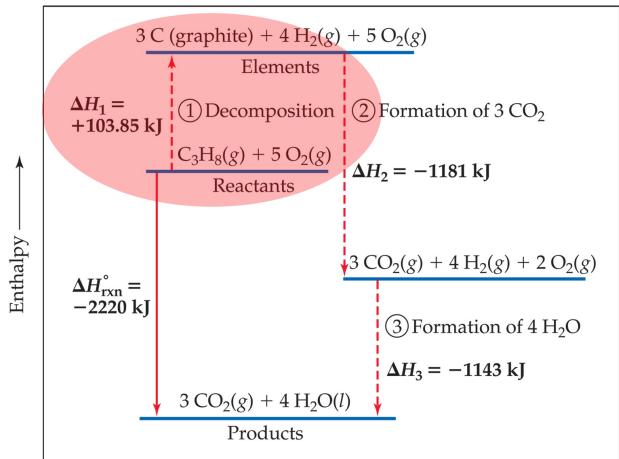
Standard enthalpies of formation, ΔH_f° , are measured under standard conditions (25°C and 1.00 atm pressure).

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	-92.30
Ammonia	$NH_3(g)$	-46.19	Hydrogen fluoride	$HF(g)$	-268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	-1207.1	Methane	$CH_4(g)$	-74.80
Calcium oxide	$CaO(s)$	-635.5	Methanol	$CH_3OH(l)$	-238.6
Carbon dioxide	$CO_2(g)$	-393.5	Propane	$C_3H_8(g)$	-103.85
Carbon monoxide	$CO(g)$	-110.5	Silver chloride	$AgCl(s)$	-127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	-947.7
Ethane	$C_2H_6(g)$	-84.68	Sodium carbonate	$Na_2CO_3(s)$	-130.9
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



Calculation of ΔH

- Calculate ΔH using the table:
- $C_3H_8 + 5 O_2 \rightarrow 3CO_2 + 4H_2O$



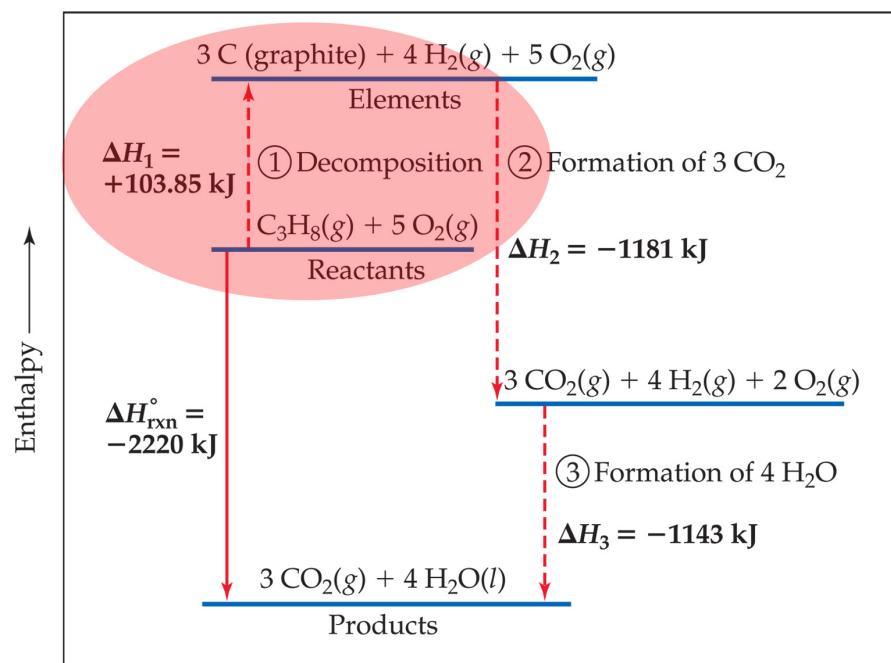
Substance	Formula	$\Delta H_f^\circ \text{ (kJ/mol)}$	Substance	Formula	$\Delta H_f^\circ \text{ (kJ/mol)}$
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	-92.30
Ammonia	$NH_3(g)$	-46.19	Hydrogen fluoride	$HF(g)$	-268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	-1207.1	Methane	$CH_4(g)$	-74.80
Calcium oxide	$CaO(s)$	-635.5	Methanol	$CH_3OH(l)$	-238.6
Carbon dioxide	$CO_2(g)$	-393.5	Propane	$C_3H_8(g)$	-103.85
Carbon monoxide	$CO(g)$	-110.5	Silver chloride	$AgCl(s)$	-127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	-947.7
Ethane	$C_2H_6(g)$	-84.68	Sodium carbonate	$Na_2CO_3(s)$	-130.9
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



Calculation of ΔH



$$\begin{aligned}\Delta H &= [3(\Delta H_f CO_2) + 4(\Delta H_f H_2O)] - [(\Delta H_f C_3H_8) + (5\Delta H_f O_2)] \\ &= [3(-393.5 \text{ kJ}) + 4(-285.8 \text{ kJ})] - [(-103.85 \text{ kJ}) + 5(0)] \\ &= [-1180.5 \text{ kJ} + (-1143.2 \text{ kJ})] - [(-103.85 \text{ kJ}) + 0 \text{ kJ}] \\ &= [-2323.7 \text{ kJ}] - [-103.85 \text{ kJ}] \\ &= -2219.9 \text{ kJ}\end{aligned}$$



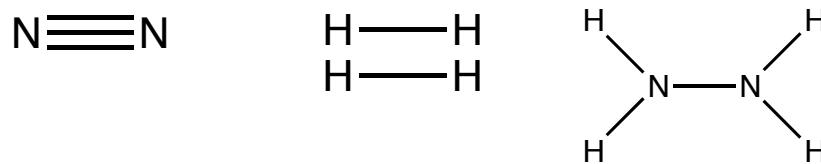
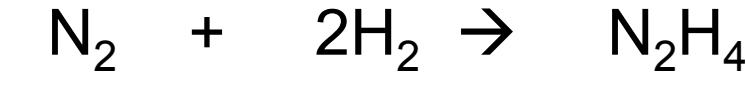
Making and Breaking bonds

i.e. a chemical reaction

- When a bond is formed, energy is released
 - An exothermic process
- When a bond is broken, energy is required
 - An endothermic process

Example

Example: Calculate the heat of formation ΔH_f of hydrazine N_2H_4
Using the bond energies given.



Need to be broken bonds made

$$\begin{aligned} & 946 + 2(436) - (159 + 4(389)) \\ & = 103 \text{ kJ} \end{aligned}$$

Example

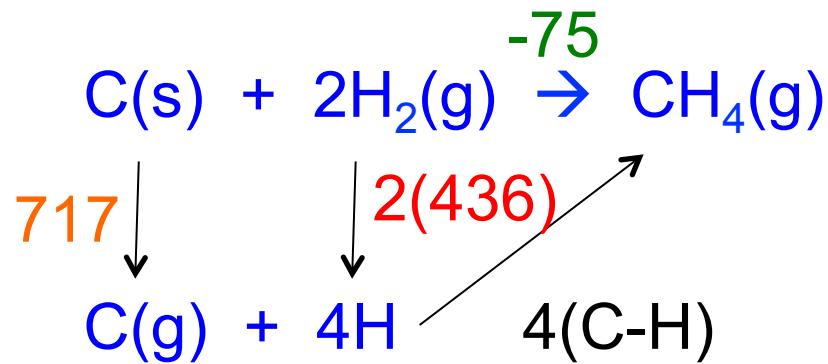
Given: $\text{H} + \text{H} \rightarrow \text{H}_2(\text{g}) \quad \Delta H = -436 \text{ kJ}$

$\text{C(s)} \rightarrow \text{C(g)} \quad \Delta H = 717 \text{ kJ}$ (sublimation)

Heat of formation of methane is: $\Delta H_f = -75 \text{ kJ mol}^{-1}$

What is the bond energy of a CH bond?

Sketch an energy cycle:



$$-75 \text{ kJ} = 717 \text{ kJ} + 2(436 \text{ kJ}) - 4(\text{C-H})$$

$$4(\text{C-H}) = 1664 \text{ kJ}$$

$$(\text{C-H}) = 416 \text{ kJ}$$



Thermochemistry