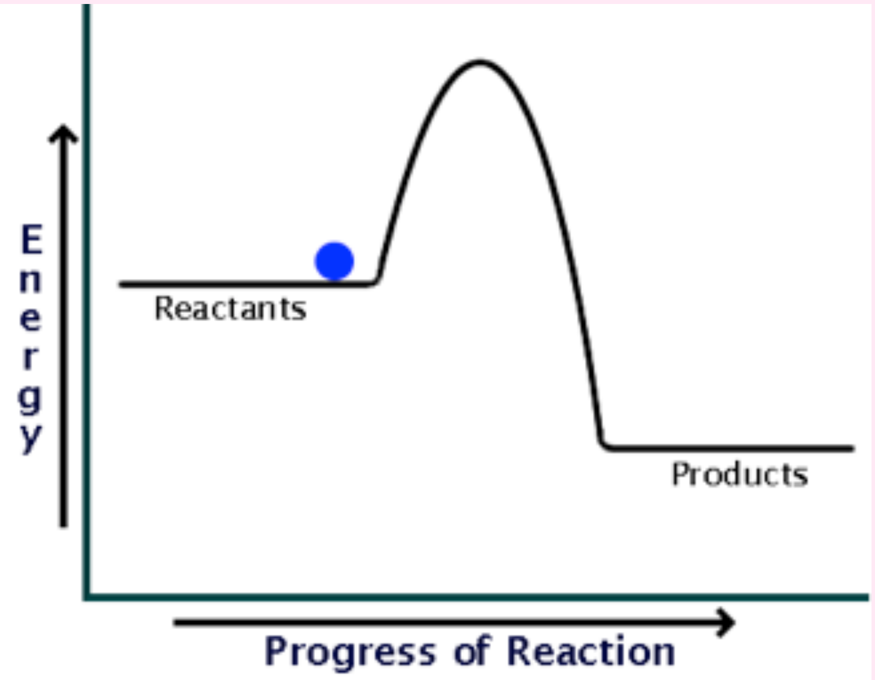
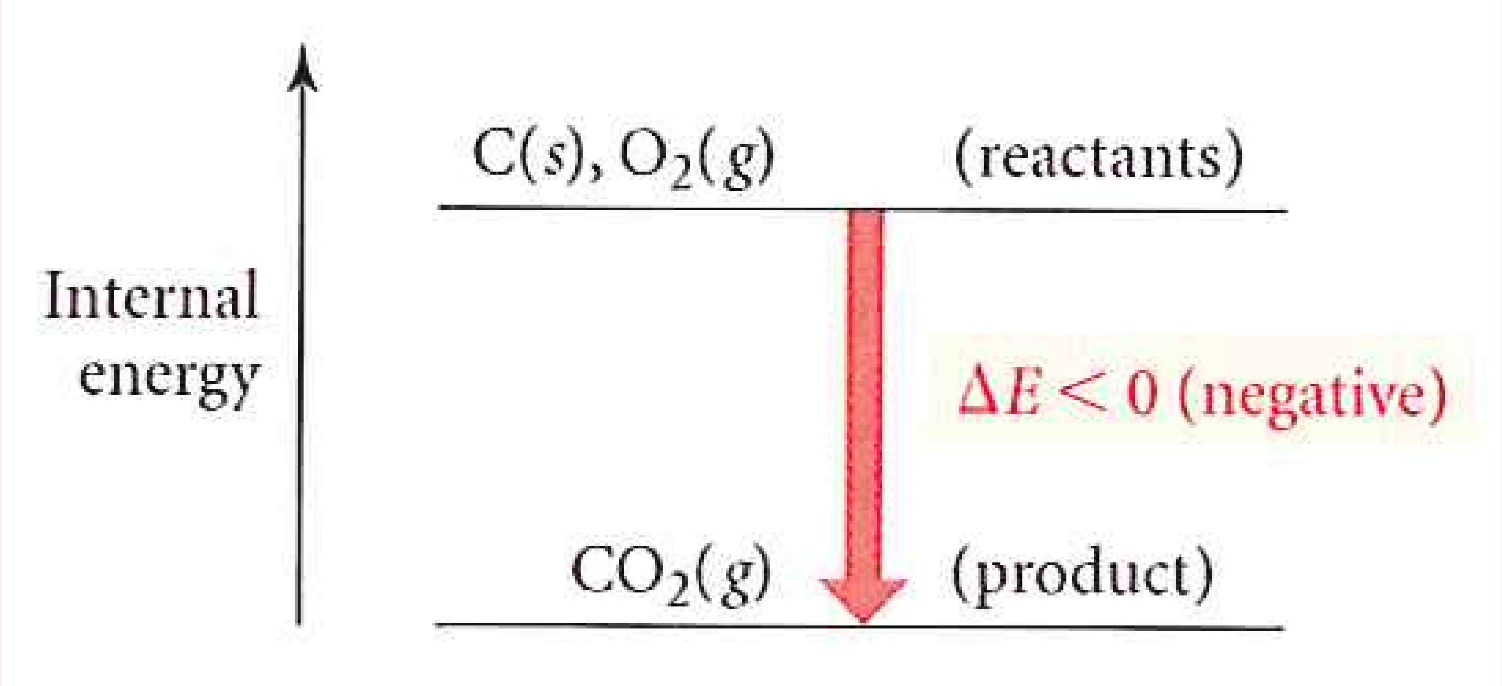
Thermochemistry

Heat Energy

Energy Diagrams

- Consider the reaction for burning coal. Energy is released during the burn. $C(s) + O_2(g) \longrightarrow CO_2(g)$
- Chemists like to draw an energy diagram to represent ΔE

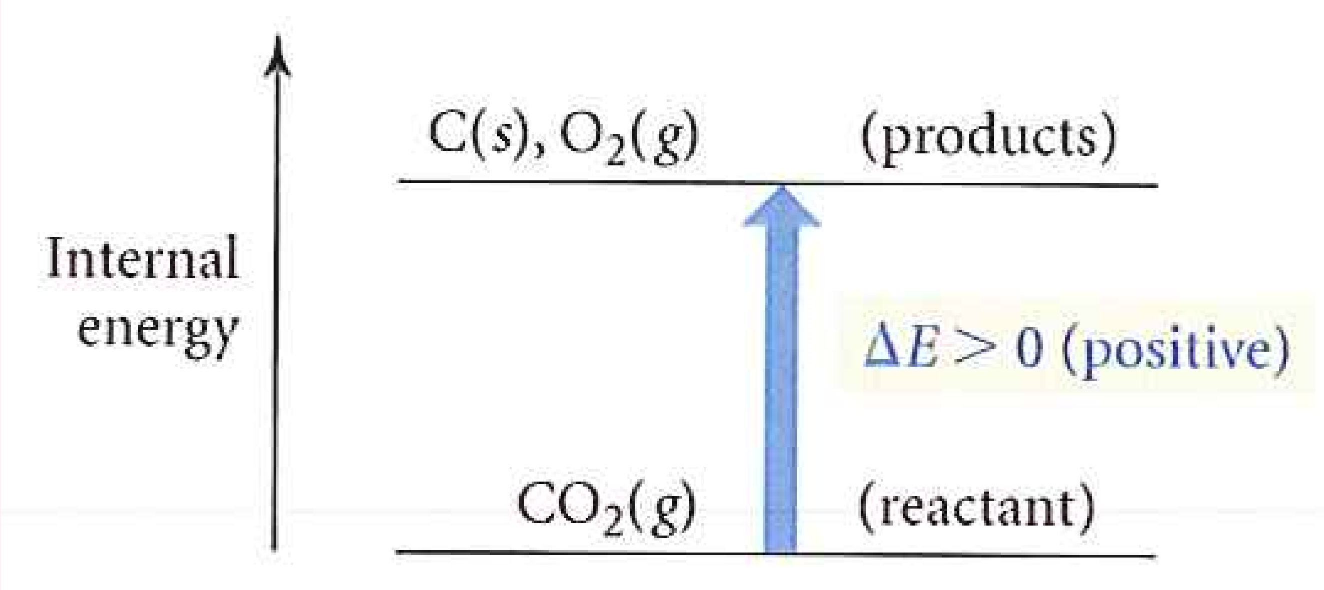


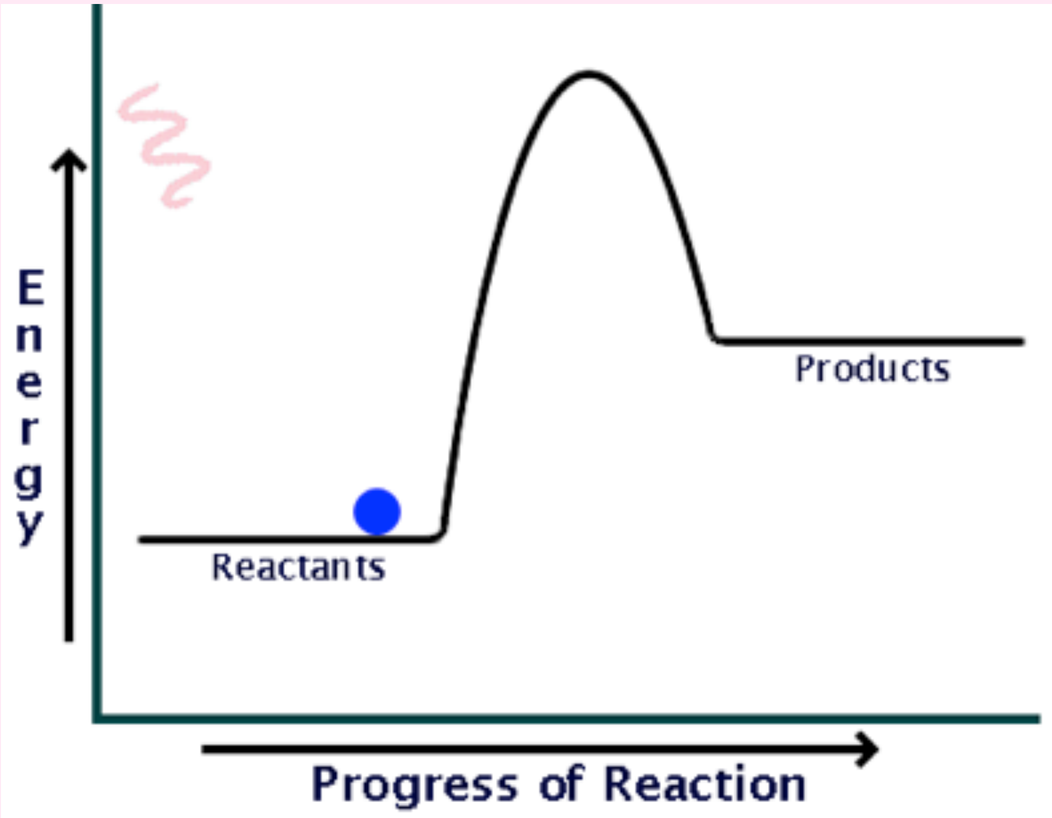


Energy Diagrams

- Consider the reverse of the coal burning reaction.
- Energy is absorbed during the reaction

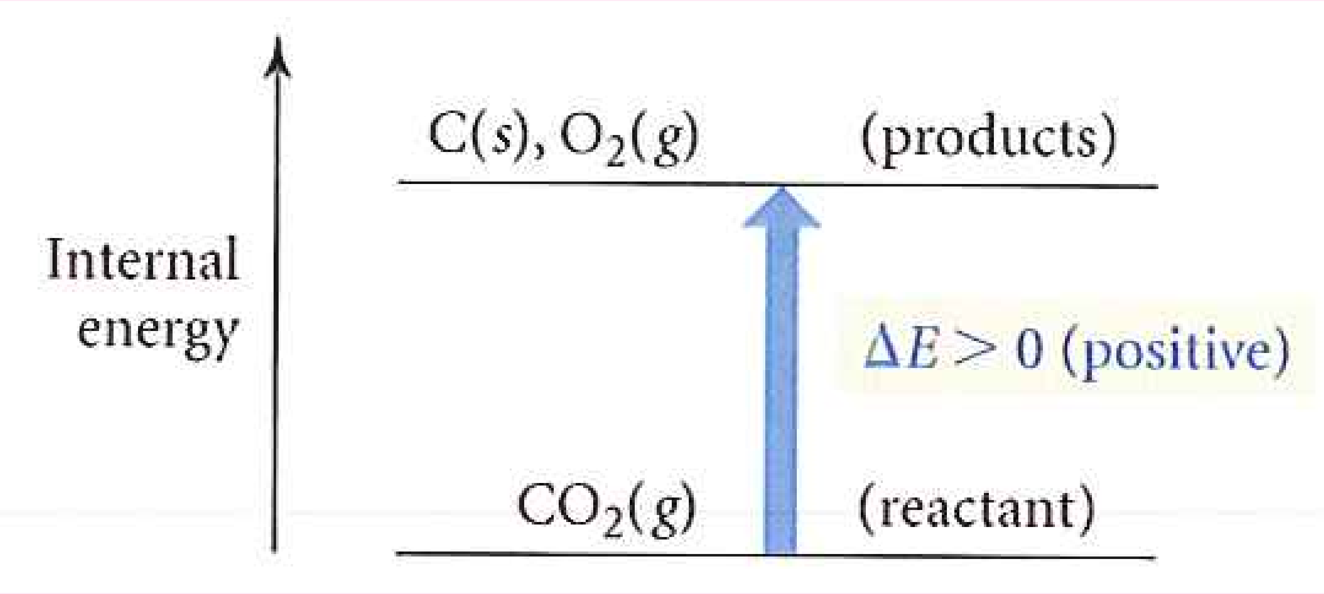
$$CO_2(g) \longrightarrow C(s) + O_2(g)$$

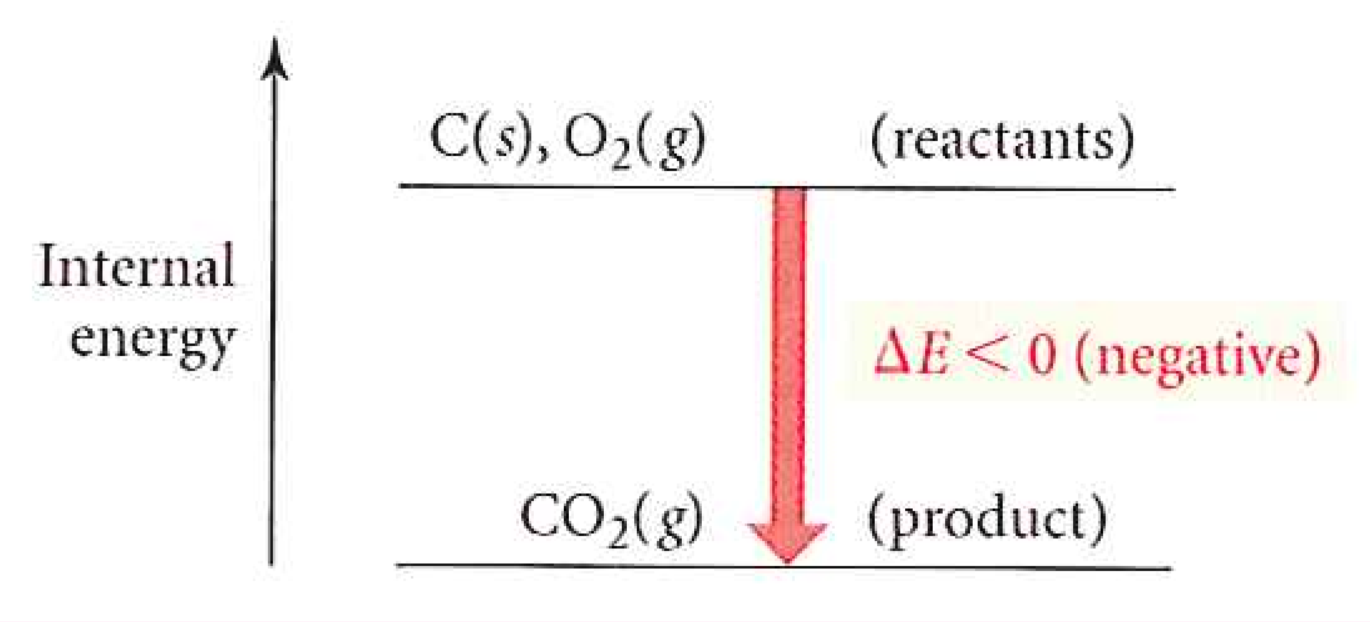




Sign: + or –

- Energy in?
  - ✓ We give the quantity a positive sign.
- Energy out?
  - ✓ We give the quantity a negative sign.

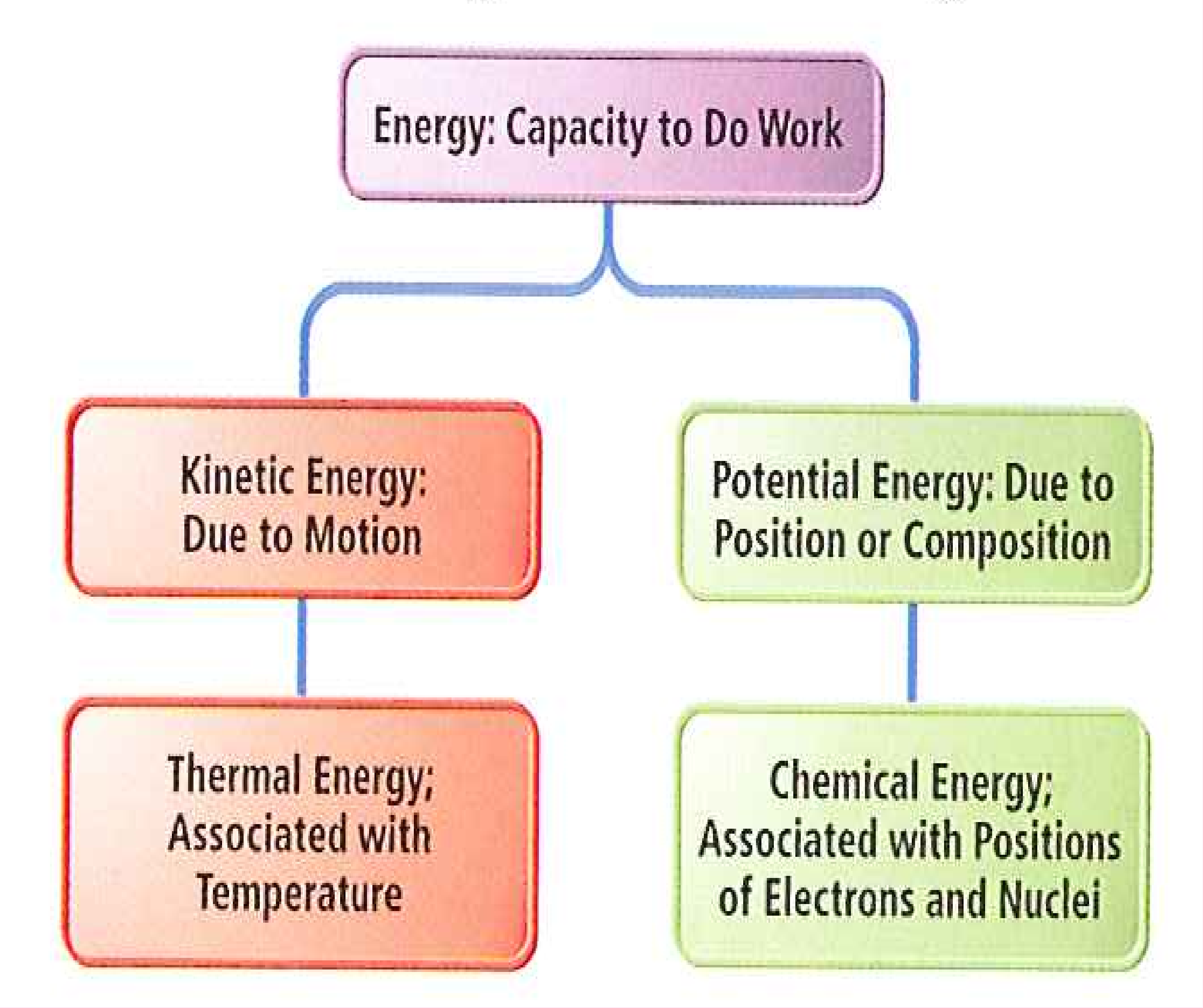




Defining Energy: The Capacity to Do Work

This year, in chemistry we will not spend any more time considering "work." We will leave that for your physics class next year.

Instead we will focus on thermal energy, chemical energy and electrical energy.



Energy: Capacity to Do Work

Kinetic Energy: Due to Motion

Potential Energy: Due to Position or Composition

Thermal Energy: Associated with Temperature

Chemical Energy: Associated with Positions of Electrons and Nuclei

We Need an Energy Unit

- So a physicist would define a Joule this way…
- A joule is defined as the kinetic energy possessed by a 2 kg mass moving at a speed of 1 meter per second.

$$KE = \frac{1}{2}mv^2 = \frac{1}{2}(2kg)\left(\frac{1m}{1s}\right)^2 = \frac{1\ kg\ m^2}{s^2} = 1\ Joule$$

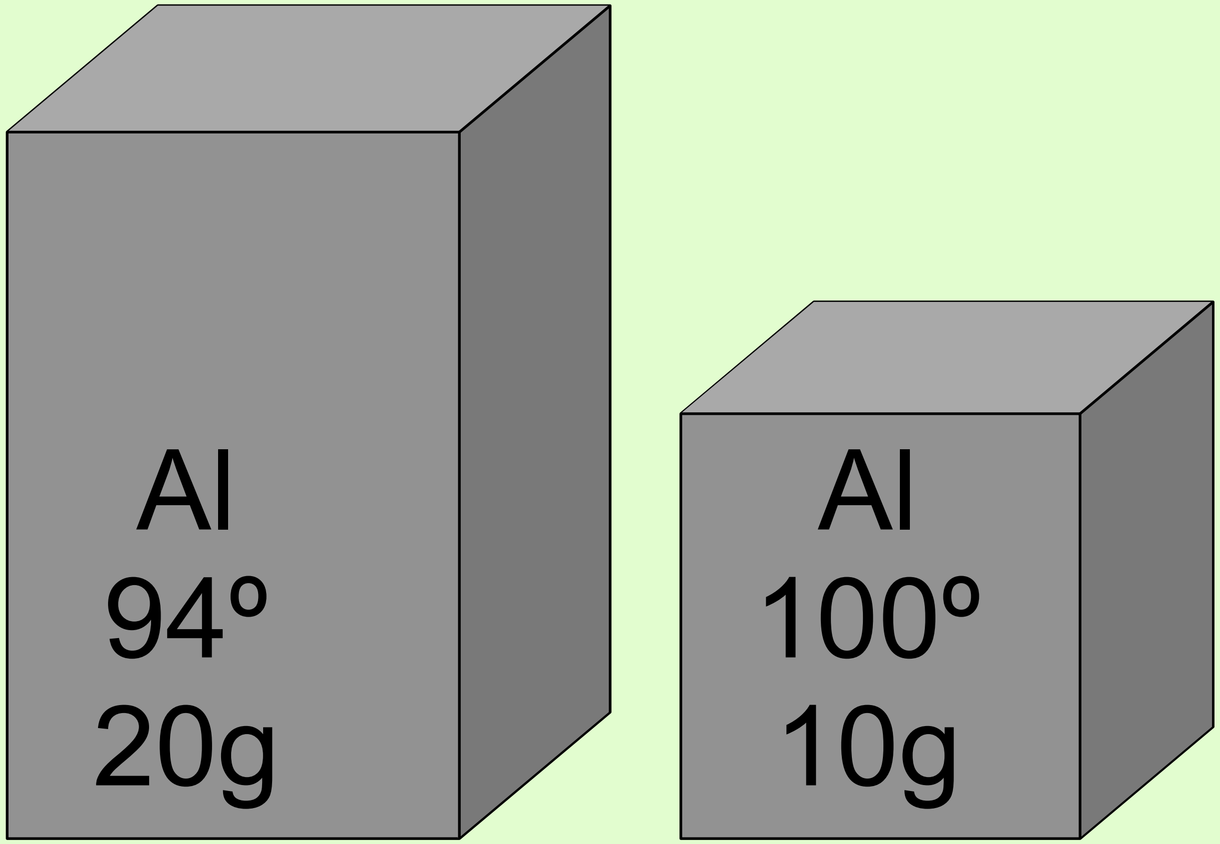
- In chemistry, we will mostly consider thermal energy and electrical energy.
- So in chemistry, thermally, 1 Joule is the amount of heat required to change the temperature of ~0.25 g of water by 1ºC.

Temperature and Heat
They are *not* the same thing

- Temperature: a measure of kinetic energy.
  - ✓ is proportional to the speed of molecules
  - ✓ measures “hotness” or “coldness”
  - ✓ tells us the direction that heat will flow
  - ✓ is measured in degrees, ºC, K, ºF
- Heat: the exchange of thermal energy caused by a temperature difference.
  - ✓ is a quantity of thermal energy (being transferred)
  - ✓ can only be measured when it is transferred
  - ✓ measured in Joules, J (calories, Calories (food), BTU)

Which block is hotter?

1. Bigger block
2. Smaller block
3. Same

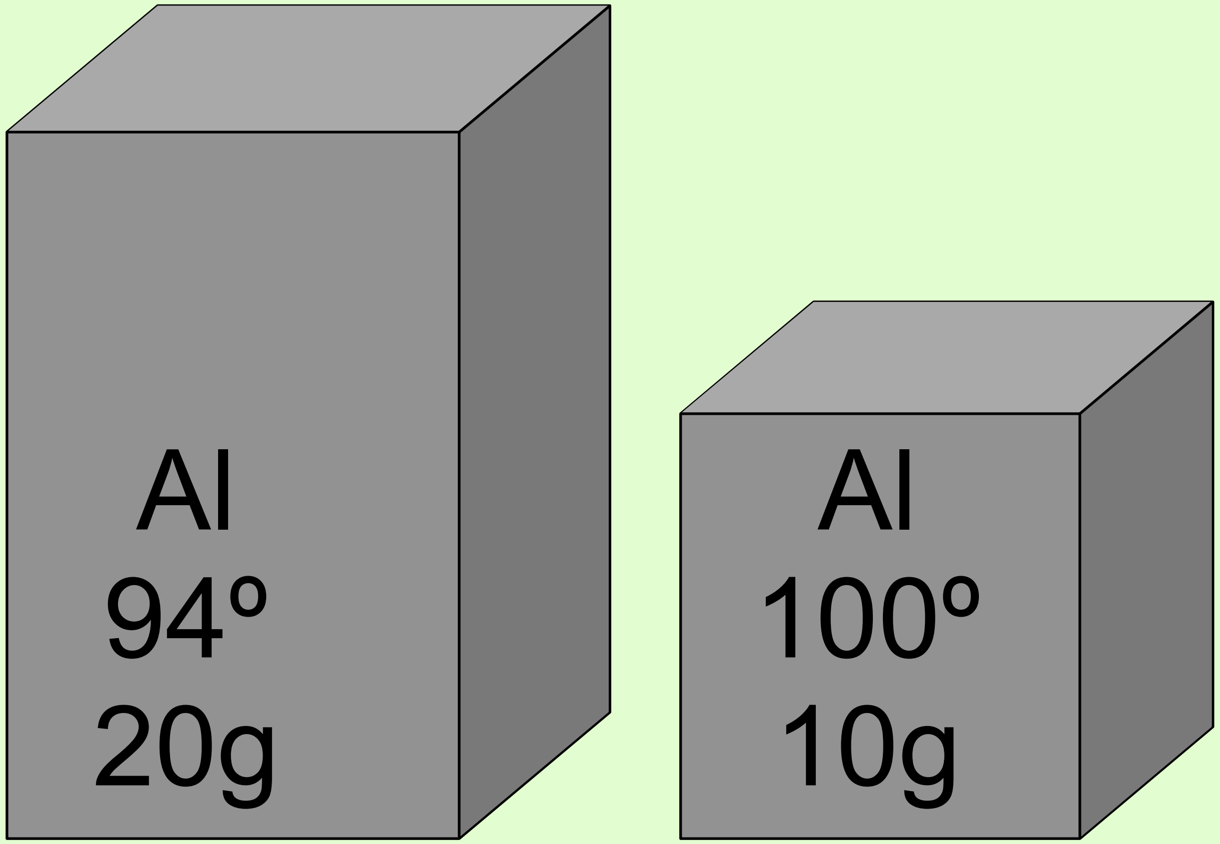


Which block is hotter?

1. Bigger block
2. Smaller block

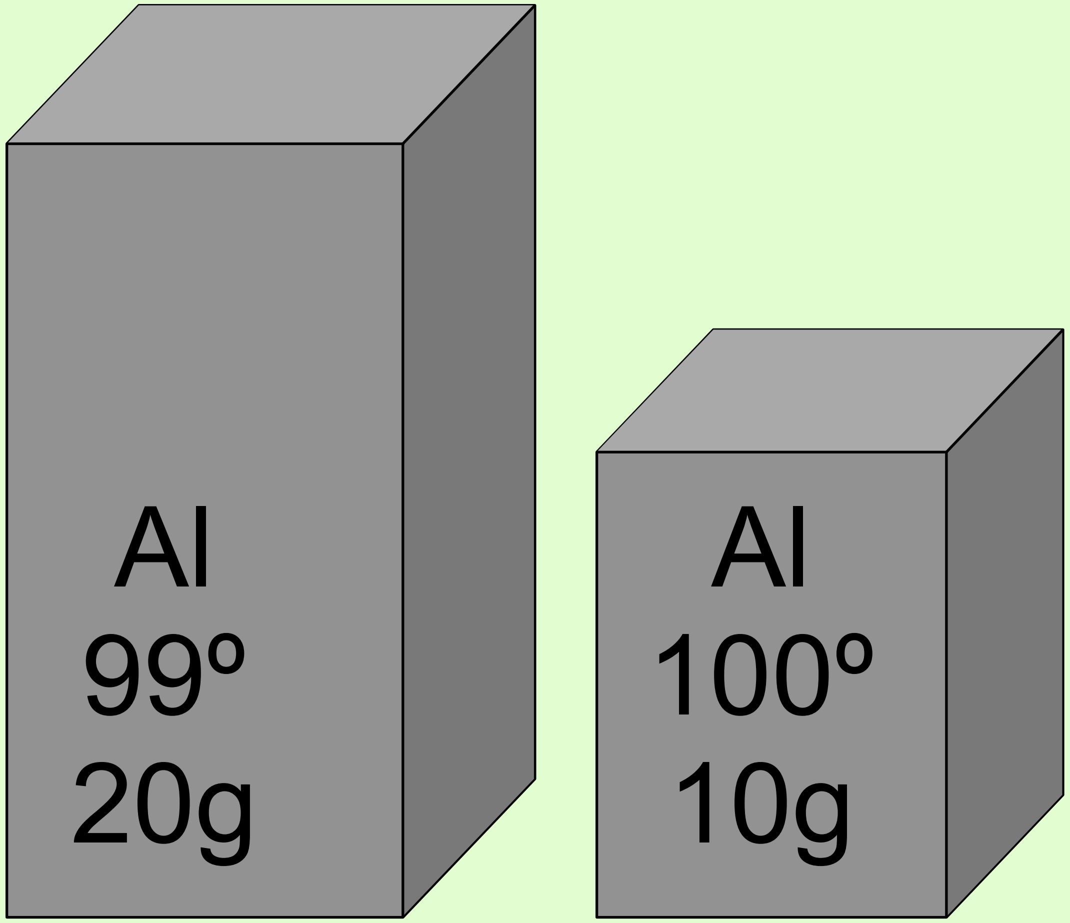
- The smaller block is at a higher temperature, and temp is a measure of hotness and coldness.

3. Same



Which block contains more thermal energy?

1. Bigger block
2. Smaller block
3. Same

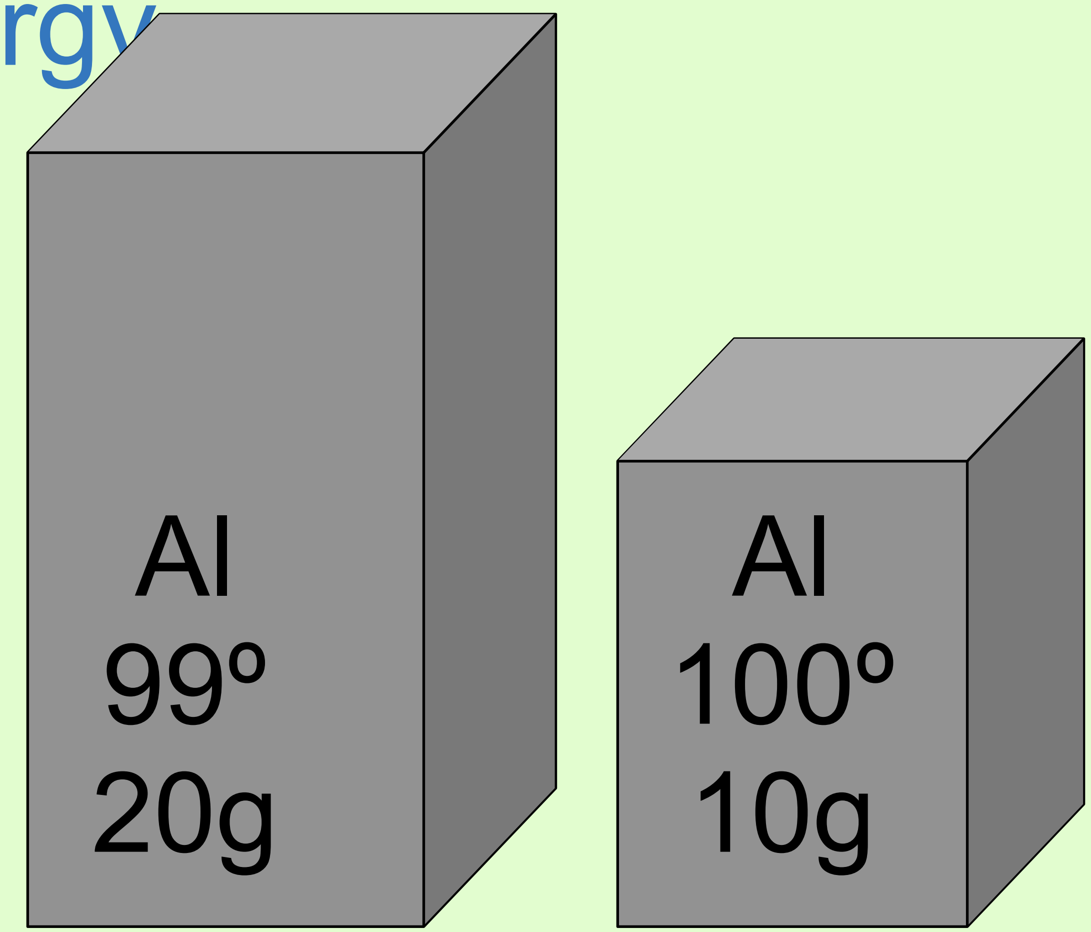


Which block contains the more thermal energy?

1. Bigger block, even though it is slightly cooler.
   - Just as a big pile of wood, would “contain” more heat (when burned). The large block would also “contain” more heat. If you dropped both blocks in equal amounts of cold water, the larger block would heat the water up much more – thus, in a sense, it contains more energy.
2. Smaller block
3. Same

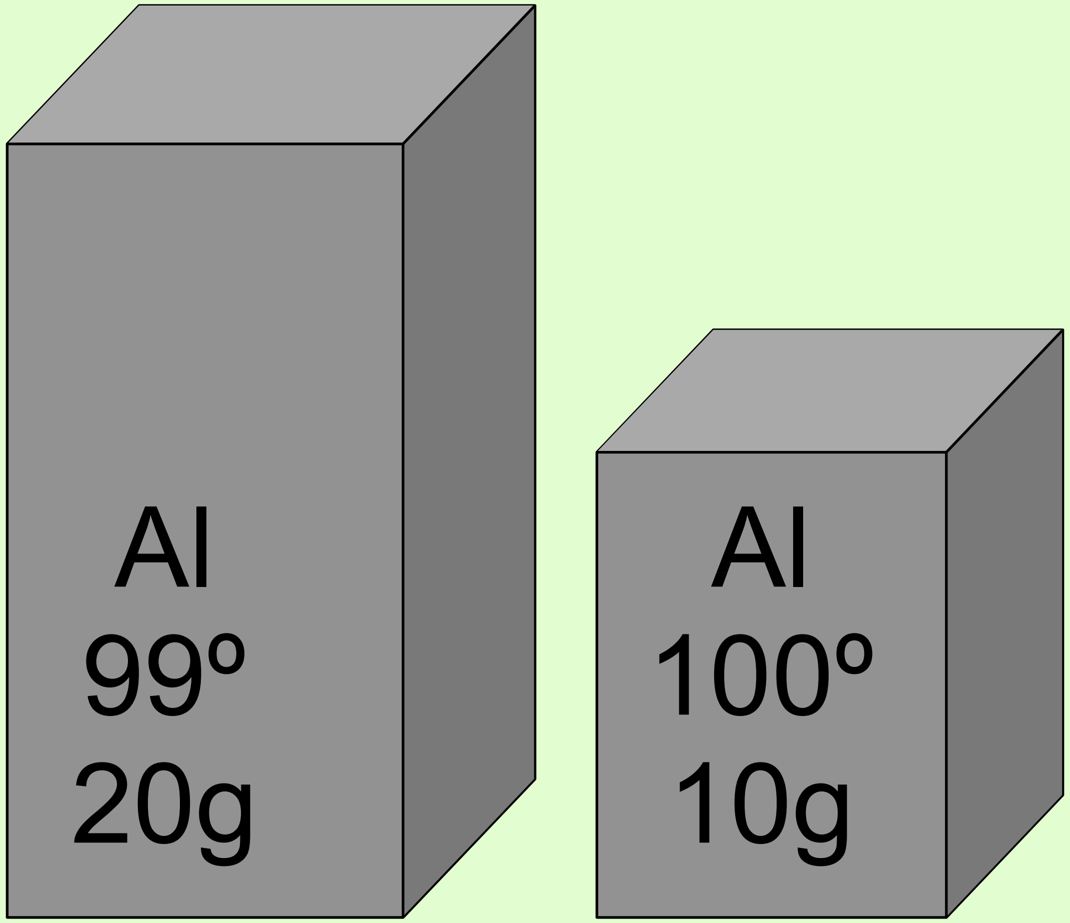
Even though it is at a lower temperature, the bigger block has a higher heat capacity, C.

$$C = \frac{\#\,Joules}{^{\circ}C}$$



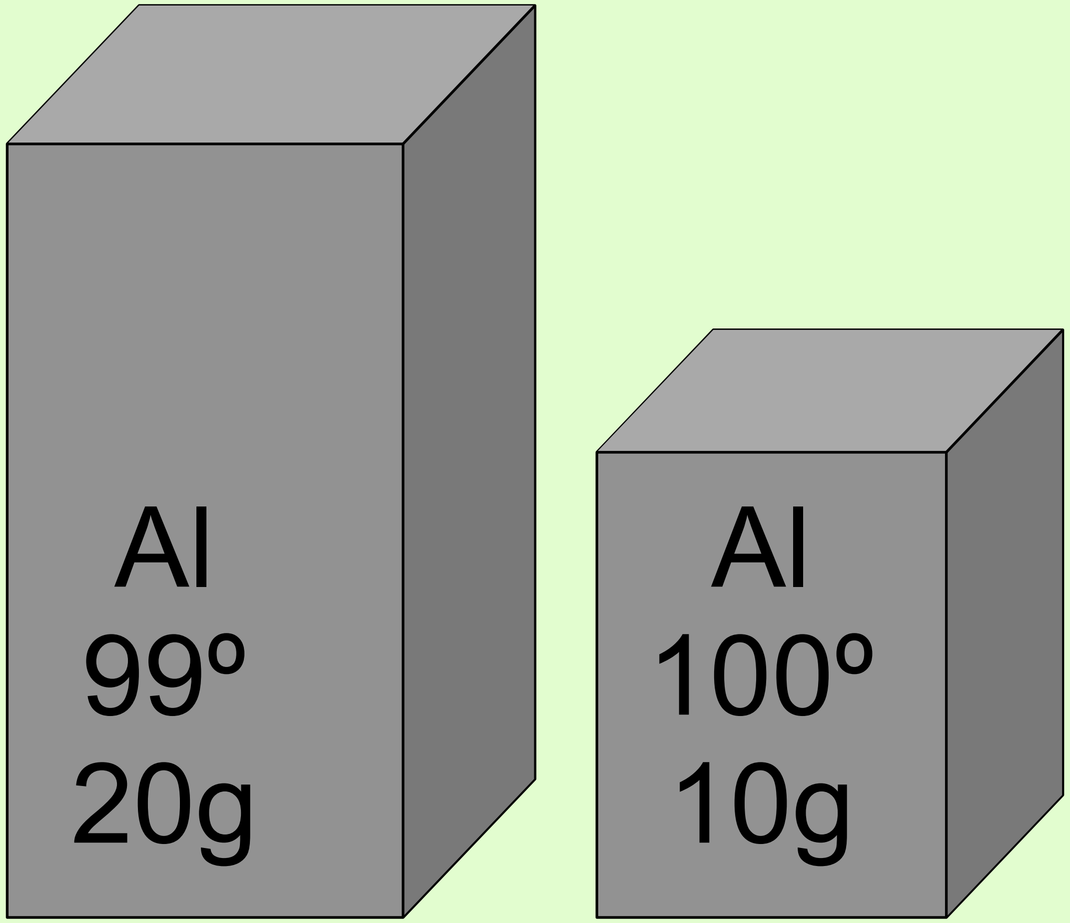
In which direction would heat flow in order to reach thermal equilibrium?

1. from big block to small block
2. from small block to big block
3. impossible to determine



In which direction would heat flow in order to reach thermal equilibrium?

1. from big block to small block
2. from small block to big block
- The Second Law of Thermodynamics tells us (among other things): Heat will always flow from hot to cold – never in the opposite direction.
3. impossible to determine



Mixing equal quantities of hot and cold water in a perfectly insulated container, aka calorimeter, the final temperature of the mixture should be

1. above the hot temperature
2. below the cold temperature
3. exactly in the middle between the two temperatures
4. closer to the hot temperature
5. closer to the cold temperature
6. not enough information to make some of the judgments previously stated

Mixing equal quantities of hot and cold water, the final temperature of the mixture should be *(Select all that apply. Be prepared to comment.)*

1. above the hot temperature
2. below the cold temperature
3. between the two temperatures - exactly in the middle

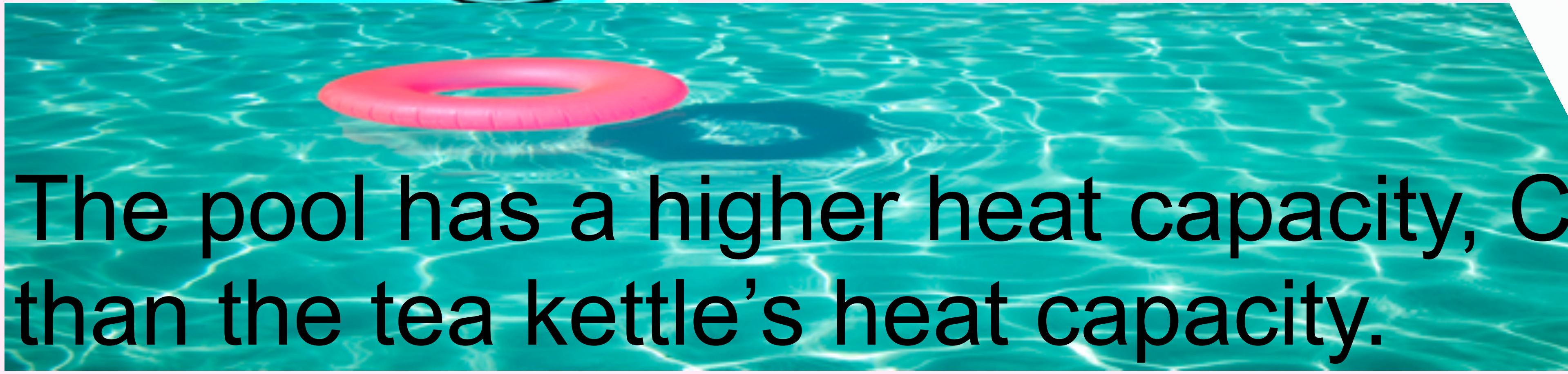
- (or just slightly below the middle temperature since some heat will be lost to the foam cup and the thermometer.)

4. closer to the hot temperature
5. closer to the cold temperature
6. not enough information to make some of the judgments previously stated

My mother in-law comes over for a swim and complains the pool is cold

- I tell her to hold on.... and run inside to heat some water in the tea kettle........

- The water in the pool and water from the tea kettle will reach thermal equilibrium
- Thermal equilibrium does not mean “in the middle” it means “same temperature”



The pool has a higher heat capacity, C, than the tea kettle’s heat capacity.

Mixing 50. g of cold water at 20.ºC with 75 g of hot water at 80.ºC in an insulated container, the final temperature (*thermal equilibrium*) of the mixture should be

(Select all that apply. Be prepared to comment.)

1. above the hot temperature
2. below the cold temperature
3. exactly in midway between the two temperatures
4. closer to the hot temperature
5. closer to the cold temperature
6. not enough information to make some of the judgments previously stated

Mixing 50. g of cold water at 20.ºC with 75 g of hot water at 80.ºC in an insulated container, the final temperature (*thermal equilibrium*) of the mixture should be

(Select all that apply. Be prepared to comment.)

1. above the hot temperature
2. below the cold temperature
3. exactly in midway between the two temperatures
4. closer to the hot temperature, because the larger mass of water has a higher heat capacity.
5. closer to the cold temperature
6. not enough information to make some of the judgments previously stated

Heat Capacity, C

- The quantity of heat required to change a system’s temperature by 1ºC

$$C = \frac{q}{\Delta T} = \frac{J}{^{\circ}C}$$

  - q = heat
  - ΔT = change in temperature

- The amount of material present will dramatically affect the heat capacity

$$q = C \Delta T$$

Mixing 50. g of *alcohol* at 20.ºC with 50. g of hot water at 80.ºC in an insulated container, the final temperature (*thermal equilibrium*) of the mixture should be

(Select all that apply. Be prepared to comment.)

1. above the hot temperature
2. below the cold temperature
3. exactly in midway between the two temperatures
4. closer to the hot temperature
5. closer to the cold temperature
6. not enough information to decide on the statements above

Mixing 50. g of alcohol at 20.ºC with 50. g of hot water at 80.ºC in an insulated container, the final temperature (*thermal equilibrium*) of the mixture should be

(Select all that apply. Be prepared to comment.)

1. above the hot temperature
2. below the cold temperature
3. exactly in midway between the two temperatures
4. closer to the hot temperature
5. closer to the cold temperature
6. not enough information to make some of the judgments previously stated

- You are correct in thinking there will be a difference in the "energy-holding capacity" of alcohol compared to water.

Specific Heat Capacity, c

A measure of the intrinsic capacity of a substance to absorb heat.

- As you may have guessed, the amount of heat needed to change a substance’s temperature may vary from substance to substance.
- *c*, the quantity of heat required to change 1 g of a substance by 1°C

$$\boxed{c = \frac{q}{m\Delta T} = \frac{J}{g\,^{o}C}}$$

- the specific heat capacity of liquid water
  - ✓ c_{water}, is 4.18 J/g°C
- the specific heat capacity of ethanol
  - ✓ $c_{ethanol}$, is 2.46 J/g°C

We will commonly use this equation rearranged

$$\boxed{q = mc\Delta T}$$

The really big assumption:

To calculate energy coming or going, we will need to assume that the amount of heat lost will equal the amount of heat gained.

$$\text{Heat lost} = \text{Heat gained}$$

$$-q_{lost} = q_{gained}$$

$$-mc\Delta T = mc\Delta T$$

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

- By convention, energy lost from a system will be negative, and energy gained by a system will be positive, thus we must include a negative sign in order to set energy lost equal to energy gained − otherwise, the energy would be equal but opposite in sign.

Let’s reconsider the previous problem with cool alcohol and warm water, and calculate:

50.0 g of cold alcohol at 20.0ºC with 50.0 g of hot water at 80.0ºC Calculate the thermal equilibrium temperature

The really big assumption:

Heat lost = Heat gained

$$-q_{lost} = q_{gained}$$

$$-mc\Delta T = mc\Delta T$$

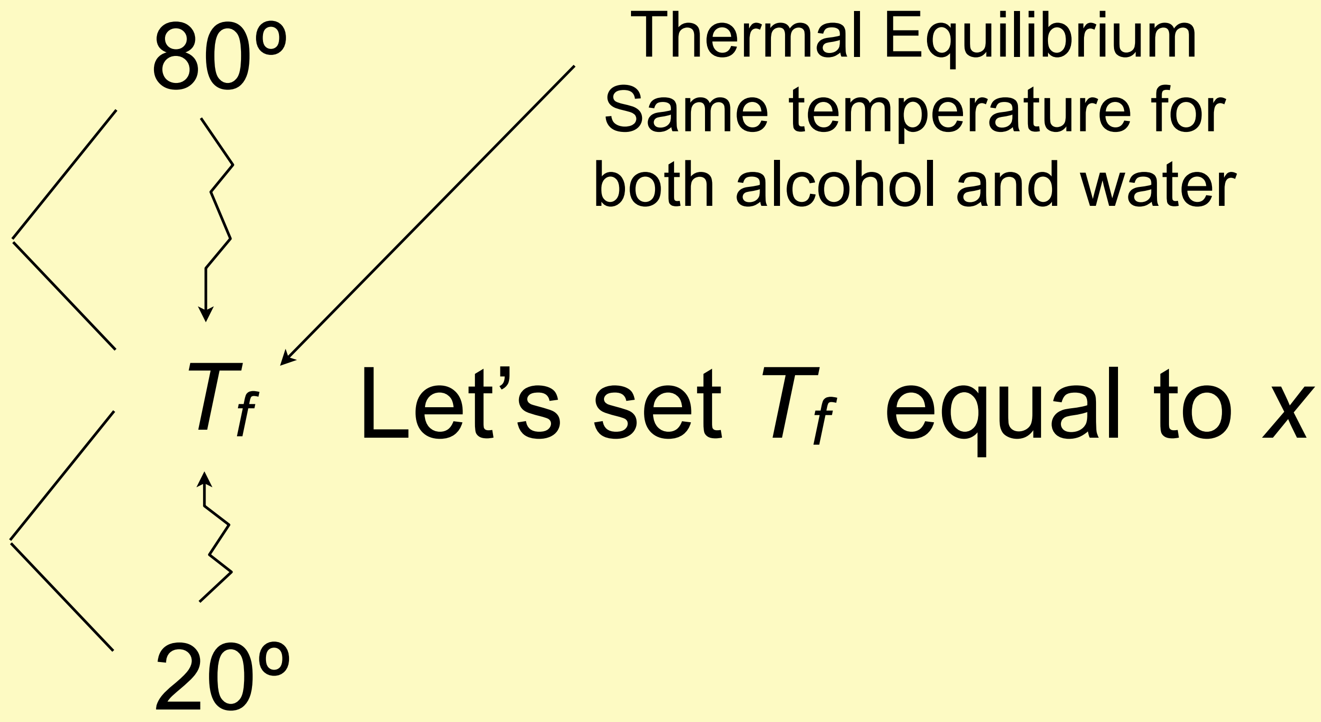
$$\Delta T = T_{final} - T_{initial}$$

- Let’s do the algebra….

50.0 g of cold ethanol at 20.0ºC with 50.0 g of hot water at 80.0ºC. Calculate the thermal equilibrium temperature.

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

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



80º

Thermal Equilibrium
Same temperature for
both alcohol and water

T_f Let's set T_f equal to x

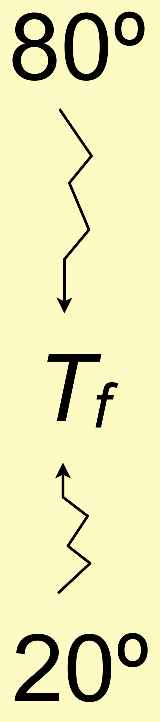
20º

$$-mc\Delta T = mc\Delta T$$

$$-\left[(50.0)(4.18J/g^{\circ}C)(x-80^{\circ})\right] = (50g)(2.46J/g^{\circ}C)(x^{\circ}-20^{\circ})$$

50.0 g of cold ethanol at 20.0ºC with 50.0 g of hot water at 80.0ºC. Calculate the thermal equilibrium temperature.

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



$$-cm\Delta T = cm\Delta T$$

$$-\left[\cancel{(50.0)}\left(4.18 J/g^{o}C\right)\left(x-80^{o}\right)\right]=\cancel{(50g)}\left(2.46 J/g^{o}C\right)\left(x^{o}-20^{o}\right)$$

Don’t distribute if you don’t have to...avoid math errors.

$$-\left(x-80^{o}\right)\left(\frac{4.18}{2.46}\right)=\left(x^{o}-20^{o}\right)$$

$$136^{o}-1.7x^{o}=x-20^{o}$$

$$156=2.7x$$

$$x=57.8^{o}$$

Suppose you are cold weather camping and you decide to bring some objects into your sleeping bag for extra warmth. Near the campfire, you heat up a jug of water and a big rock of equal mass, both reaching a temperature of 43ºC. If you could bring only one into your sleeping bag, which one should you choose to keep you the warmest through the night?

1. Water jug
2. Rock

Suppose you are cold weather camping and you decide to bring some objects into your sleeping bag for extra warmth. Near the campfire, you heat up a jug of water and a big rock of equal mass, both reaching a temperature of 43ºC. If you could bring only one into your sleeping bag, which one should you choose to keep you the warmest through the night?

1. Water jug
   - Water has higher specific heat capacity, c, and as it cools to thermal equilibrium with you, the water will release more energy per gram per degree.
2. Rock

REVIEW “Opener”

1. How many kilojoules of energy are required to change the temperature of 36 g of water from 5ºC to 65ºC?

2. Determine the starting temperature of the hot water when 128 g of water at 11ºC is mixed with 95 g of water and the final temperature is 28ºC.

LAD C.1

Specific Heat Capacity of Various Metals

LAD C1 – Heat Capacity of Various Metals

Let's make some measurements of the specific heat capacity of various metals, by dropping hot metals into cool water and measuring the temp changes.

We will use 4.18 J/g°C as the specific heat capacity of water.

1. What are we calculating?

$$-m_m \boxed{c_m} \Delta T_m = m_w c_w \Delta T_w$$

2. What do we need to measure?
   - Set up a data table on lined paper.

The really big assumption:

Heat lost = Heat gained

−heat lost by hot = heat gained by cold

$-q_{hot} = q_{cold}$

$$-mc\Delta T = mc\Delta T$$

LAD C.1 Temp Diagram

T_H _____

ΔT_H ________

T_{equil} _____

ΔT_C ________

T_C _____

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

Enthalpy
Heat of Reaction

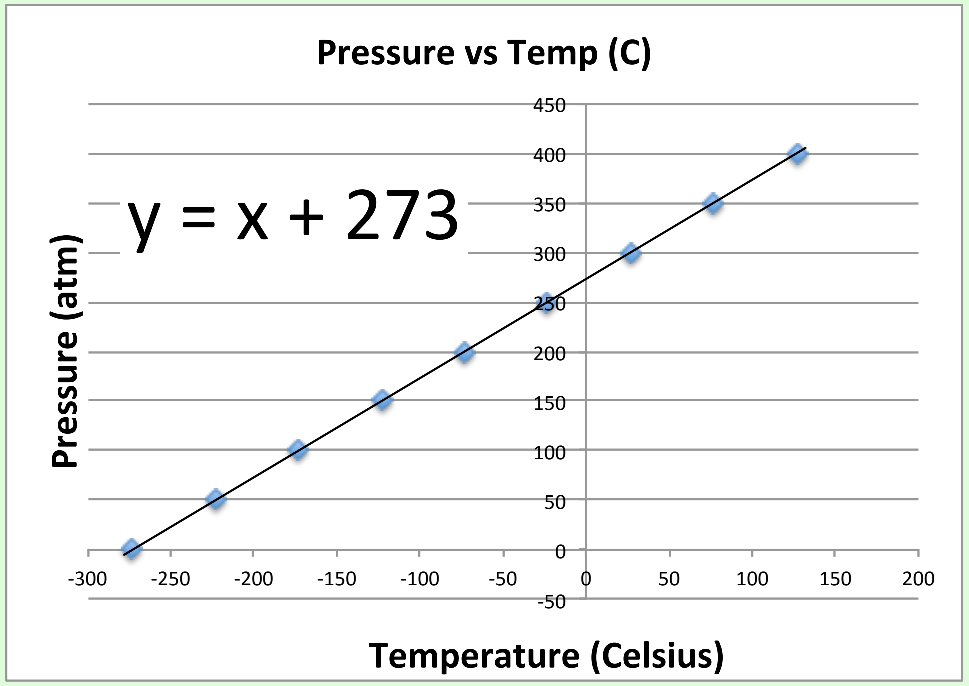
So we have discussed the energy changes when materials are warming and cooling simply because the materials were simply at different temperatures, but what about the energy changes caused by a chemical reaction?

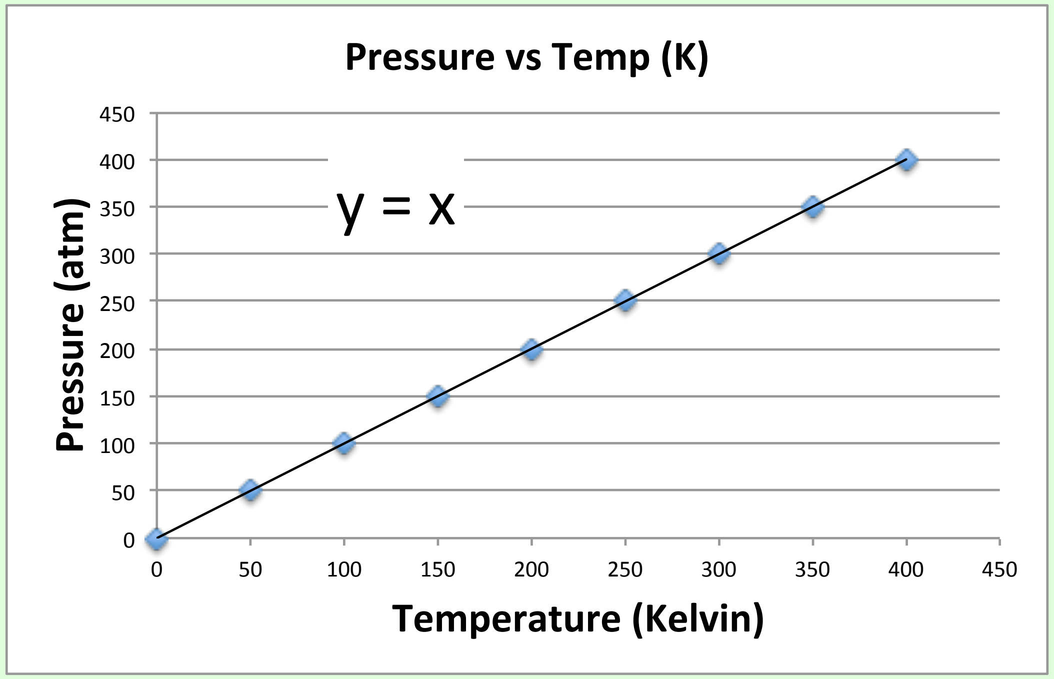
LAD C2 - ΔH

If you got less than 50% efficiency, you should go run another trial.
Work hard to try to avoid energy loss in any way you can.

Why must Gas Laws must be calculated in Kelvin? Yet Energy calculations can be Celsius or Kelvin?

- Gas calculations involve $PV = nRT$ $\quad \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$
  - ✓ $\frac{50atm}{50^\circ C} = \frac{P}{100^\circ C}$ $\quad \frac{50atm}{323K} = \frac{P}{373K}$
- Energy calculations involve $\Delta T = T_f - T_i$
  - ✓ since the “size” of a Kelvin and a ºC are the same subtractions will yield the same value.
  - ✓ 50ºC - 30ºC = 20 and 323K - 303K = 20





The Molecular View

- Where *does* the energy come from during chemical reactions?
  - ✓ It does not come simply from the kinetic energy of the particles of the system.
- It comes from the chemical potential energy that arises from the electrostatic forces of the protons and electrons within or between the particles.
- During the reaction, bonds break, atoms rearrange, bonds form resulting in a different arrangement.
  - ✓ A new arrangement might result in lower potential energy, more stable, and more favorable. But that energy has to go somewhere. The energy leaves as heat. We call this exothermic and we represent the leaving energy as negative.
  - ✓ OR a new arrangement might result in higher potential energy, less stable, and less favorable. But that energy has to come from somewhere. The energy steals that energy from the kinetic energy of nearby molecules (sometimes even from their own kinetic energy). We call this endothermic and we represent the coming energy as positive.

The Energy of Bonds

- Bond breaking
  - ✓ Endothermic

time for the wax demo?

- Bond forming
  - ✓ exothermic
- $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + E$
  - ✓ For this reaction the net result of the energy in for bonds broken combined with the energy out from bonds formed, give off heat energy.

The Energy of Bonds

- Bond breaking
  - ✓ Endothermic
- Bond forming
  - ✓ exothermic
- ATP + water → ADP + Phosphate-water + E
  - ✓ For this reaction the net result of the energy in for bonds broken combined with the energy out from bonds formed, give off heat energy.

Measuring thermal heat of a reaction.

- Symbolized by ΔH_{Rx} Called Enthalpy
  - ✓ The amount of heat released or absorbed during a chemical reaction.
  - ✓ ΔH_{Rx} positive (+), means energy is absorbed (temp goes down)
  - ✓ ΔH_{Rx} negative (−), means energy is released (temp goes up)
- $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ + Energy
- $\Delta H_{combustion} = -802$ kJ/mol$_{rxn}$ (1mol of CH_4)
- Thus $q = \Delta H_{Rx} \times amount$
- ΔH is intensive (notice, joules per mole)
- q is extensive (notice, just joules)
- *On Wed, we will experimentally measure and calculate Heat of Combustion of Butane, LAD C.2*

Relationships involving ΔH_{Rx}

- If a chemical equation is multiplied by some factor, the ΔH_{Rx} is also multiplied by the same factor.

- $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 802\ \text{kJ}$
- $\Delta H_{combustion} = -802\ \text{kJ/mol}_{rxn}$ (of 1 mol CH_4)

- $2CH_4 + 4O_2 \rightarrow 2CO_2 + 4H_2O + 1604\ \text{kJ}$
- $\Delta H_{combustion} = -1604\ \text{kJ/ 2 mol of } CH_4$

Relationships involving ΔH_{Rx}

- If a chemical equation is reversed, then the ΔH_{Rx} changes sign.

- $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 802\ \text{kJ}$
- $\Delta H_{combustion} = -802$ kJ/mol of CH_4

- $CO_2 + 2H_2O + 802\ \text{kJ} \rightarrow CH_4 + 2O_2$
- $\Delta H_{reaction} = +802$ kJ/mol of CH_4

Relationships involving ΔH_{Rx}

- If a chemical equation can be expressed as the sum of a series of steps, then the ΔH_{Rx} for the overall equation is the sum of the heats of reactions for each step.
- This is Hess' Law…..
  - ✓ what does this mean? how can we use this?

Hess' Law

- Given the following data

$N_2 + 2O_2 \rightarrow 2NO_2 \qquad \Delta H^o = 68\ \text{kJ}$

$N_2 + 2O_2 \rightarrow N_2O_4 \qquad \Delta H^o = 10.\ \text{kJ}$

- calculate ΔH^o for the reaction below:

$2NO_2 \rightarrow N_2O_4$

Hess' Law

- Given the following data

reverse: $N_2 + 2O_2 \rightarrow 2NO_2 \quad \Delta H^o = 68\text{ kJ}$

$$2NO_2 \rightarrow N_2 + 2O_2 \quad \Delta H^o = -68\text{ kJ}$$

$$N_2 + 2O_2 \rightarrow N_2O_4 \quad \Delta H^o = 10.\text{ kJ}$$

then add them together, and add the ΔH values

$$2NO_2 \rightarrow \cancel{N_2} + \cancel{2O_2} \quad \Delta H^o = -68\text{ kJ}$$

$$\cancel{N_2} + \cancel{2O_2} \rightarrow N_2O_4 \quad \Delta H^o = 10.\text{ kJ}$$

- calculate ΔH^o for the reaction:

$$2NO_2 \rightarrow N_2O_4 \quad \Delta H^o = -58\text{ kJ}$$

$\Delta H_{formation}$ values

- Check out the Thermodynamic Table
- Look at the first column ΔH^o_f (kJ/mol)
- What does $^o{}_f$ mean, and per mole of what?
  - ✓ ΔH = Enthalpy,
  - ✓ f = of formation of the substance listed, from its elements in their standard condition
  - ✓ ^{o} = at standard conditions (1 M and 1 atm)
  - ✓ measured at 25ºC

$\Delta H_{formation}$ *Reactions*

- Look up gaseous butane
- ΔH^{o}_{f} = −124.73 kJ/mol
- Δ tells us change, but change for what??
  - ✓ For a reaction….but what reaction?

- For the formation of gaseous butane from its elements
- $4C + 5H_2 \rightarrow C_4H_{10(g)}$ $\Delta H = -124.73$ kJ/mol

$\Delta H_{formation}$ Reactions

- Look up calcium hydroxide
- $\Delta H^o_f = -986.2$ kJ/mol
- For what reaction?
- For the formation of gaseous solid calcium hydroxide from its elements
- $Ca + O_2 + H_2 \rightarrow Ca(OH)_{2(s)} \quad \Delta H = -986.2$ kJ/mol

$\Delta H^o{}_f$ By Definition

- Chemists have compiled long lists of energy values for formation reactions.
  - ✓ A formation reaction is defined as: The formation of one mole of a substance from the substances' elements in their standard state.
- Formation of liquid water?
  - ✓ $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(L)}$ $\Delta H_f^o = -286$ kJ/mol
- Formation of solid sugar?
  - ✓ $6C_{s(graphite)} + 6H_{2(g)} + 3O_{2(g)} \rightarrow C_6H_{12}O_{6(s)}$ $\Delta H_f^o = -1{,}273$ kJ/mol
- These values can be used to calculate the energy for many reactions using Hess' Law.
- Let's try it…..

ΔH_{Rxn} for combustion of ethanol

Look up values from the ΔH_f^o table for compounds in the reaction of the burning of ethanol vapor.

Using Hess' Law, rearrange these reactions so they will add up to the desired reaction.

$C_2H_5OH_{(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$

ΔH_{Rxn} for combustion of ethanol

Look up values from the ΔH_f^o table for compounds in the reaction of the burning of ethanol vapor.

$2C + 3H_2 + \frac{1}{2}O_2 \rightarrow C_2H_5OH_{(g)}$ $\Delta H = -235$ kJ/mol

$C + O_2 \rightarrow CO_{2(g)}$ $\Delta H = -394$ kJ/mol

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{(g)}$ $\Delta H = -242$ kJ/mol

$O_2 \rightarrow O_2$ $\Delta H = 0$ kJ/mol

Rearrange these reactions so they will add up to the desired reaction.

$C_2H_5OH_{(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$

Look up values from the ΔH_f^o table for compounds in the burning of butane reaction.

$2C + 3H_2 + ½O_2 \rightarrow C_2H_5OH_{(g)}$ ΔH = −235 kJ/mol

$C + O_2 \rightarrow CO_{2(g)}$ ΔH = −394 kJ/mol

$H_2 + ½O_2 \rightarrow H_2O_{(g)}$ ΔH = −242 kJ/mol

$O_2 \rightarrow O_2$ ΔH = 0 kJ/mol

Rearrange and "fix" the stoichiometry of these reactions so they will add up to the desired reaction.

$C_2H_5OH_{(g)} \rightarrow 2C + 3H_2 + ½O_2$ ΔH = +235 kJ/mol

$2C + 2O_2 \rightarrow 2CO_{2(g)}$ ΔH = 2(−394 kJ/mol) = −788

$3H_2 + 1½O_2 \rightarrow 3H_2O_{(g)}$ ΔH = 3(−242 kJ/mol) = −726

add up the reactions, and add up the ΔH values

$C_2H_5OH_{(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$ ΔH = −1279 kJ/mol

ΔH for combustion of ethanol

Whew...that was tedious, how about a nifty formula?

Wait...what? We have a nifty formula?

This rearranging gets tedious, not to worry, there is a shortcut. When using heats of **formation** values, we can apply the formula:

$$\Delta H_{rx} = \Sigma n\Delta H^{o}_{f\ products} - \Sigma n\Delta H^{o}_{f\ reactants}$$

$$\Delta H = [\ 2(-394) + 3(-242)\ ] - [\ (-235) + 3\tfrac{1}{2}(0)\ ] = -1279$$

This works of course, because subtracting the reactant ΔH values, is the same as flipping and changing the sign when we wrote out Hess' Law.

$C_2H_5OH_{(g)} \rightarrow 2C + 3H_2 + \tfrac{1}{2}O_2$ $\Delta H = +235$ kJ/mol

$2C + 2O_2 \rightarrow 2CO_{2(g)}$ $\Delta H = 2(-394$ kJ/mol$) = -788$

$3H_2 + 1\tfrac{1}{2}O_2 \rightarrow 3H_2O_{(g)}$ $\Delta H = 3(-242$ kJ/mol$) = -726$

$C_2H_5OH_{(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$ $\Delta H = -1279$ kJ/mol

More Practice

Calculating ΔH_{rxn}

Write a reaction for the combustion of ethane, C_2H_6. Then calculate the $\Delta H_{combustion}$.

Write a balanced equation to represent the combustion of ethane, C_2H_6.

- $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O \quad \Delta H_{comb} = ?$
- or $C_2H_6 + 3\frac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O \quad \Delta H_{comb} = ?$

Calculate the heat associated with the combustion of ethane, C_2H_6. Determine the $\Delta H_{combustion}$ using ΔH_f reactions.

1. Break out the thermo sheets to look up the heat of formation for each substance in the chemical equation.
2. $C_2H_{6(g)}$ $\Delta H^o_f = -85$ kJ
3. $O_{2(g)}$ $\Delta H^o_f = 0$ kJ
4. $CO_{2(g)}$ $\Delta H^o_f = -394$ kJ
5. $H_2O_{(g)}$ $\Delta H^o_f = -242$ kJ
6. So what do these numbers mean?

Calculate the heat associated with the combustion of ethane, C_2H_6. Determine the $\Delta H_{combustion}$ using Hess's Law and ΔH_f reactions.

1. A formation reaction is one that describes the formation of a chemical *from* its elements
2. $2C + 3H_2 \rightarrow C_2H_6$ $\Delta H_f = -85$ kJ
3. $C + O_2 \rightarrow CO_2$ $\Delta H_f = -394$ kJ
4. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{(g)}$ $\Delta H_f = -242$ kJ
5. $O_2 \rightarrow O_2$ $\Delta H_f = 0$ kJ
   - really there is no need to look up the ΔH_f of an element as it will always = 0. Forming an element from itself, is to say, no reaction thus no energy change.
6. Use these reactions to "build" the desired reaction.
7. $C_2H_6 + 3\frac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O$ $\Delta H_{comb} = ?$
8. Reverse any reactions and adjust the stoichiometry as necessary to produce the reaction below - changing the ΔH as necessary.

Calculate the heat associated with the combustion of ethane, C_2H_6. Determine the $\Delta H_{combustion}$ using Hess's Law and ΔH_f reactions.

1. $2C + 3H_2 \rightarrow C_2H_6$ $\Delta H_f = -85$ kJ
2. $C + O_2 \rightarrow CO_2$ $\Delta H_f = -394$ kJ
3. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $\Delta H_f = -242$ kJ
4. $O_2 \rightarrow O_2$ $\Delta H_f = 0$ kJ

5. $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$ $\Delta H_{comb} = ?$

6. $C_2H_6 + 3\frac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O$ $\Delta H_{comb} = ?$

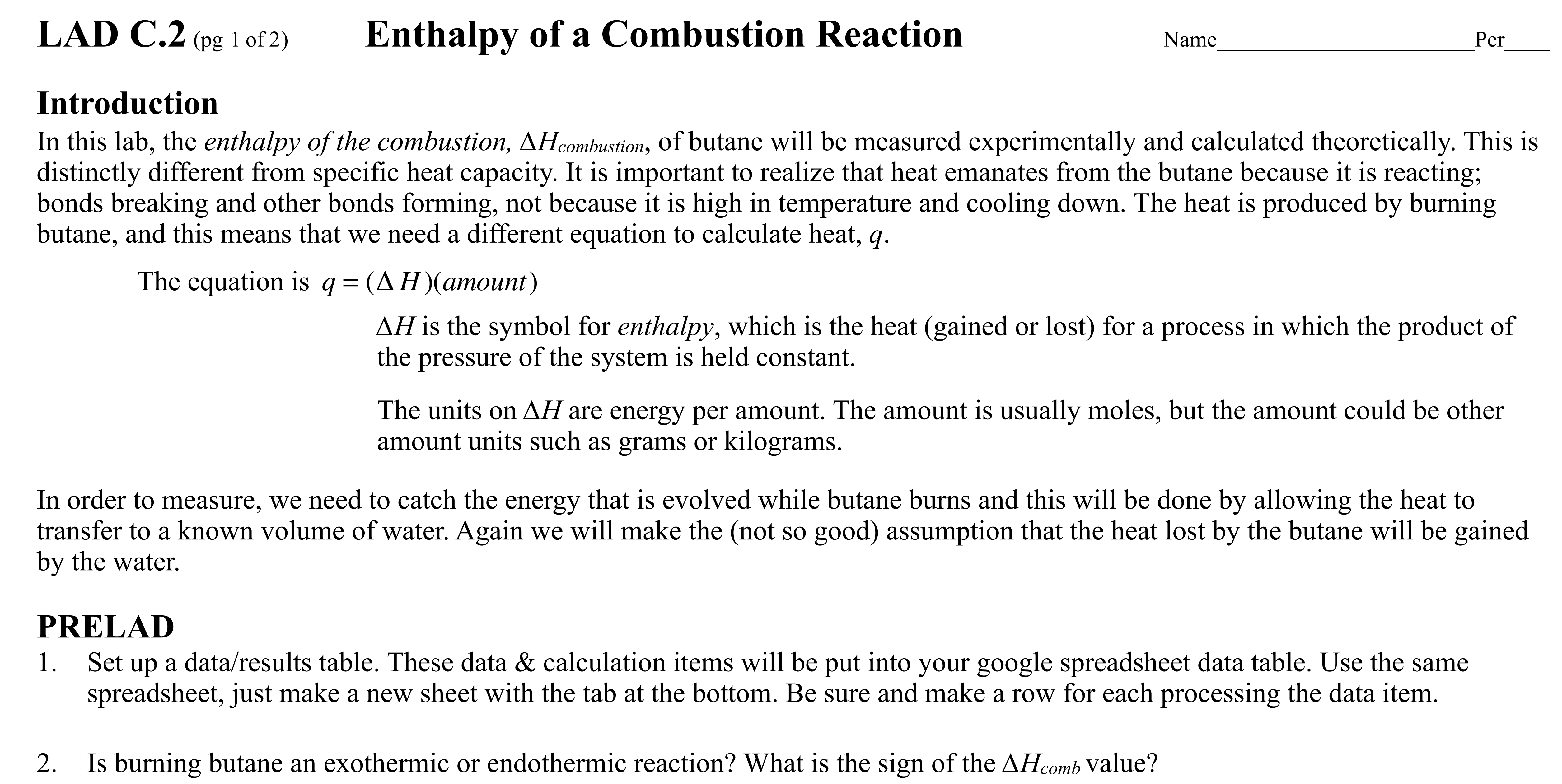
Calculate the heat associated with the combustion of ethane, C_2H_6. Determine the $\Delta H_{combustion}$ using Hess's Law and ΔH_f reactions.

1. $2C + 3H_2 \rightarrow C_2H_6$ $\Delta H_f = -85\ kJ$
2. $C + O_2 \rightarrow CO_2$ $\Delta H_f = -394\ kJ$
3. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $\Delta H_f = -242\ kJ$
4. $O_2 \rightarrow O_2$ $\Delta H_f = 0\ kJ$
5. Shortcut calculation: $\Sigma n\Delta H_{f\ products} - \Sigma n\Delta H_{f\ reactants}$

6. $C_2H_6 + 3\frac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O$ $\Delta H_{comb} = ?$

LAD C.2 – Enthalpy of Combustion

- Here we go…..
- Let's do the preLAD



LAD C.2 (pg 1 of 2) Enthalpy of a Combustion Reaction

Name______________________Per____

Introduction

In this lab, the *enthalpy of the combustion,* $\Delta H_{combustion}$, of butane will be measured experimentally and calculated theoretically. This is distinctly different from specific heat capacity. It is important to realize that heat emanates from the butane because it is reacting; bonds breaking and other bonds forming, not because it is high in temperature and cooling down. The heat is produced by burning butane, and this means that we need a different equation to calculate heat, *q*.

The equation is $q = (\Delta H)(amount)$

ΔH is the symbol for *enthalpy*, which is the heat (gained or lost) for a process in which the product of the pressure of the system is held constant.

The units on ΔH are energy per amount. The amount is usually moles, but the amount could be other amount units such as grams or kilograms.

In order to measure, we need to catch the energy that is evolved while butane burns and this will be done by allowing the heat to transfer to a known volume of water. Again we will make the (not so good) assumption that the heat lost by the butane will be gained by the water.

PRELAD

1. Set up a data/results table. These data & calculation items will be put into your google spreadsheet data table. Use the same spreadsheet, just make a new sheet with the tab at the bottom. Be sure and make a row for each processing the data item.

2. Is burning butane an exothermic or endothermic reaction? What is the sign of the ΔH_{comb} value?

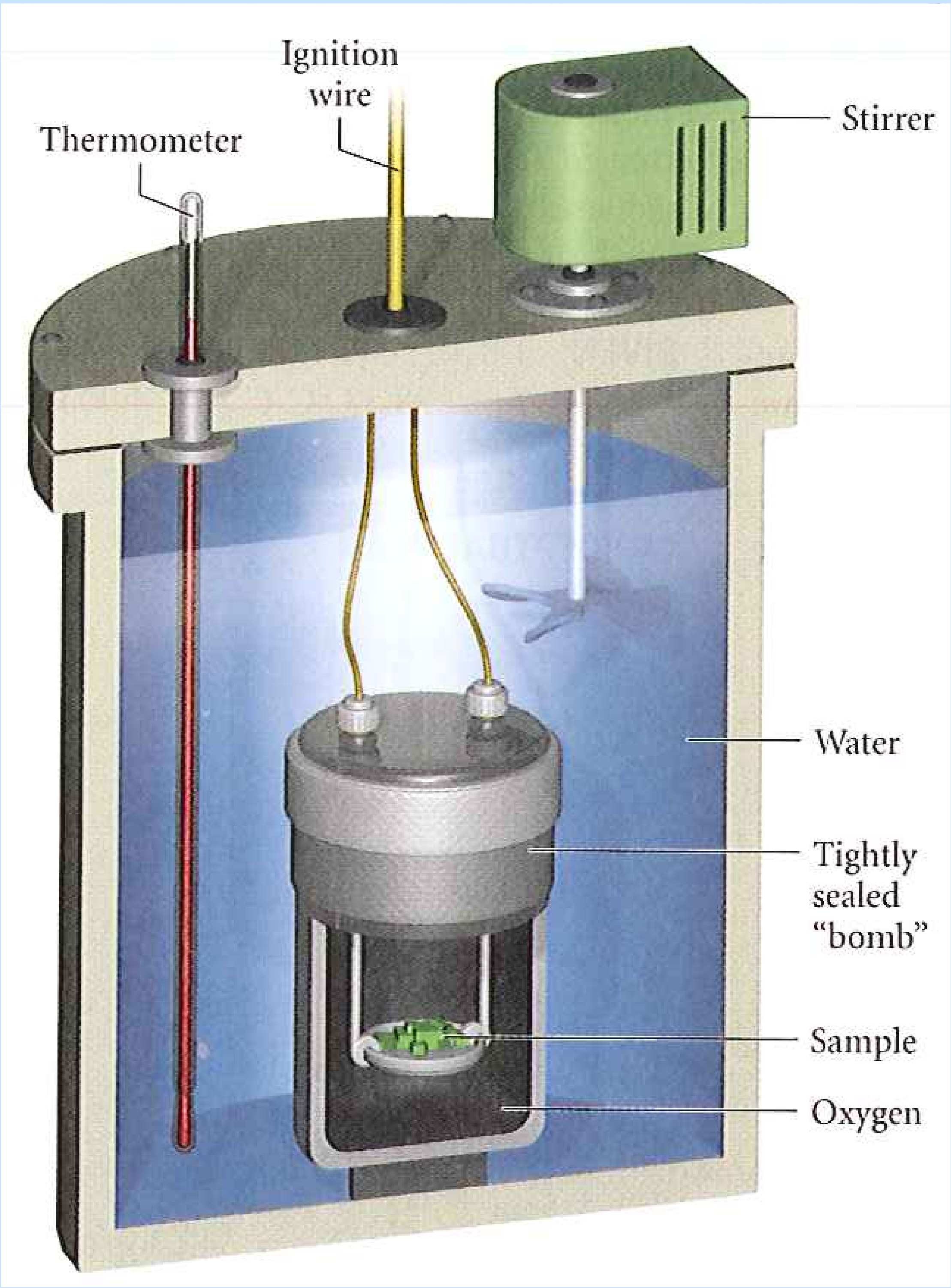
LAD C.2 – Enthalpy of Combustion

- In this Lab, we noticed that our results were especially low, only about 50% of the energy that we expected to be evolved from the reaction, was actually captured by the water.
- Our set up lent itself to so much energy evolved into the air.
- Also, the gases were expanding and “doing work” on the atmosphere. We did not measure that energy.
- To more accurately measure energy evolved during a reaction involving gases, we should use a “bomb” calorimeter which allows the pressure to remain constant, and thus very little energy will be lost as work.

Heat Evolved at Constant Volume

- $\Delta E = q + w$
- but if there is no change in volume, there is no change in work.
- thus $\Delta E = \Delta H$
- We do not have a bomb calorimeter, so all of our energy measurements will be taken in unsealed containers at constant volume.

The Bomb Calorimeter



Energy of Chemical Reactions

- When chemical reactions occur, the internal energy of reactants compared to products is nearly always different, thus there is a ΔE.
- So what's the difference between ΔE and ΔH?
  - ✓ ΔH is a measure of the heat exchanged
  - ✓ ΔE is a measure all the energy exchanged, heat and work, however….
- conceptually and often numerically, they are very similar.
- For this course, we will not worry about any small differences, and use them interchangeably.

Bond Dissociation Energy

Using Bond Dissociation Energies to Estimate ΔH_{rx}

Bond breaking & Bond Forming

Bond Breaking	Bond Forming
Endo	Exo
+	–

break out your Thermodynamic Quantities Sheets

Let’s take a moment to consider how we might represent bonded atoms.

Lewis Structures

1. H_2
2. O_2
3. H_2O
4. CO_2
5. CH_4
6. C_3H_8
7. N_2
8. NH_3

Using bond energies (not using ΔH_f) to estimate ΔH_{rx}

Use bond energy values to estimate the ΔH for $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$

1. Draw Lewis Structure for all molecules.

2. Take an inventory of the bonds breaking (endothermic) and look up bond energy values.

3. Take an inventory of the bonds forming (exothermic) and look up bond energy values.

4. (+bonds breaking) + (−bonds forming) = ΔH_{rx}

   reactants *products*

Using bond energies to estimate ΔH_{rx} Use bond energy values to estimate the ΔH for $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$

- Take an inventory of the bonds breaking (endothermic) and bonds forming (exothermic)
- $2[+(H\text{-}H)] + [+(O{=}O)] + 4[-(H\text{-}O)]$

  bonds breaking bonds forming
- $2[+(436)] + [+(495)] + 4[-(463)] = -485\ \text{kJ/mol}_{rxn}$
- If you look up the heat of formation, 2x(ΔH^o_f) which is 2x(*-241.82) so* for this reaction, you'll get
  - $\Delta H^o_f = -483.64\ \text{kJ/}_{rxn}$....nearly the same

Use the bond dissociation energies (NOT ΔH_f) to estimate ΔH_{comb} for the burning of propane.

1. Write a balanced equation.
2. Draw Lewis Structure for all molecules.
3. Take an inventory of the bonds breaking (endothermic) and look up bond energy values.
4. Take an inventory of the bonds forming (exothermic) and look up bond energy values.
5. (+bonds breaking) + (−bonds forming) = ΔH_{rx}

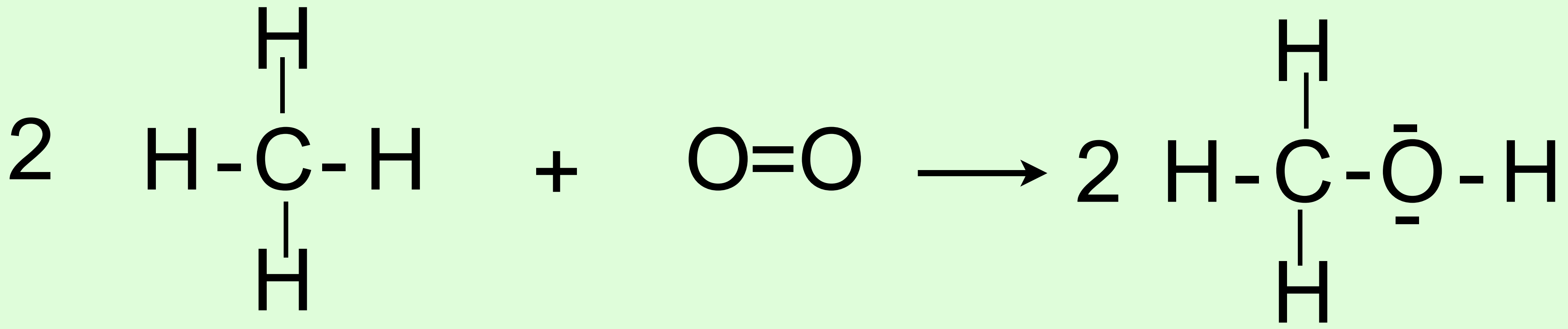
   reactants *products*

Use the bond energies to estimate ΔH_{comb} for the burning of propane.

1. $C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$
2. bonds breaking
   - 2x C−C(348) + 8x C−H(413) + 5x O=O(495) = +6475
3. bonds forming
   - 6x C=O(799) + 8x O−H(463) = -8498
4. (+breaking) + (−forming) = ΔH
   - ΔH_{comb} = (−8498) + (+6475) = −2,023 kJ/mol propane
5. calculate ΔH_{comb} using ΔH^o_f values
   - $\Delta H_{rx} = \Sigma n \Delta H^o_{f\ products} - \Sigma n \Delta H^o_{f\ reactants}$
   - ΔH_{comb} = −2044kJ/mol propane....pretty close to the previous calc
   - What might be causing the difference?
     - ✓ the fact that bond dissociation values are averages and not exact values for the molecules in the reaction. Strength of bonds are affected by nearby atoms and bonds.

Use bond dissociation energies to estimate ΔH_{rxn} for the following reaction: $2\ CH_4 + O_2 \rightarrow 2\ CH_3OH$

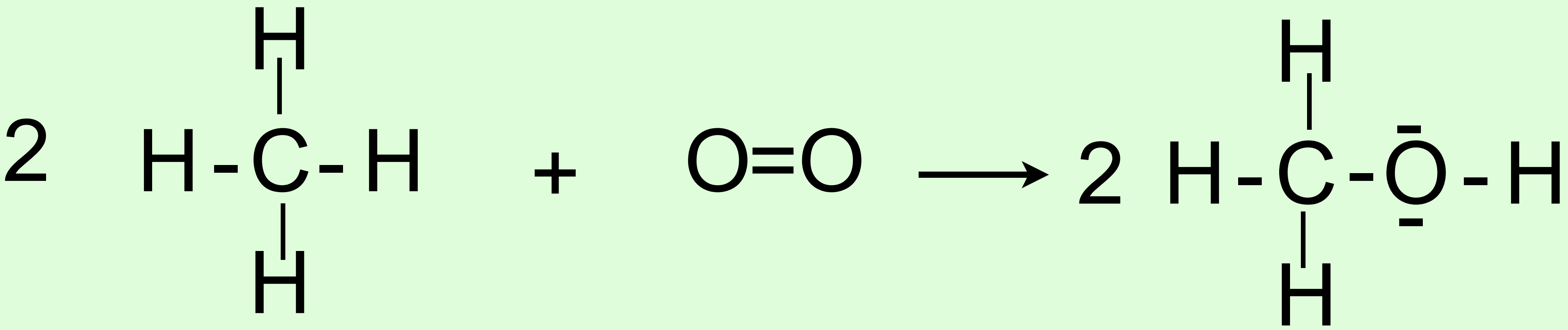
Use bond dissociation energies to estimate ΔH_{rxn} for the following reaction: $2\ CH_4 + O_2 \rightarrow 2\ CH_3OH$



$$2\ \mathrm{H{-}\overset{H}{\underset{H}{C}}{-}H} + \mathrm{O{=}O} \longrightarrow 2\ \mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{-}{\underset{-}{O}}{-}H}$$

1. First lets take a bond inventory.

Use bond dissociation energies to estimate ΔH_{rxn} for the following reaction: $2\,CH_4 + O_2 \rightarrow 2\,CH_3OH$

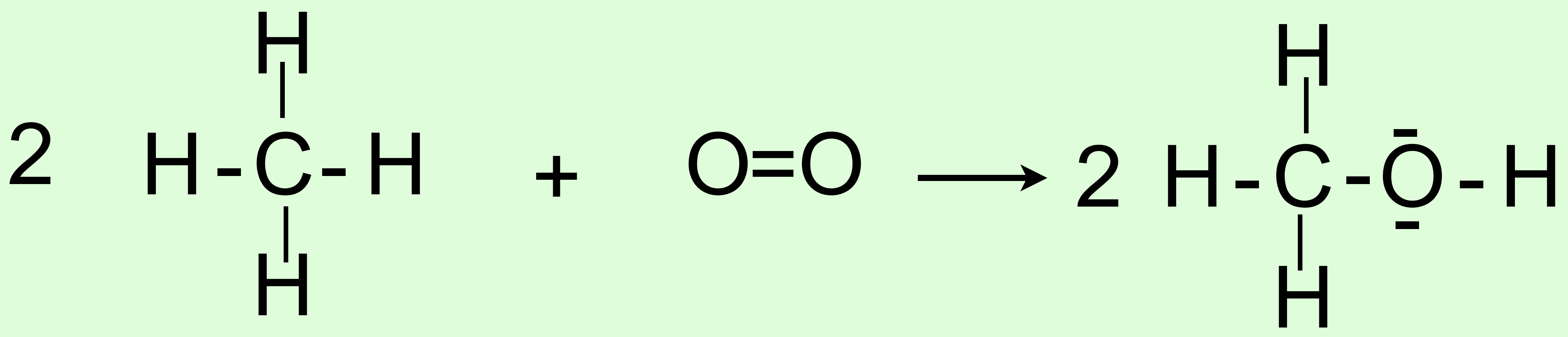


$$2\ \mathrm{H{-}\overset{H}{\underset{H}{C}}{-}H} \quad + \quad \mathrm{O{=}O} \longrightarrow 2\ \mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{-}{\underset{-}{O}}{-}H}$$

1. First lets take a bond inventory.

- C-H 413
- O=O 495
- C-O 358
- O-H 463

Use bond dissociation energies to estimate ΔH_{rxn} for the following reaction: $2\,CH_4 + O_2 \rightarrow 2\,CH_3OH$



$$2\;\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H} \;+\; \mathrm{O{=}O} \longrightarrow 2\;\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}\overline{\underline{O}}{-}H}$$

1. First lets take a bond inventory.

- C-H 413 x8
- O=O 495 x1
- C-O 358 x2
- O-H 463 x2
- C-H 413 x6

Use bond dissociation energies to estimate ΔH_{comb} for the following reaction: $2\ CH_4 + O_2 \rightarrow 2\ CH_3OH$

1. -321 kJ/mol_{rxn}

Use bond dissociation energies to estimate ΔH_{comb} for the following reaction: $H_2 + Br_2 \rightarrow 2\ HBr$

1. First lets take a bond inventory.

Use bond dissociation energies to estimate ΔH_{comb} for the following reaction: $H_2 + Br_2 \rightarrow 2\ HBr$

1. -103 kJ/mol$_{rxn}$

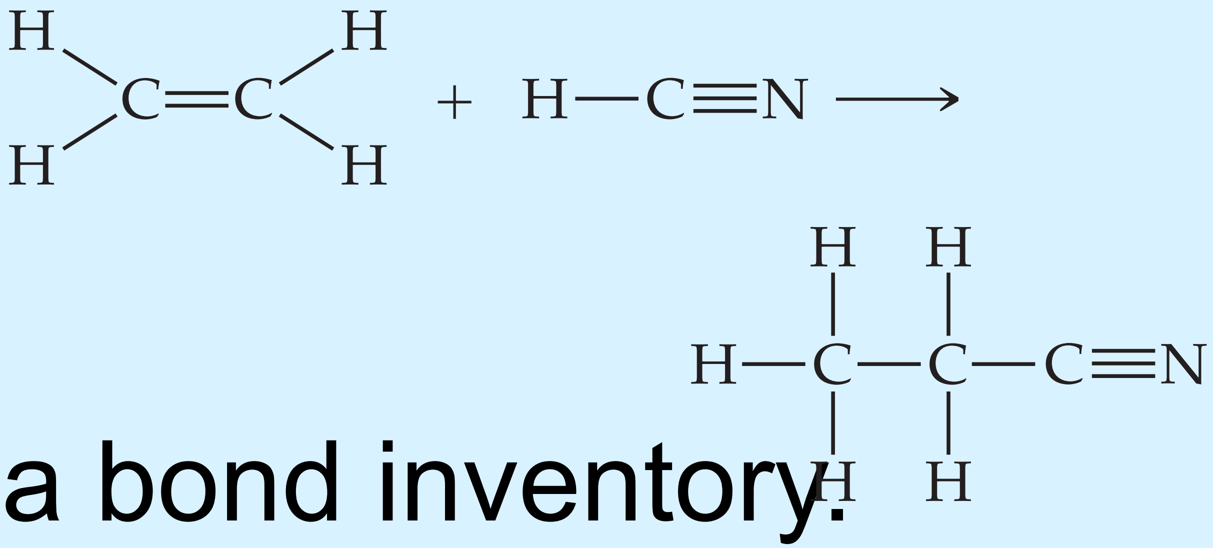
Use bond dissociation energies to estimate ΔH_{comb} for the following reaction: $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$

1. First lets take a bond inventory.

Use bond dissociation energies to estimate ΔH_{comb} for the following reaction: $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$

1. -203 kJ/mol$_{rxn}$

Use bond dissociation energies to estimate ΔH_{comb} for the following reaction:



1. First lets take a bond inventory.

Energy of Dissolving

$\Delta H_{dissolving}$

$\Delta H_{dissolution}$

$\Delta H_{solvation}$

$\Delta H_{sol'n}$

Endo- and Exo- Dissolving

- Sodium hydroxide dissolving is exothermic.
  - ✓ $NaOH_{(s)} \rightarrow Na^+ + OH^- + E$
- potassium sulfate dissolving is endothermic.
  - ✓ $E + K_2SO_{4(s)} \rightarrow 2K^+ + SO_4^{2-}$

- There is no sure way of looking at the chemical formula of a substance and knowing if the dissolving process is exo- or endothermic.

- You might be asking yourself “why is the NaOH exothermic?” After all, it seems as if this is a bond breaking process.

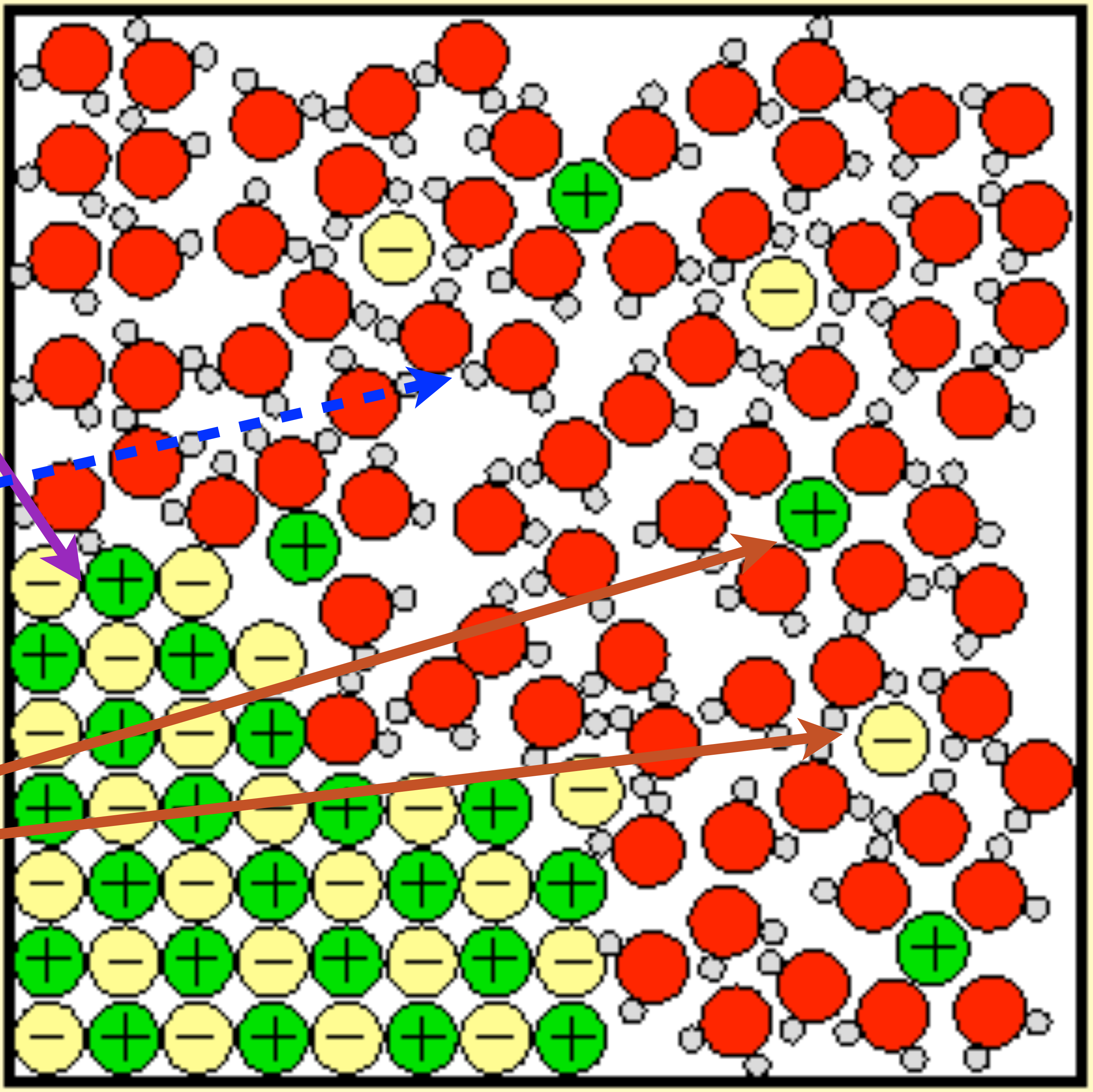
Just what is going on during the dissolving process?

- Since the dissolving of some salts is exo thermic, there must be more going on than just breaking the ionic bonds of the crystal.

✓ $NaOH_{(s)} \rightarrow Na^{+} + OH^{-} + E$

- Actually, there are three separate processes involved. Let's take a look...

A Static Look at Hydration



1. Energy IN to break apart the crystal structure,

2. Energy IN to separate the hydrogen bonding" between water molecules,

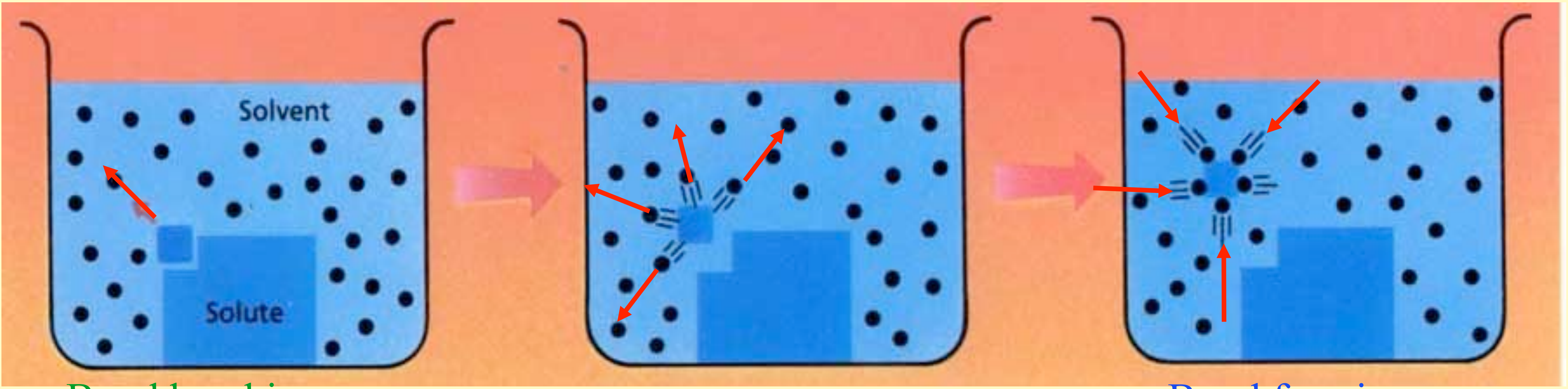
3. Energy out as the cations and anions make "bonds" with the water molecules

Intermolecular forces that occur during solution formation

- Bonds between *solute* particles (the crystal) to be broken
  - ✓called Lattice Energy of the ionic crystal, ENDO-
- “Bonds” between *solvent* molecules (water) are broken
  - ✓called dipole–dipole interactions ENDO-
- “Bonds” between the *solute* and the *solvent* particles (+/- ions and polar water) are formed
  - ✓called ion–dipole interactions   EXO-

Enthalpy of Dissolving Process

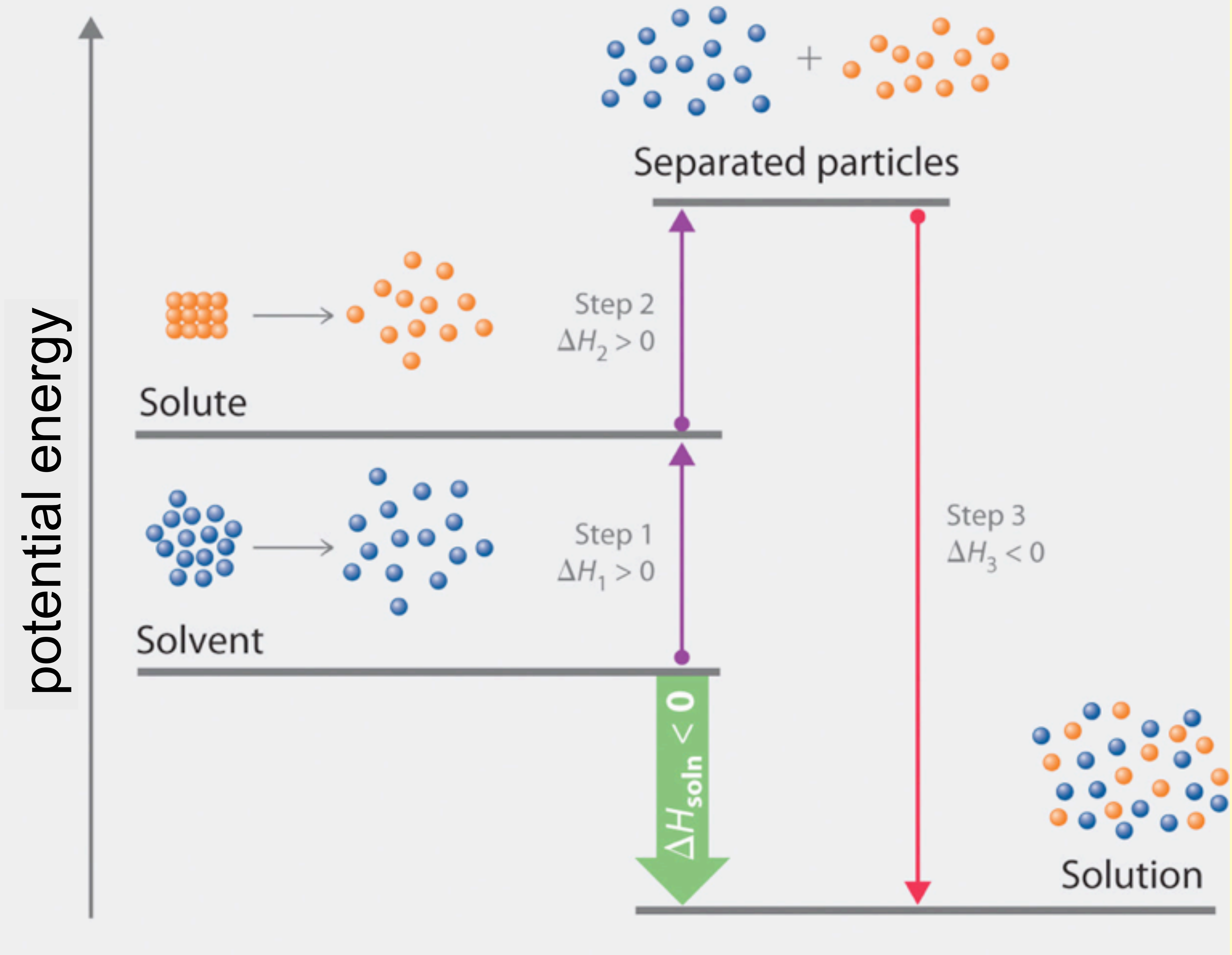
ΔH_1 + ΔH_2 + ΔH_3 −



Bond breaking "Bond" breaking Bond forming

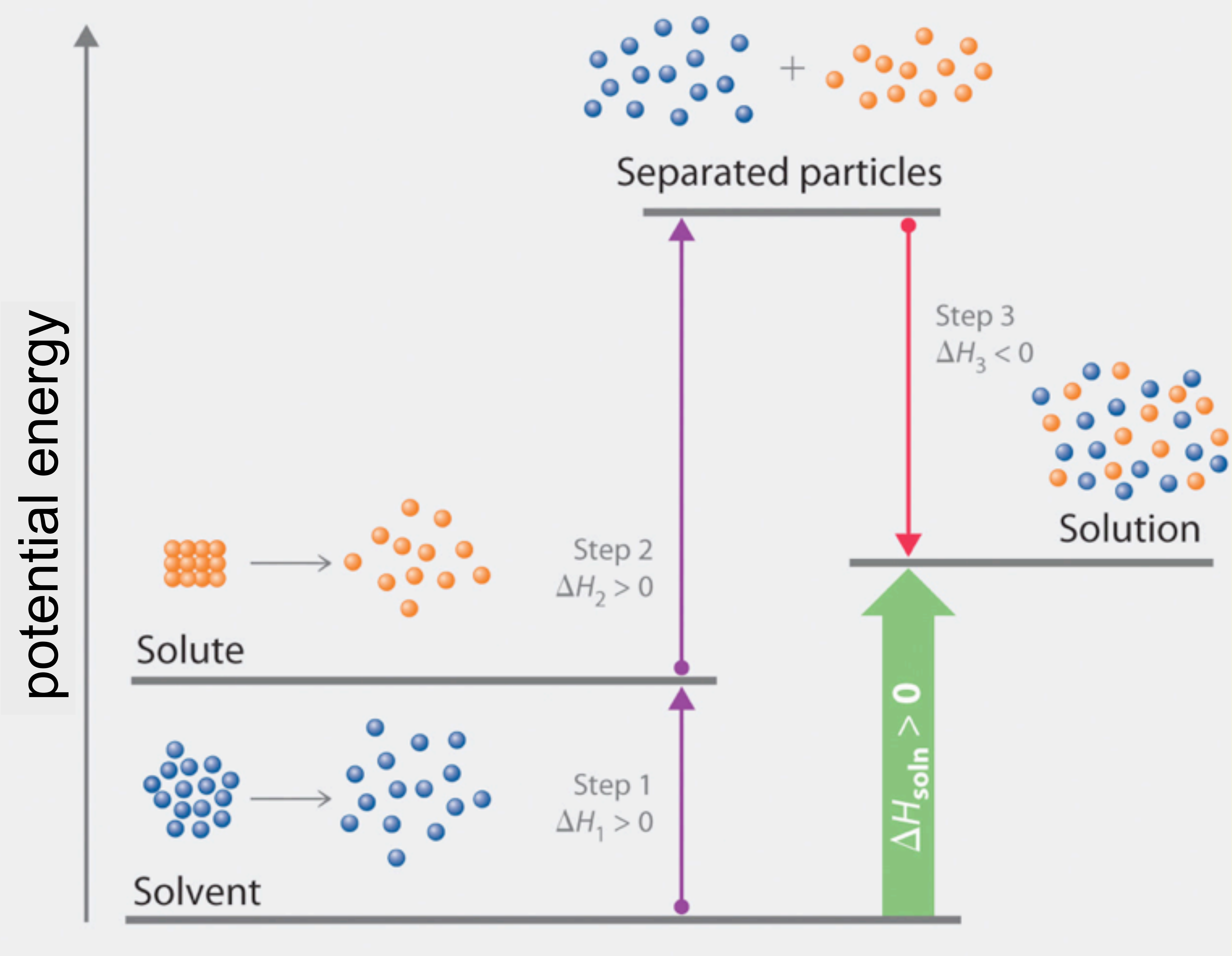
- ΔH_1 = lattice energy (endothermic) [bond breaking]
- ΔH_2 = solvent IMF (endothermic) ["bond" breaking]
- ΔH_3 = energy of solvation (exothermic) ["bond" forming]
- $\Delta H_{sol'n} = \Delta H_1 + \Delta H_2 + \Delta H_3$
- The sign of the $\Delta H_{sol'n}$ depends on the magnitude of the endothermic processes compared to the exothermic process.

Exothermic



- *two parts endo, one part exo: net result = exo*

Endothermic



- *two parts endo, one part exo*

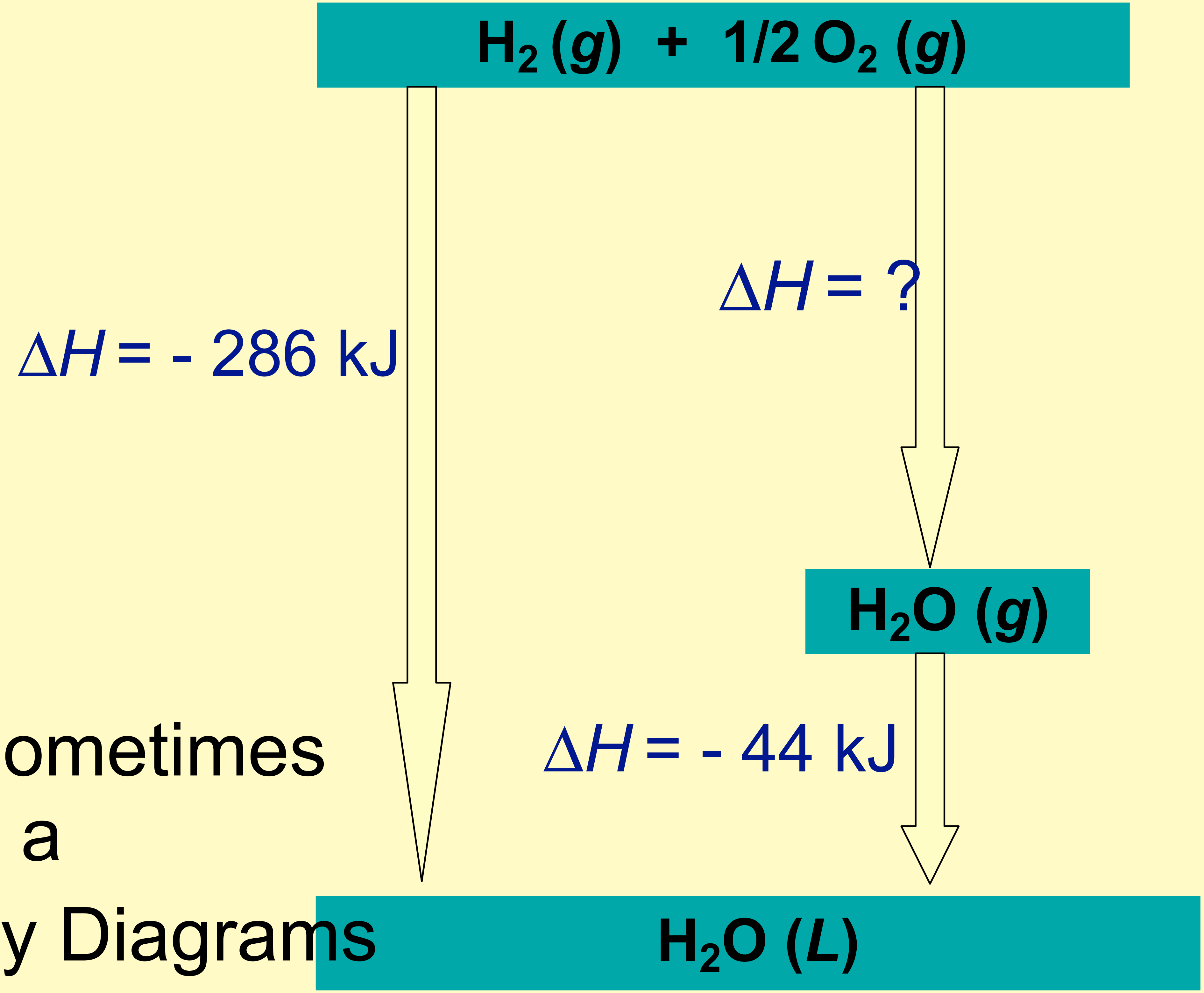
LAD C.3 Hess' Law

Let's do an experiment in which it is easier for us to contain the heat, and there are no gases formed, in hopes of obtaining better $\Delta H_{reaction}$ values.

More Clicker Questions

What is the value of the unknown ΔH in the *Energy Diagram* below?

1. +330 kJ
2. -330 kJ
3. +286 kJ
4. -242 kJ
5. +242 kJ



The AP Exam sometimes refers to this as a *Potential* Energy Diagrams

What is the value of the unknown ΔH in the energy diagram below?

1. +330 kJ
2. -330 kJ
3. +286 kJ
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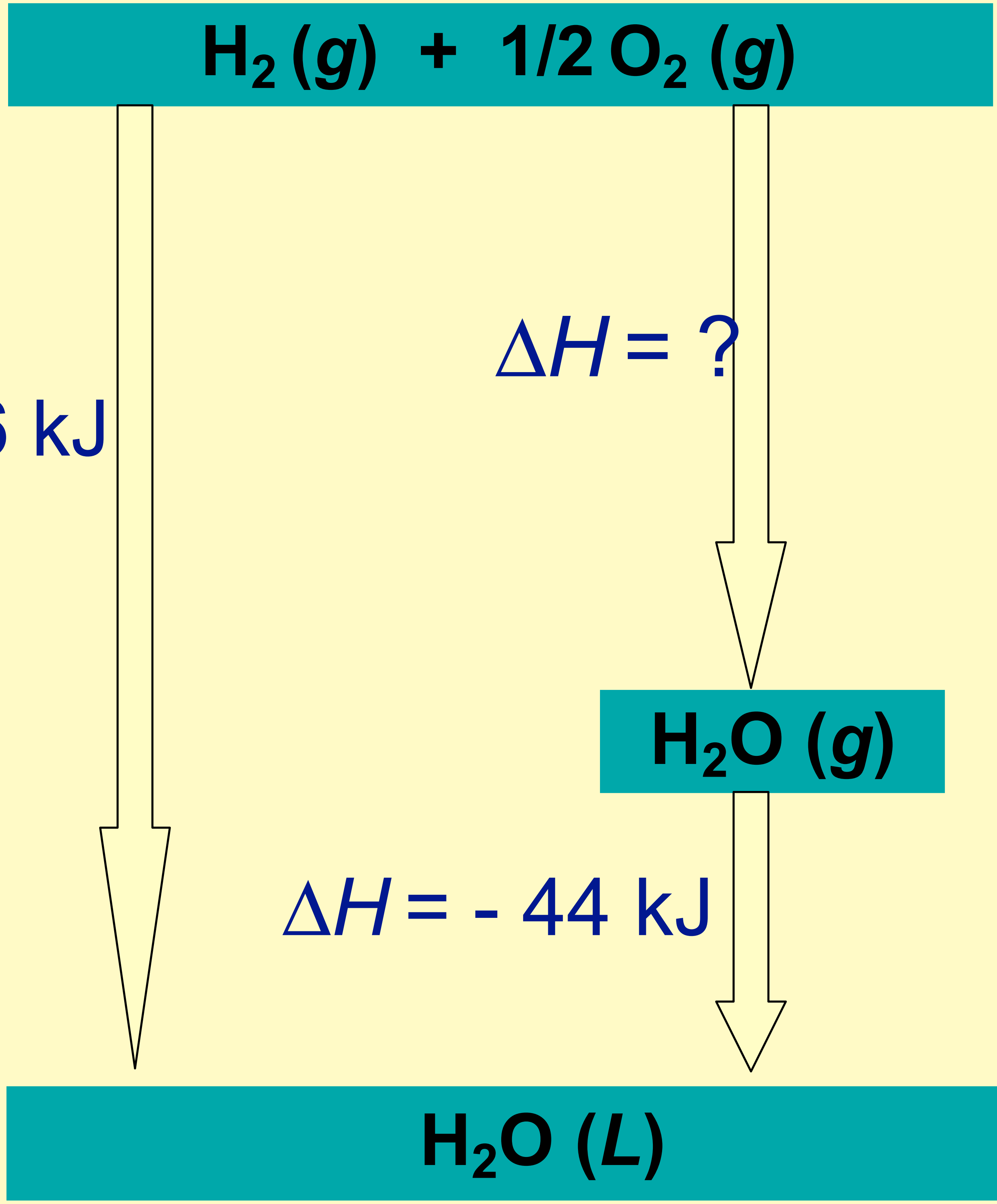


$H_2\,(g)\ +\ 1/2\,O_2\,(g)$

$\Delta H = -\,286$ kJ

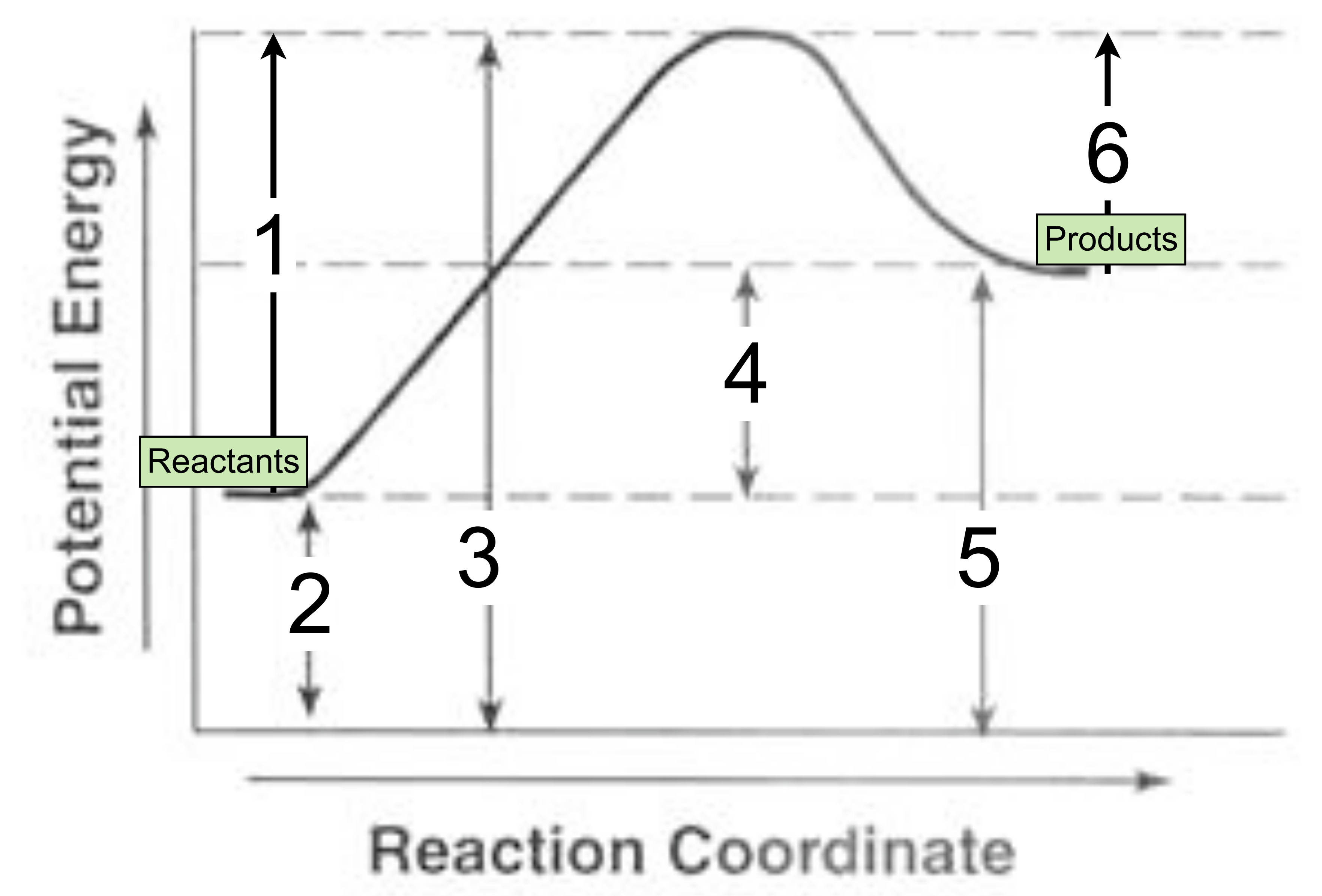
$\Delta H = ?$

$H_2O\,(g)$

$\Delta H = -\,44$ kJ

$H_2O\,(L)$

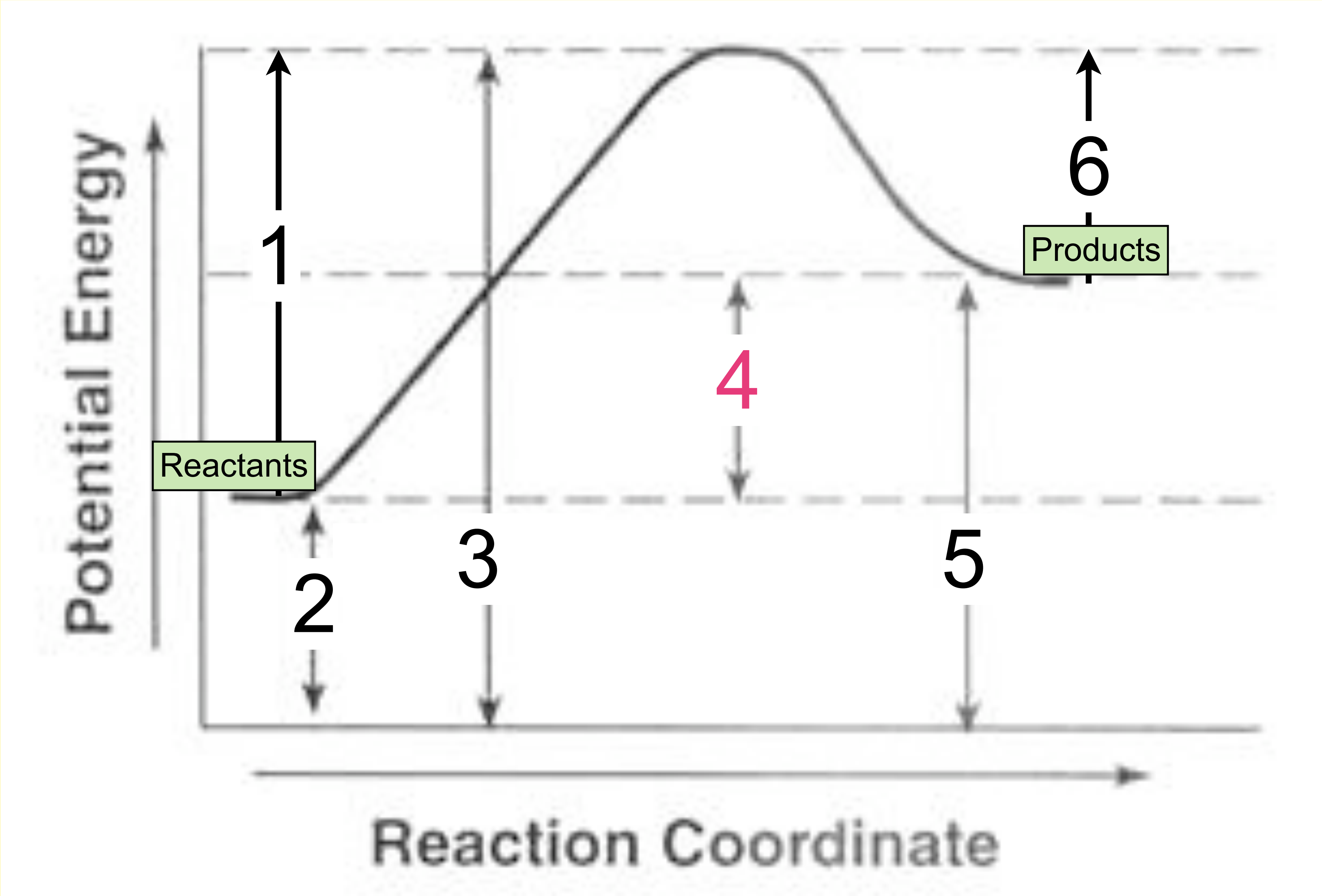
Which number in the potential energy diagram shown below, represents the heat of the reaction, ΔH?



or time, or progress of reaction

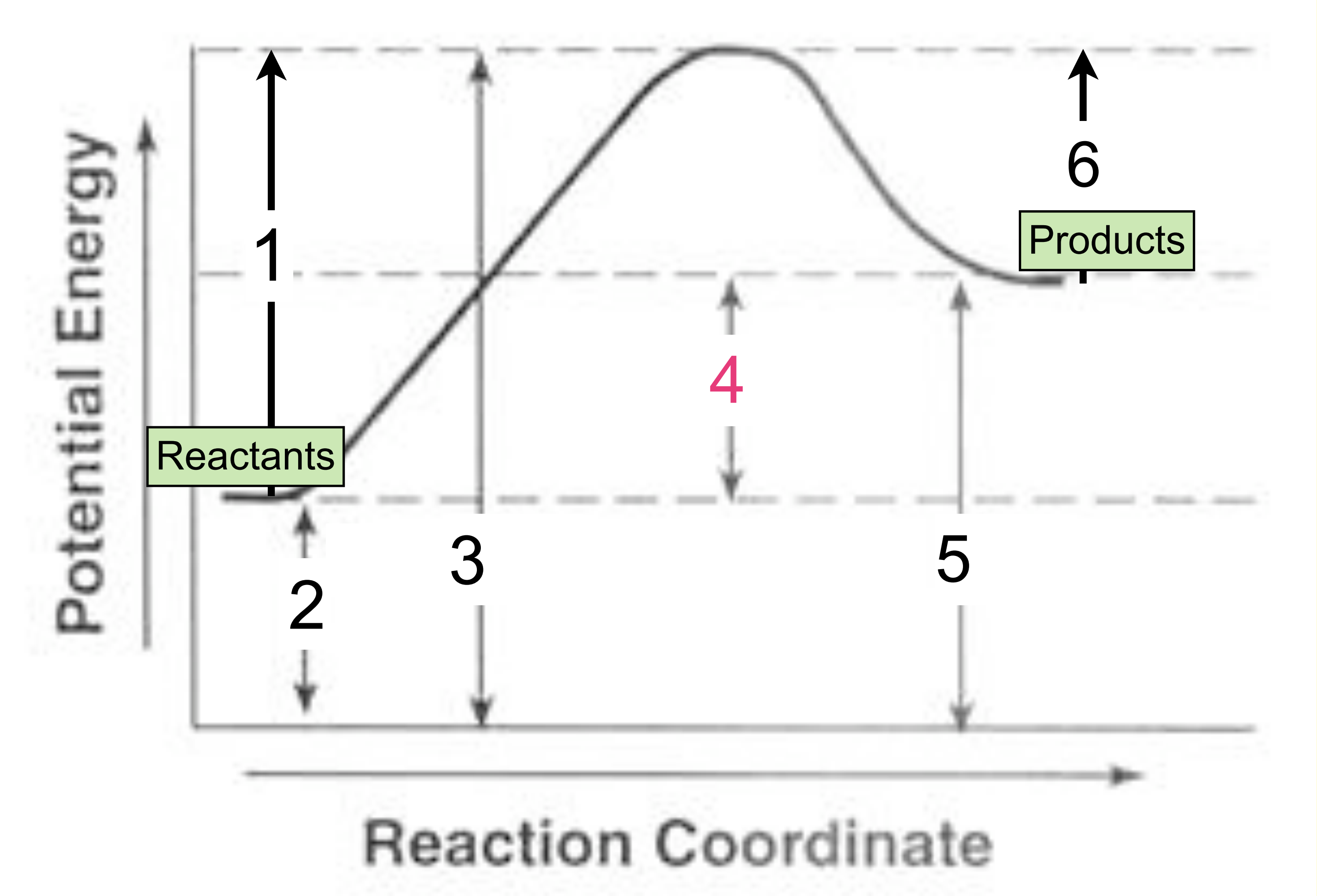
Which letter in the potential energy diagram shown below, represents the heat of the reaction, ΔH?

- ΔH represents the “net” energy difference between he reactants and the products



The reaction represented by this graph

1. is exothermic
2. is endothermic
3. There is not enough information to determine the energetics of this reaction.



In a chemical reaction, the difference between the potential energy of the products and the potential energy of the reactants is defined as

1. activation energy
2. ionization energy
3. heat of vaporization
4. heat of reaction
5. kinetic energy
6. lattice energy

In a chemical reaction, the difference between the potential energy of the products and the potential energy of the reactants is defined as

1. activation energy
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The reaction represented by this graph

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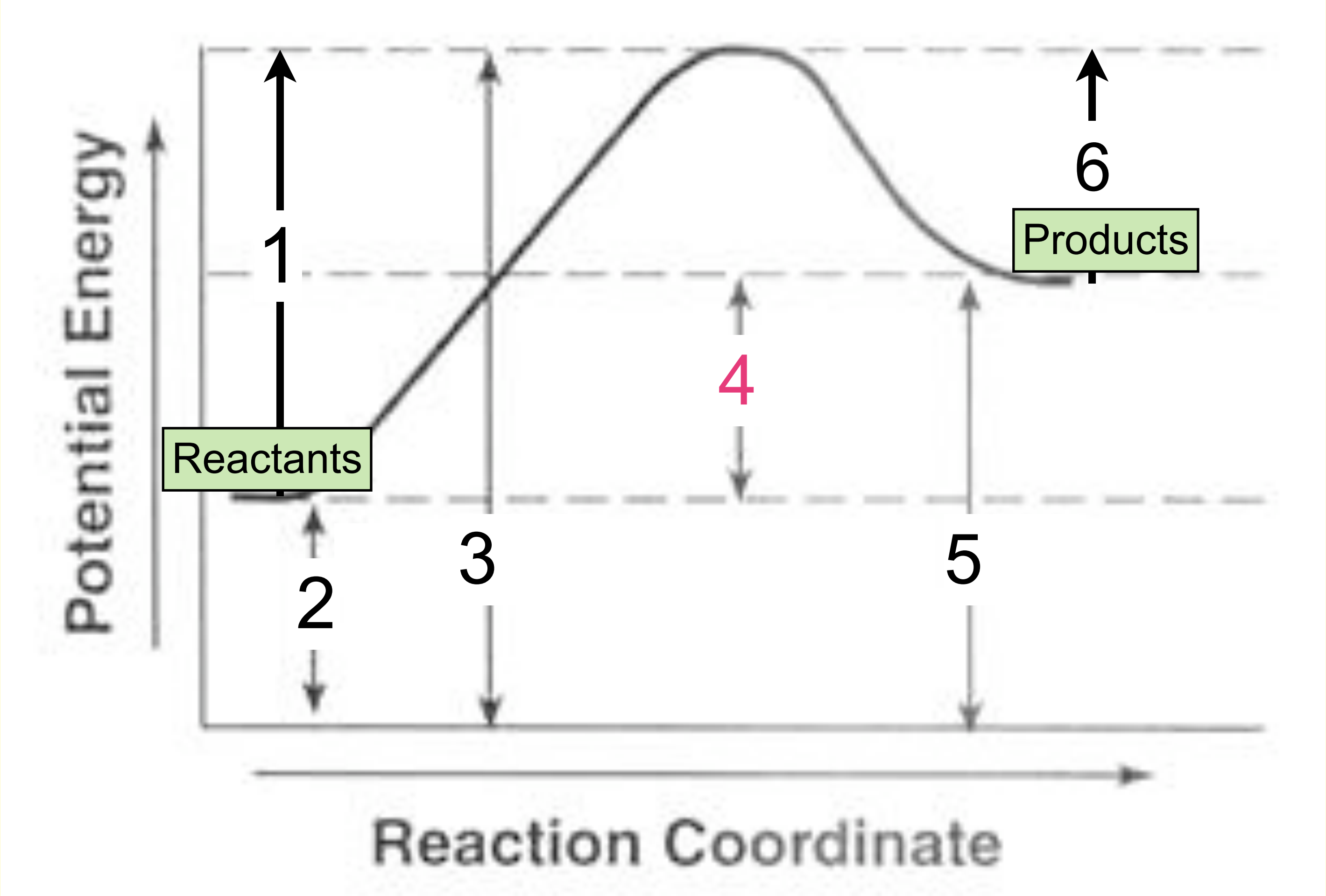
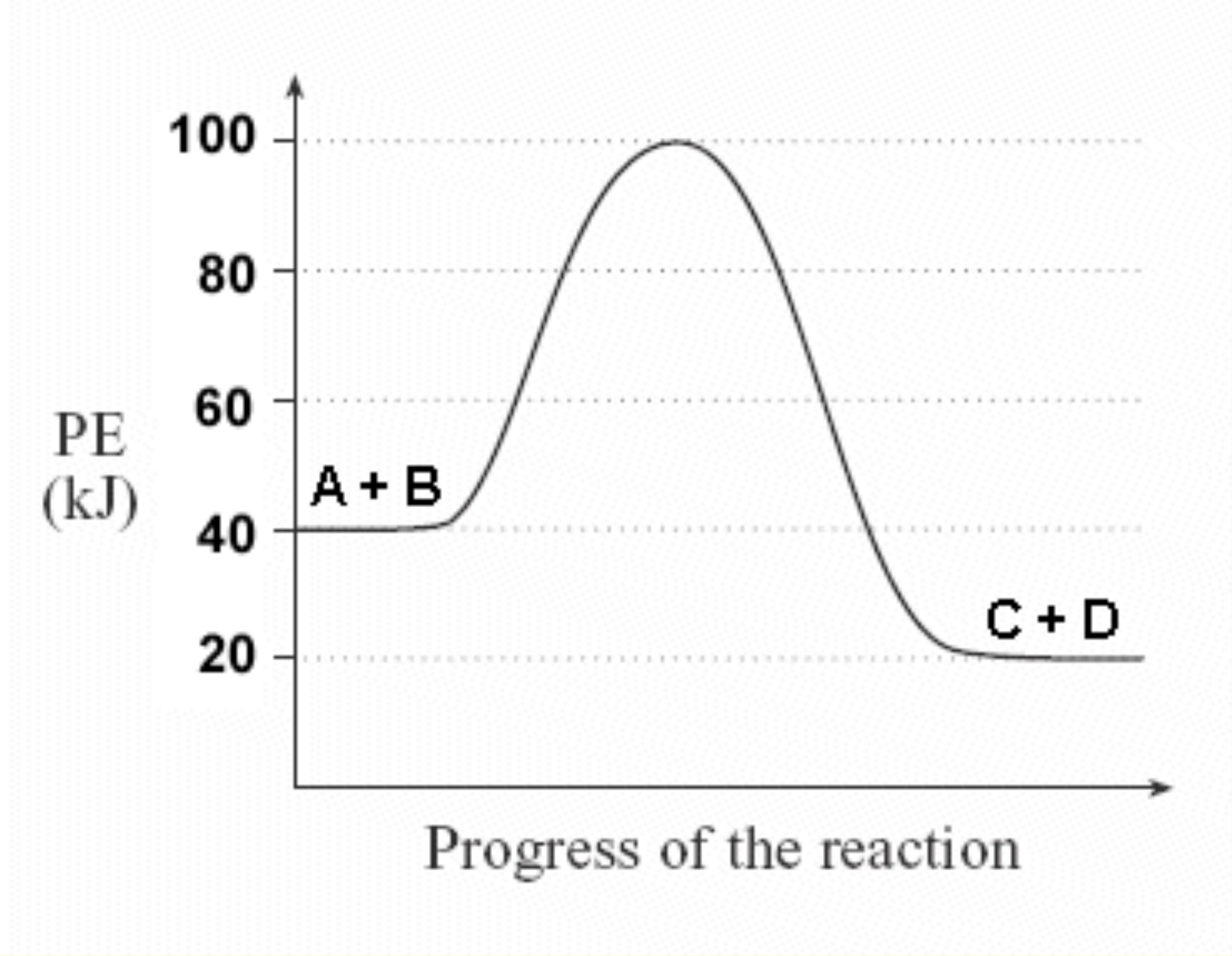


For the reaction represented by the potential energy diagram below, the total bond dissociation energy of the products (C + D) is __________ the bond dissociation energy of the reactants (A + B).

1. greater than
2. less than
3. the same as
4. none of the above, because this cannot be determined from this graph.



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1. greater than
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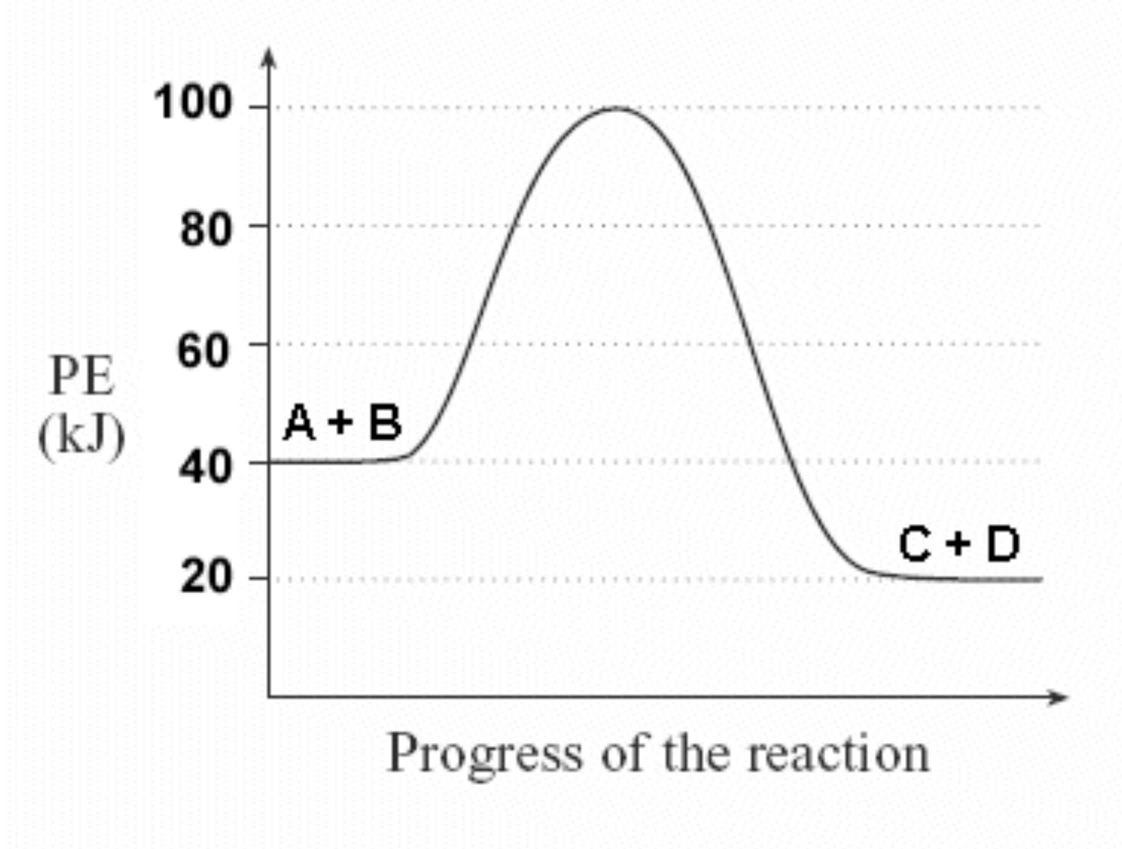
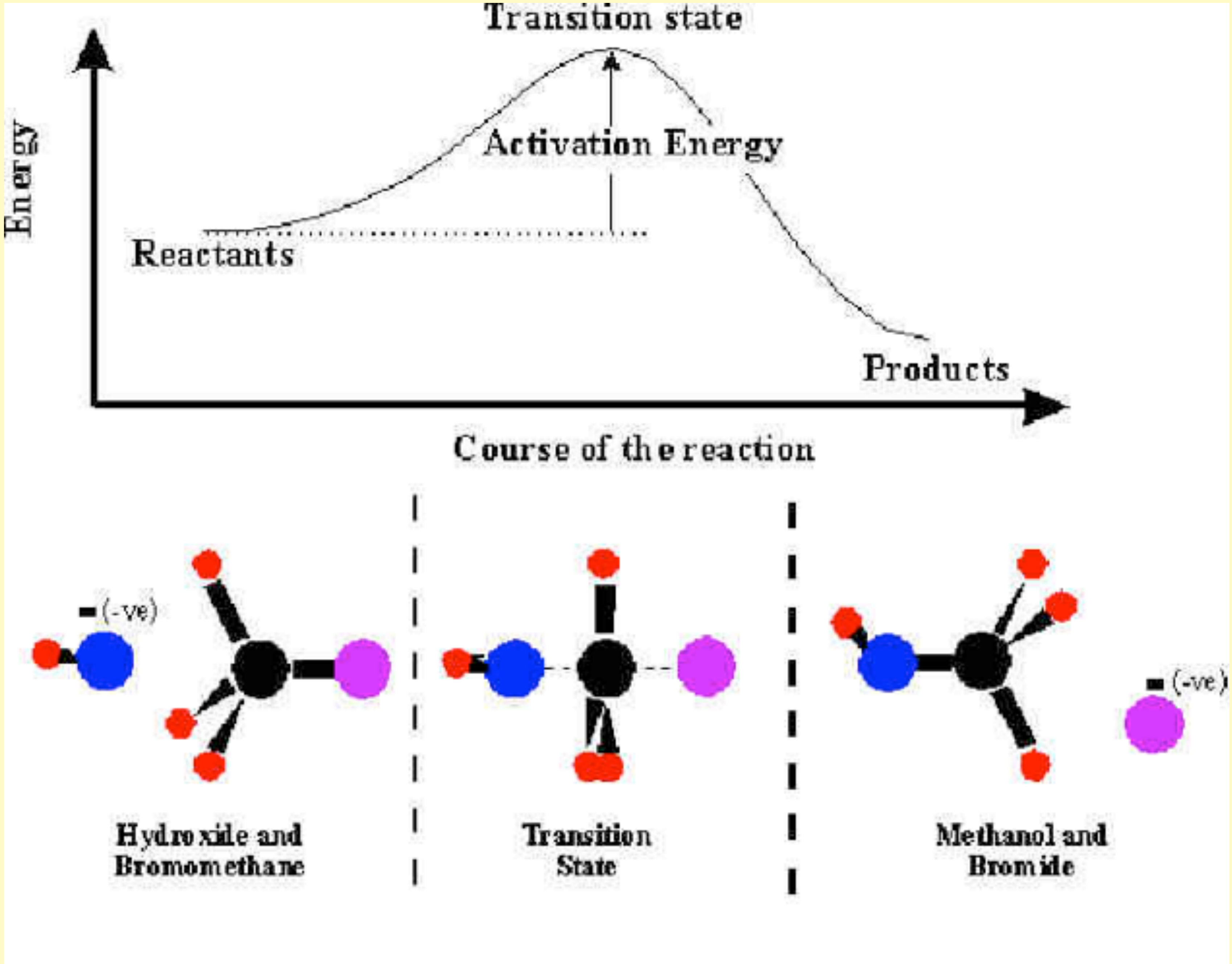
4. none of the above, because this cannot be determined from this graph.

$$BDE_{react} + (-BDE_{prod}) = \Delta H$$



- We know this because there is more energy produced by the formation of the products than needed to break the reactants.

Why is there a peak on these potential energy graphs and what’s going on there?



The heat of formation for *liquid* benzene is represented below

$6C_{(graphite)} + 3H_{2(g)} \rightarrow C_6H_{6(L)} \quad \Delta H^o_f = +49 \text{ kJ}$

The ΔH^o_f for *gaseous* benzene would be

1. greater positive value
2. smaller positive value
3. more likely to be negative
4. unable to determine

The heat of formation for liquid benzene is represented below

$6C_{(s)} + 3H_{2(g)} \rightarrow C_6H_{6(L)} \quad \Delta H^o_f = +49\ \text{kJ}$

The ΔH^o_f for gaseous benzene is

1. greater positive value

- you could use Hess' Law to consider this…
- $6C_{(s)} + 3H_{2(g)} \rightarrow C_6H_{6(L)} \quad \Delta H^o_f = +49\ \text{kJ}$
- $C_6H_{6(L)} \rightarrow C_6H_{6(g)} \quad \Delta H^o_{vaporization} = +$

2. smaller positive value
3. more likely to be negative
4. unable to determine

Consider the following thermochemical equation:

$2H_2O_{(L)} + 570\ \text{kJ} \rightarrow 2H_{2(s)} + O_{2(g)}$

The ΔH^o_f for liquid water is

1. $(+570)^2$
2. $(-570)^2$
3. $(+570)^{½}$
4. $(-570)^{½}$
5. $\frac{-570}{2}$
6. -570
7. $+570$
8. $\frac{+570}{2}$

Consider the following thermochemical equation:

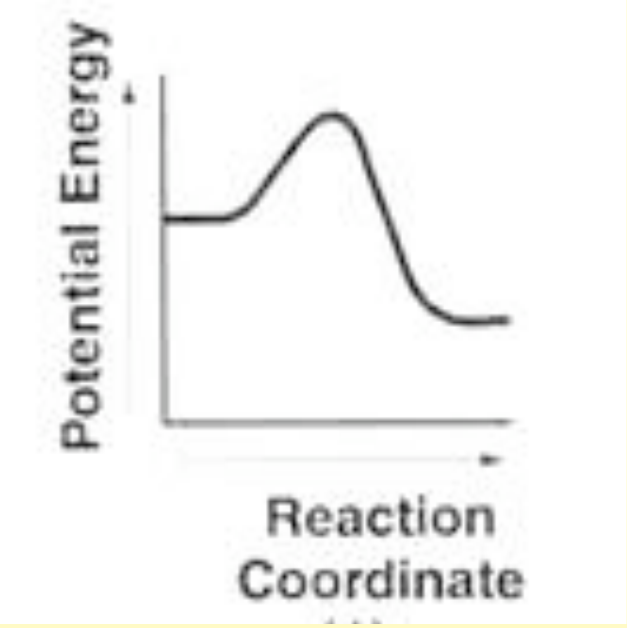
$2H_2O_{(L)} + 570\text{ kJ} \rightarrow 2H_{2(s)} + O_{2(g)}$

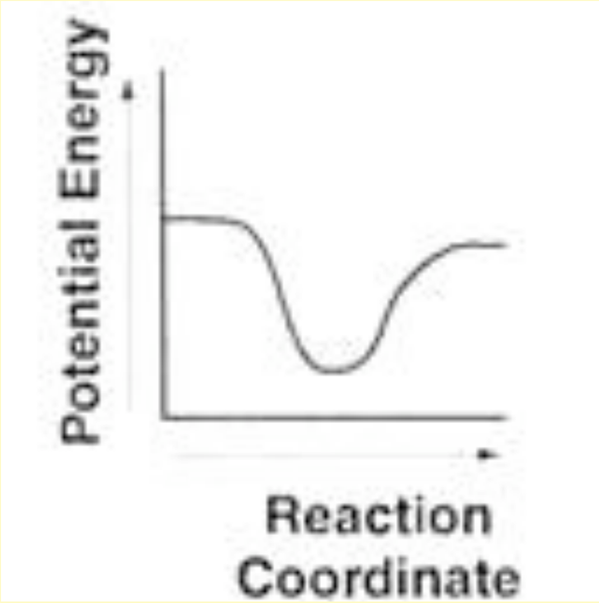
The $\Delta H^o{}_f$ for liquid water is

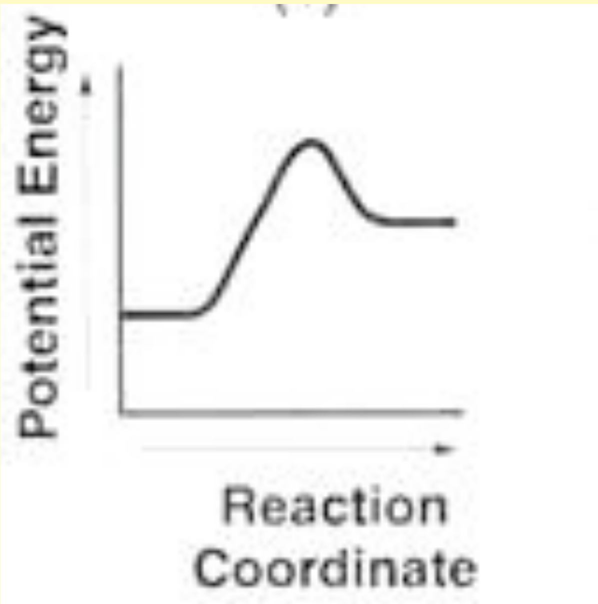
1. $(+570)^2$
2. $(-570)^2$
3. $(+570)^{½}$
4. $(-570)^{½}$
5. $\frac{-570}{2}$
6. -570
7. $+570$
8. $\frac{+570}{2}$

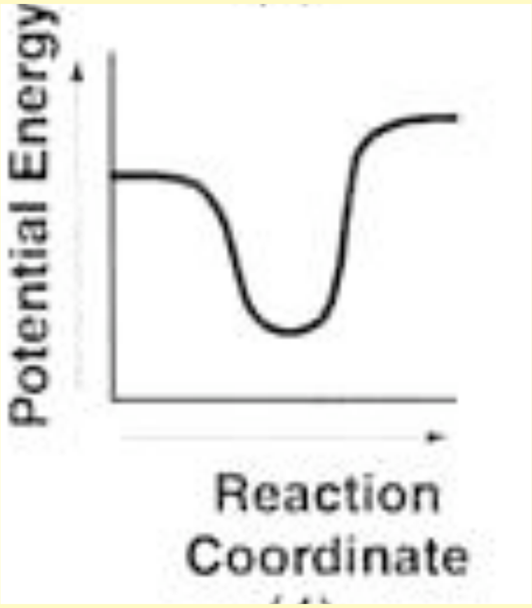
- When you take the thermochemical value out of the equation above, because it is exothermic, you need to represent it as negative.
- In addition, $\Delta H^o f$ values are always per mole of whatever is being formed from its elements.

Which energy diagram below best represents the formation of liquid water?

1. 

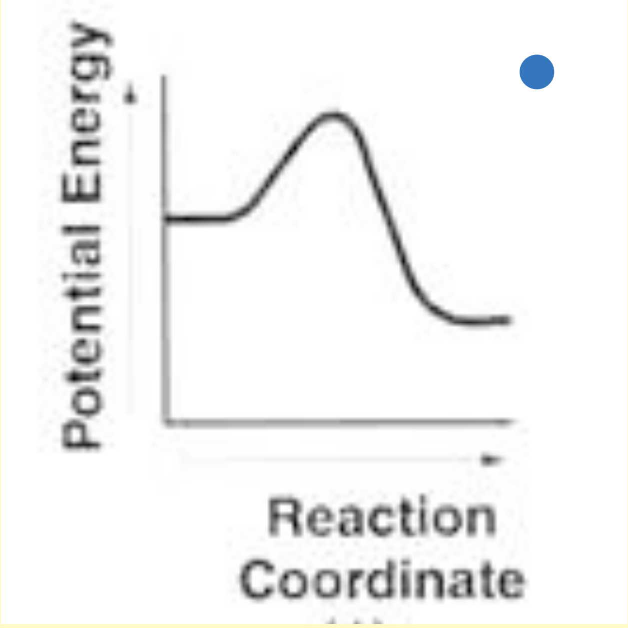
2. 

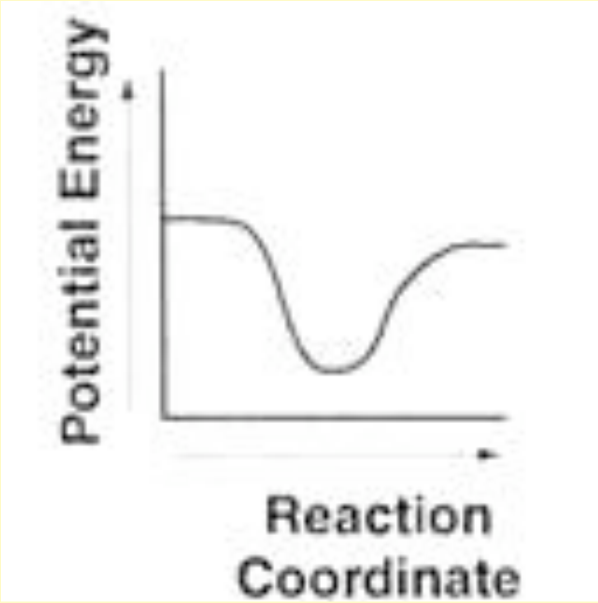
3. 

4. 

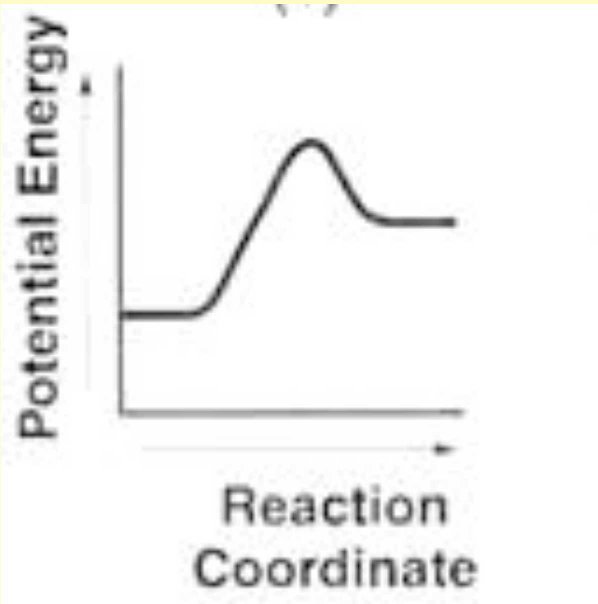
5. None of the choices are valid.

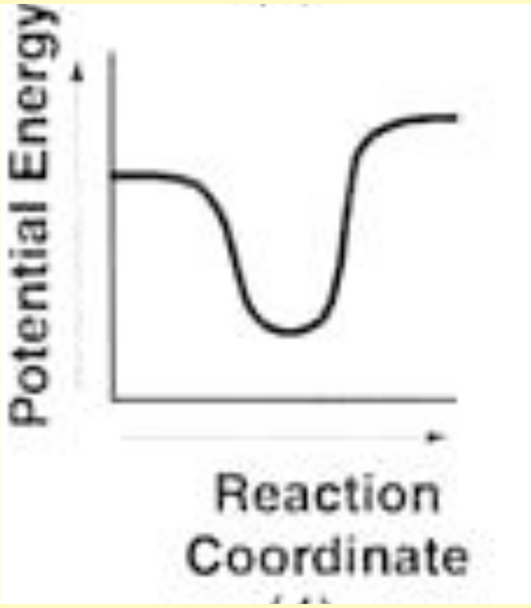
Which energy diagram below best represents the formation of liquid water?

1.


2.


- since we learned in the last slide that the formation of liquid water is exothermic.

3.


4.


5. None of the choices are valid.

Use your Thermodynamic Tables to calculate the ΔH for the process of vaporizing solid iodine, I_2

Input your numeric answer.

Use your Thermodynamic Tables to calculate the ΔH for the process of vaporizing solid iodine, I_2

$I_{2(s)} \rightarrow I_{2(g)}$

$\Delta H_{vap} = \Sigma n \Delta H^{o}_{f\,\mathrm{products}} - \Sigma n \Delta H^{o}_{f\,\mathrm{reactants}}$

+62.25 kJ/mole - 0 kJ/mole

thus $\Delta H_{vap} = +62.25/\text{mole } I_{2(s)}$

Use your Thermo Tables, and the enthalpy for the reaction given below to calculate the ΔH^o_f for gaseous propanol.

$C_3H_7OH_{(g)} + {}^9/_2O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$

$\Delta H_{combustion} = -2061$ kJ/mole alcohol

Enter a value rounded to the nearest whole number.

Use your Thermo Tables, and the enthalpy for the reaction given below to calculate the ΔH^o_f for gaseous propanol.

$C_3H_7OH_{(g)} + {}^9/_2O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(g)}$

$\Delta H_{combustion} = -2061$ kJ/mole

- $\Delta H_{rx} = \Sigma n\Delta H^o_{f\ products} - \Sigma n\Delta H^o_{f\ reactants}$
- $[3(-393.5) + 4(-241.82)] - [(x) + (0)] = -2061$ kJ
- $x = H^o_f$ for $C_3H_7OH_{(g)} = -87$ kJ

Which reaction best represents the ΔH^o_f reaction for solid sodium nitrate?

1. $Na^+_{(aq)} + NO_3^-{}_{(aq)} \rightarrow NaNO_{3(aq)}$
2. $Na^+_{(aq)} + NO_3^-{}_{(aq)} \rightarrow NaNO_{3(s)}$
3. $Na^+_{(g)} + NO_{3(g)} \rightarrow NaNO_{3(s)}$
4. $Na_{(s)} + NO_{3(s)} \rightarrow NaNO_{3(s)}$
5. $2Na_{(s)} + N_{2(g)} + 3O_{2(g)} \rightarrow 2NaNO_{3(s)}$
6. $Na_{(s)} + \frac{1}{2}N_{2(g)} + {}^{3}/_{2}O_{2(g)} \rightarrow NaNO_{3(s)}$

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- Heat of formation reactions are always per mole of the “formed” chemical.

$2B_{(s)} + 3H_{2(g)} \rightarrow B_2H_{6(g)}$

Use the reactions below to determine the ΔH for formation of diborane shown above.

$2B_{(s)} + {}^{3}/_{2}O_{2(g)} \rightarrow B_2O_{3(s)}$ $\Delta H = a$

$B_2H_{6(g)} + 3O_{2(g)} \rightarrow B_2O_{3(s)} + 3H_2O_{(g)}$ $\Delta H = b$

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(L)}$ $\Delta H = c$

$H_2O_{(L)} \rightarrow H_2O_{(g)}$ $\Delta H = d$

1. a+b+c+d
2. a-b+3c
3. a-b+3c+3d
4. b-a+c^3
5. b-a+3d
6. b-a-3c-3d
7. some other sum not listed above

$2B_{(s)} + 3H_{2(g)} \rightarrow B_2H_{6(g)}$

Use the reactions below to determine the ΔH for formation of diborane shown above.

$2B_{(s)} + {}^3/_2O_{2(g)} \rightarrow B_2O_{3(s)}$ $\Delta H=a$

$B_2H_{6(g)} + 3O_{2(g)} \rightarrow B_2O_{3(s)} + 3H_2O_{(g)}$ $\Delta H=b$

$H_{2(g)} + ½O_{2(g)} \rightarrow H_2O_{(L)}$ $\Delta H=c$

$H_2O_{(L)} \rightarrow H_2O_{(g)}$ $\Delta H=d$

1. a+b+c+d
2. a-b+3c
3. a-b+3c+3d
4. b-a+c^3
5. b-a+3d
6. b-a-3c-3d
7. some other sum not listed above

Select the unit label(s) that would be appropriate for ΔH^o_f

1. kJ
2. kJ/mole
3. kJ/mole°C
4. J/g
5. J/°C
6. J/g°C
7. calories/mg

Select the unit label(s) that would be appropriate for ΔH°_{f}

1. kJ
2. kJ/mole
3. kJ/mole°C
4. J/g
5. J/°C
6. J/g°C
7. calories/mg