Thermochemistry

Dr. Ron Rusay

Energy

Joules (J) / calorie (cal) : (4.184 J = 1 cal)

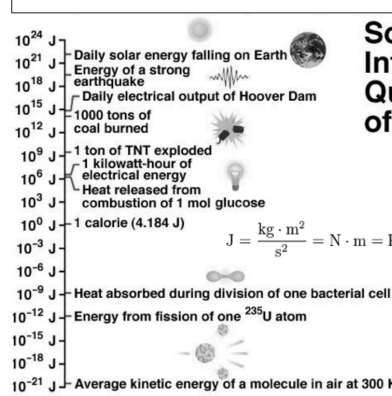
- *Can be defined as the capacity to do work.*
- *Chemical energy is defined as heat.*
- *Name five other types of Energy.*

$$J = \frac{kg \cdot m^2}{s^2} = N \cdot m = Pa \cdot m^3 = W \cdot s = C \cdot V$$

Two Types of Energy

- *Potential: due to an object's position or material's composition - which can be converted to work*
- *Kinetic: due to motion of an object*
  - *$KE = \frac{1}{2} mv^2$*
  - *(m = mass, v = velocity)*

Some Interesting Quantities of Energy



$$J = \frac{kg \cdot m^2}{s^2} = N \cdot m = Pa \cdot m^3 = W \cdot s = C \cdot V$$

Law of Conservation of Energy

- Different forms of energy can be inter-converted but can neither be created nor destroyed.
- ($E_{universe}$ is constant)
- Describe three inter-conversions of energy.

Temperature v. Energy

- Temperature reflects random motions of particles; i.e. the kinetic energy of a system.
- Heat involves a transfer of energy between 2 objects due to different energies and temperature differences.

Always: HOT → cold

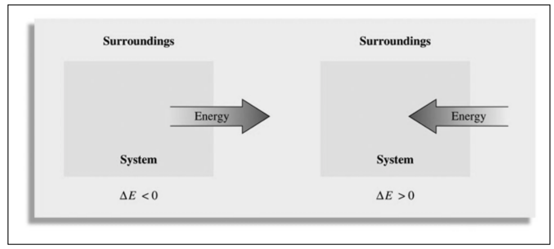
Heat (Energy) Loss

Energy: A State Function

- Depends **only** on the state of the system - not the path of how it arrived at that state.
- It is independent of pathway.

System and Surroundings

- *System: That on which we focus attention*
- *Surroundings: Everything else in the universe*
  - *Universe = System + Surroundings*



Defining Energy Change
Exo- and Endo- thermic
(*Exergonic and Endergonic*)

- *Two types of energy change :*
- *Exothermic: Heat flows* ***out of*** *the system (to the surroundings)….negative sign*
- *Endothermic: Heat flows* ***into*** *the system (from the surroundings)….positive sign*

First of Three Laws of Thermodynamics

- *First Law of Thermodynamics: The energy of the universe is constant or "energy is conserved".*

Heat Capacity (Specific Heat)

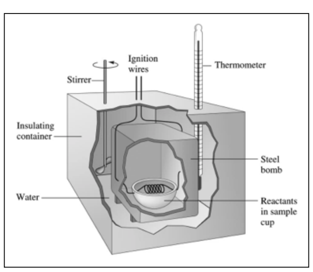
$$C_P = \frac{\text{heat absorbed}}{\text{increase in temperature}} = \frac{\text{J}}{^\circ\text{C}} \text{ or } \frac{\text{J}}{\text{K}}$$

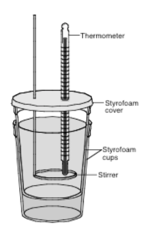
http://chemconnections.org/general/chem120/Flash/specific_heat_s.swf

Terminology

- *Specific heat capacity*
  heat capacity per gram = J/°C g or J/K g
- *Molar heat capacity*
  heat capacity per mole = J/°C mol or J/K mol

Calorimeters





http://chemconnections.org/general/chem120/Flash/calorimetry_s.html

QUESTION

What is the specific heat capacity of gold if it requires 48.8 J to raise the temperature of 15 grams of gold 25°C?

A. 29 J/g°C
B. 0.13 J/g°C
C. 79 J/g°C
D. 0.011 J/g°C
E. none of these

Heat Capacities

Substance	Specific Heat J / °C · g
$H_2O_{(l)}$	4.18
$H_2O_{(s)}$	2.03
$Al_{(s)}$	0.89
$Fe_{(s)}$	0.45

QUESTION

If 5.0 kJ of energy is added to a 15.5-g sample of water at 10.°C, the water is:

A) boiling.
B) completely vaporized.
C) frozen solid.
D) decomposed.
E) still a liquid.

Specific Heat $H_2O_{(l)}$ J / °C · g
4.18

Why can you burn the top of your mouth with hot pizza and not the bottom?

(The top & bottom are at the same temperature!)

http://www.dailymotion.com/video/x3hfwx_the-science-of-pizza_people

Why can you burn the top of your mouth with hot pizza and not the bottom? (The top & bottom are at the same temperature.)

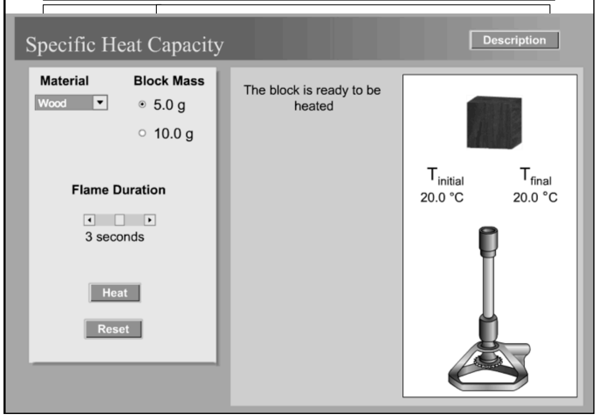
Specific Heat Capacities of Some Elements

Substance	Specific Heat Capacity (J/g · K)*
Elements	
Aluminum, Al	0.900
Graphite, C	0.711
Iron, Fe	0.450
Copper, Cu	0.387
Gold, Au	0.129
Compounds	
Ammonia, $NH_3(l)$	4.70
Water, $H_2O(l)$	4.184
Ethyl alcohol, $C_2H_5OH(l)$	2.46
Ethylene glycol, $(CH_2OH)_2(l)$	2.42
Carbon tetrachloride, $CCl_4(l)$	0.862
Solid materials	
Wood	1.76
Cement	0.88
Glass	0.84
Granite	0.79
Steel	0.45

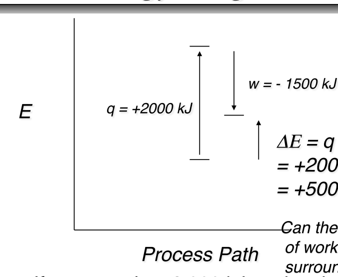
*At 298 K (25°C).

(Cp) on body fat. In obese mice (fat content 52.76% body wt) the heat capacity was 2.65 kJ kg-1 K-1 and in lean mice (fat content 7.55% body wt) the heat capacity was 3.66 kJ kg-1 K-1.

Specific Heat Interactive



Energy diagrams

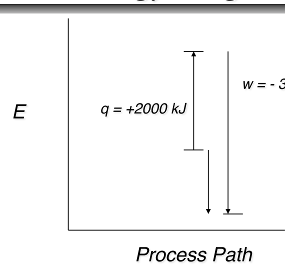


$\Delta E = q + w$
$= +2000kJ + (-1500kJ)$
$= +500kJ$

Can the system do 3000 kJ of work on the surroundings?

If a system has 2,000 kJ put into it and the system does work of 1500 kJ on the surroundings, what is ΔE?

Energy diagrams



Can the system do 3000 kJ of work on the surroundings?

QUESTION

A gas absorbs 0.0 J of heat and then performs 15.2 J of work. The change in internal energy of the gas is:

A) –24.8 J.
B) 14.8 J.
C) 55.2 J.
D) –15.2 J.
E) none of these.

Sign Conventions Used and the Relationship Among q, w, and ΔE

Sign Convention for q:	Sign of $\Delta E = q + w$
$q > 0$: Heat is transferred from the surroundings to the system	$q > 0$ and $w > 0$: $\Delta E > 0$
$q < 0$: Heat is transferred from the system to the surroundings	$q > 0$ and $w < 0$: The sign of ΔE depends on the magnitudes of q and w
Sign Convention for w:	$q < 0$ and $w > 0$: The sign of ΔE depends on the magnitudes of q and w
$w > 0$: Work is done by the surroundings on the system	
$w < 0$: Work is done by the system on the surroundings	$q < 0$ and $w < 0$: $\Delta E < 0$

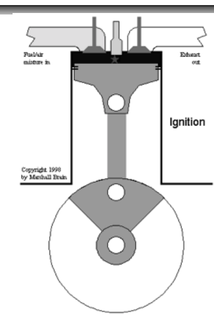
QUESTION

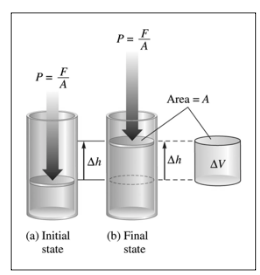
For a particular process q = 20 kJ and w = 15 kJ. Which of the following statements is true?

A) Heat flows from the system to the surroundings.
B) The system does work on the surroundings.
C) ΔE = 35 kJ.
D) All of these are true.
E) None of these are true.

Work of
Gas Expansion

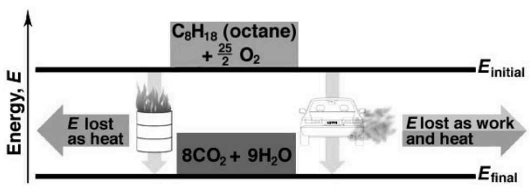
Energy
The Gas Combustion Engine





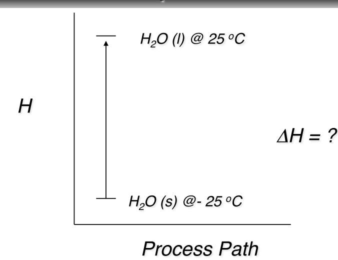
http://chemconnections.org/general/movies/html-swf/workversusenergyflow.htm

Two Different Paths for the Energy Change of a System



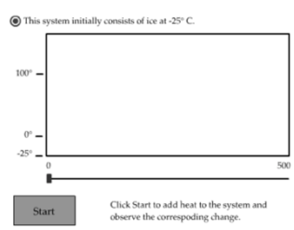
Enthalpy diagrams

$q_p = \Delta H$



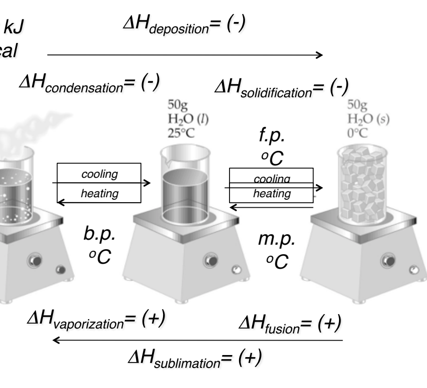
If 50.0 g of ice @ -25 °C warms to 25 °C what is ΔH of the process?

Substance	Specific Heat J / °C · g
$H_2O_{(l)}$	4.18
$H_2O_{(s)}$	2.03



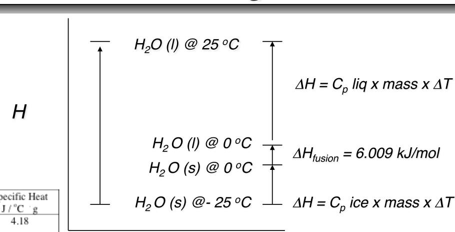
http://chemconnections.org/general/movies/HeatingCurves.swf

ΔH = J or kJ
cal or kcal



Enthalpies $\Delta H_?$

$s \leftrightarrow l \leftrightarrow g$



Substance	Specific Heat J / °C g
$H_2O_{(l)}$	4.18
$H_2O_{(s)}$	2.03
$Al_{(s)}$	0.89
$Fe_{(s)}$	0.45

Process Path $\Delta H = \Delta H_{ice} + \Delta H_{fusion} + \Delta H_{liq}$

If 50.0 g of ice @ -25 °C warms to 25 °C what is ΔH of the process? $\Delta H = ?$

QUESTION

You take 200. g of a solid at 30.0°C and let it melt in 400. g of water. The water temperature decreases from 85.1°C to 30.0°C. Calculate the heat of fusion of this solid.

A) 125 J/g
B) 285 J/g
C) 461 J/g
D) 518 J/g
E) cannot without the heat capacity of the solid

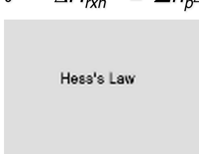
"Heat of Reaction"

http://chemconnections.org/general/movies/hesslaw.mov

Change in Enthalpy

- *The heat of any reaction can be calculated from enthalpies of formation of reactants and products.("Hess's Law")*

- $\Delta H_{rxn}° = \Sigma n_p \Delta H_f°(\text{products}) - \Sigma n_r \Delta H_f°(\text{reactants})$



QUESTION

Consider the following standard heats of formation:

$P_4O_{10}(s)$ = –3110 kJ/mol
$H_2O(l)$ = –286 kJ/mol
$H_3PO_4(s)$ = –1279 kJ/mol

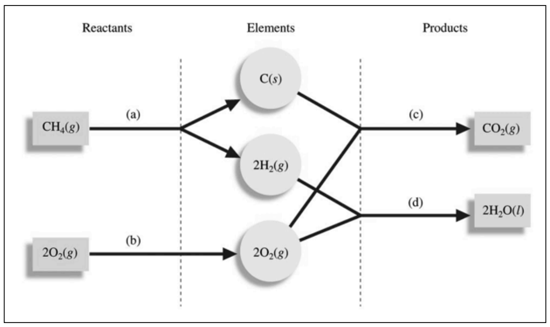
Calculate the change in enthalpy for the following process:

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(s)$

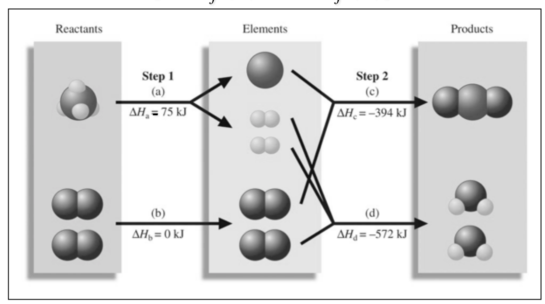
A) 4675 kJ *B) -1545 kJ* *C) -290 kJ*
D) -1720 kJ

Ex. Combustion of Methane

$CH_{4\,(g)} + 2\ O_{2\,(g)} \rightarrow CO_{2\,(g)} + \ 2\ H_2O\ _{(g)}$



$\Delta H_{rxn}° \ = \ [1\Delta H_f°(c) + 2\Delta H_f°(d)] -$
$[1\Delta H_f°(a) + 2\Delta H_f°(b)]$



$\Delta H_{rxn}°= [-394kJ+(-572kJ)]-[-75kJ+0kJ]= -891kJ$

QUESTION

The heat of formation of Fe_2O_3(s) is –826 kJ/mol. Calculate the heat of the reaction $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$ when a 55.8-g sample of iron is reacted.

A) –206 kJ
B) –413 kJ
C) –826 kJ
D) –1650 kJ
E) -3.30×10^3 kJ

Exo- and Endo- thermic
(***Exergonic and Endergonic***)

ð *Heat exchange accompanies chemical reactions.*

ð *Exothermic: Heat flows* ***out of*** *the system (to the surroundings)….negative sign*

ð *Endothermic: Heat flows* ***into*** *the system (from the surroundings)….positive sign*

QUESTION

In the lab, two solutions (each originally at the same temperature) are mixed and the temperature of the resulting solution decreases. Which of the following is true?

A) The chemical reaction is releasing energy.
B) The energy released is equal to $Cp \times m \times T$.
C) The chemical reaction is absorbing energy.
D) The energy absorbed is equal to $Cp \times m \times T$.
E) More than one of these.

Remember from earlier slides:
http://chemconnections.org/general/chem120/Flash/specific_heat_s.swf

(Cp) of a body: In obese mice (fat content 52.76% body wt) the heat capacity was 2.65 kJ kg^{-1} K^{-1} and in lean mice (fat content 7.55% body wt) the heat capacity was 3.66 kJ kg^{-1} K^{-1}.

Substance	Specific Heat Capacity (J/g · K)*
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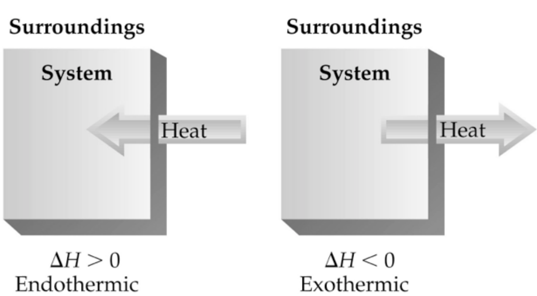
Solid materials	
Wood	1.76
Cement	0.88
Glass	0.84
Granite	0.79
Steel	0.45

*At 298 K (25°C).

http://chemconnections.org/general/chem120/Flash/heat_transfer_s.swf



How does the relative (Cp) of the body of an obese person compared to that of a lean person relate to their relative rise in body temperatures if both persons exercise at exactly the same level?

"Heat of Reaction"

Change in Enthalpy

- *The heat of any reaction can be calculated from enthalpies of formation of reactants and products.("Hess's Law")*

$$\Delta H_{rxn}^\circ = \Sigma n_p \Delta H_f^\circ(\text{products}) - \Sigma n_r \Delta H_f^\circ(\text{reactants})$$

http://chemconnections.org/general/chem120/Flash/hess_law_s.swf

Thermochemistry Lab

Neutralization Reactions / Hess's law

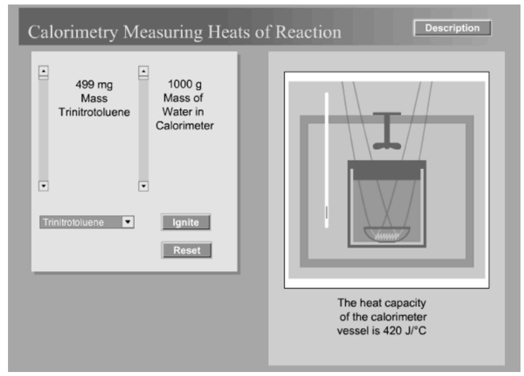
$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$

$HNO_{3(aq)} + NaOH_{(aq)} \longrightarrow NaNO_{3(aq)} + H_2O_{(l)}$

$NaOH_{(s)} + H_2O_{(l)} \longrightarrow NaOH_{(aq)}$

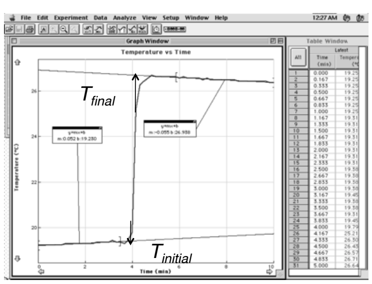
$HCl_{(aq)} + NaOH_{(s)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$

Calorimetry (Interactive)



Thermochemistry Lab

Neutralization Reactions / Hess's law



QUESTION

In this Thermochemistry lab, 50.0 mL of 1.0M HCl(aq) is added to 50.0 mL of 1.0M NaOH (each originally at the same temperature). The temperature increases 5.50 oC . Which of the following is true?

A) The chemical reaction is releasing energy.
B) The energy released is equal to $Cp \times m \times T$.
C) The chemical reaction is absorbing energy.
D) The energy absorbed is equal to $Cp \times m \times T$.
E) More than one of these.

Report Table

Vol. Solution (mL)	Density Solution (g/mL)	Mass Solution (g)	Specific Heat Solution (J/g °C)	T_f (°C)	T_i (°C)	Δ T (°C)	Δ H_{rxn} (J)	Δ H_{rxn} (kJ/mol)

Results/Conclusions: answer questions #3,4,& 6 pg. 41 (DVC Lab Manual)

QUESTION

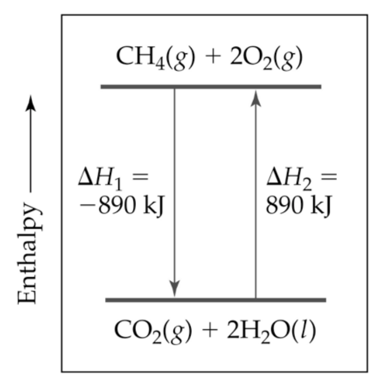
In the neutralization experiment, 50.0 mL of 1.0M HCl(aq) was added to 50.0 mL of 1.0M NaOH. The temperature increased 5.50 °C . The density of the resulting solution of products was 1.02 g/mL and the heat capacity 4.0 J/g °C. The heat for the experiment is:

A) -2200 kJ
B) +2200 kJ
C) -2200 J
D) +2200 J

QUESTION

In the neutralization experiment, 50.0 mL of 1.0M HCl(aq) was added to 50.0 mL of 1.0M NaOH. The temperature increased 5.50 °C . The density of the resulting solution of products was 1.02 g/mL and the heat capacity 4.0 J/g °C. The heat of neutralization for the experiment is:

A) -45 kJ/mol
B) -22 kJ/mol
C) -4500 J/mol
D) -220 J/mol



Exothermic Reaction

http://www.youtube.com/watch?v=rdCsbZf1_Ng

Heats of Combustion of Some Fats and Carbohydrates

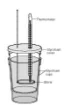
Substance	ΔH_{comb} (kJ/g)
Fats	
Vegetable oil	37.0
Margarine	30.1
Butter	30.0
Carbohydrates	
Table sugar (sucrose)	16.2
Brown rice	14.9
Maple syrup	10.4

Heats of Combustion

- *Combustion of octane releases 5,470 kJ per mole of octane (ΔH_{comb} = -5,470 kJ/mol)*
- *How many gallons of water can be boiled by burning 1 gallon of gasoline? (Assume the water is at 25^{o}C)*
- *How many grams of fat have the equivalent combustion energy as 1 gallon of gasoline?*
- *How many pounds of CO_2 are added to atmosphere from burning 1 gallon of gasoline? (This question relates to the Greenhouse Gas Workshop.)*

Endothermic Reaction

QUESTION



If a student performs an endothermic reaction in a calorimeter, how does the calculated value of ΔH differ from the actual value if the heat exchanged with the calorimeter is not taken into account?

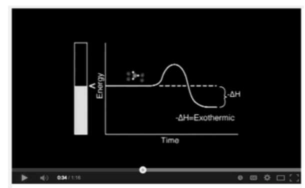
A) ΔH_{calc} would be more negative because the calorimeter always absorbs heat from the reaction.
B) ΔH_{calc} would be less negative because the calorimeter would absorb heat from the reaction.
C) ΔH_{calc} would be more positive because the reaction absorbs heat from the calorimeter.
D) ΔH_{calc} would be less positive because the reaction absorbs heat from the calorimeter.
E) ΔH_{calc} would equal the actual value because the calorimeter does not absorb heat.

http://chemconnections.org/general/chem120/Flash/calorimetry_s.swf

Activation Energy (Ea) & Chemical Reactions

ð $CH_{4\,(g)} + 2\,O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2\,H_2O_{\,(g)}$

ð $N_{2\,(g)} + O_{2\,(g)} \rightarrow 2\,NO_{\,g)}$



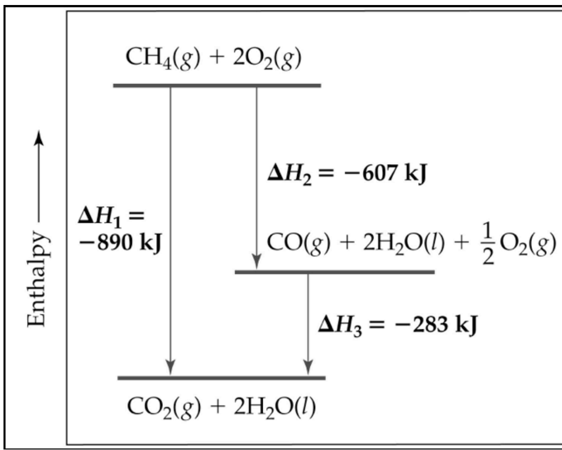
ð *NOTE: Ea depends on pathway.*

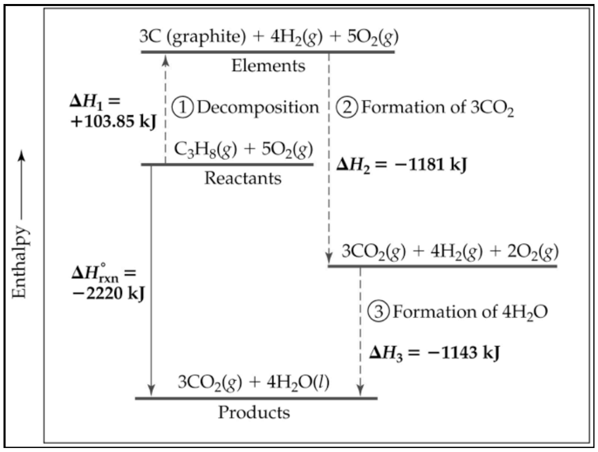
Hess's Law Continued

ð *Reactants → Products*

ð *ΔH = + (endothermic); ΔH = - (exothermic)*

ð *The change in enthalpy is the same whether the reaction takes place in one step or a series of steps.*





Calculations via Hess's Law

- *1. If a reaction is reversed, ΔH is also reversed.*
  - *$N_2(g) + O_2(g) \rightarrow 2\ NO(g)$ $\Delta H = 180$ kJ*
  - *$2\ NO(g) \rightarrow N_2(g) + O_2(g)$ $\Delta H = -180$ kJ*
- *2. If the coefficients of a reaction are multiplied by an integer, ΔH is multiplied by that same integer.*
  - *$6\ NO(g) \rightarrow 3\ N_2(g) + 3\ O_2(g)$ $\Delta H = -540$ kJ*

QUESTION

Consider the following numbered processes:

1. $A \rightarrow 2B$
2. $B \rightarrow C + D$
3. $E \rightarrow 2D$

ΔH for the process $A \rightarrow 2C + E$ is

A) $\Delta H_1 + \Delta H_2 + \Delta H_3$
B) $\Delta H_1 + \Delta H_2$
C) $\Delta H_1 + \Delta H_2 - \Delta H_3$
D) $\Delta H_1 + 2\Delta H_2 - \Delta H_3$
E) $\Delta H_1 + 2\Delta H_2 + \Delta H_3$

QUESTION

Enthalpies of formation data are not always experimentally easy to obtain. However, enthalpies of combustion data are readily available. Calculate the enthalpy of formation of methane from the combustion data provided.

$C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^0_{comb} = -393.5$ kJ

$H_2(g) + ½\ O_2(g) \rightarrow H_2O(l)$ $\Delta H^0_{comb} = -285.8$ kJ

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ $\Delta H^0_{comb} = -890.3$ kJ

A) –19.4 kJ/mol ***B) –74.8 kJ/mol***

C) –221.9 kJ/mol ***D) –296.0 kJ/mol***