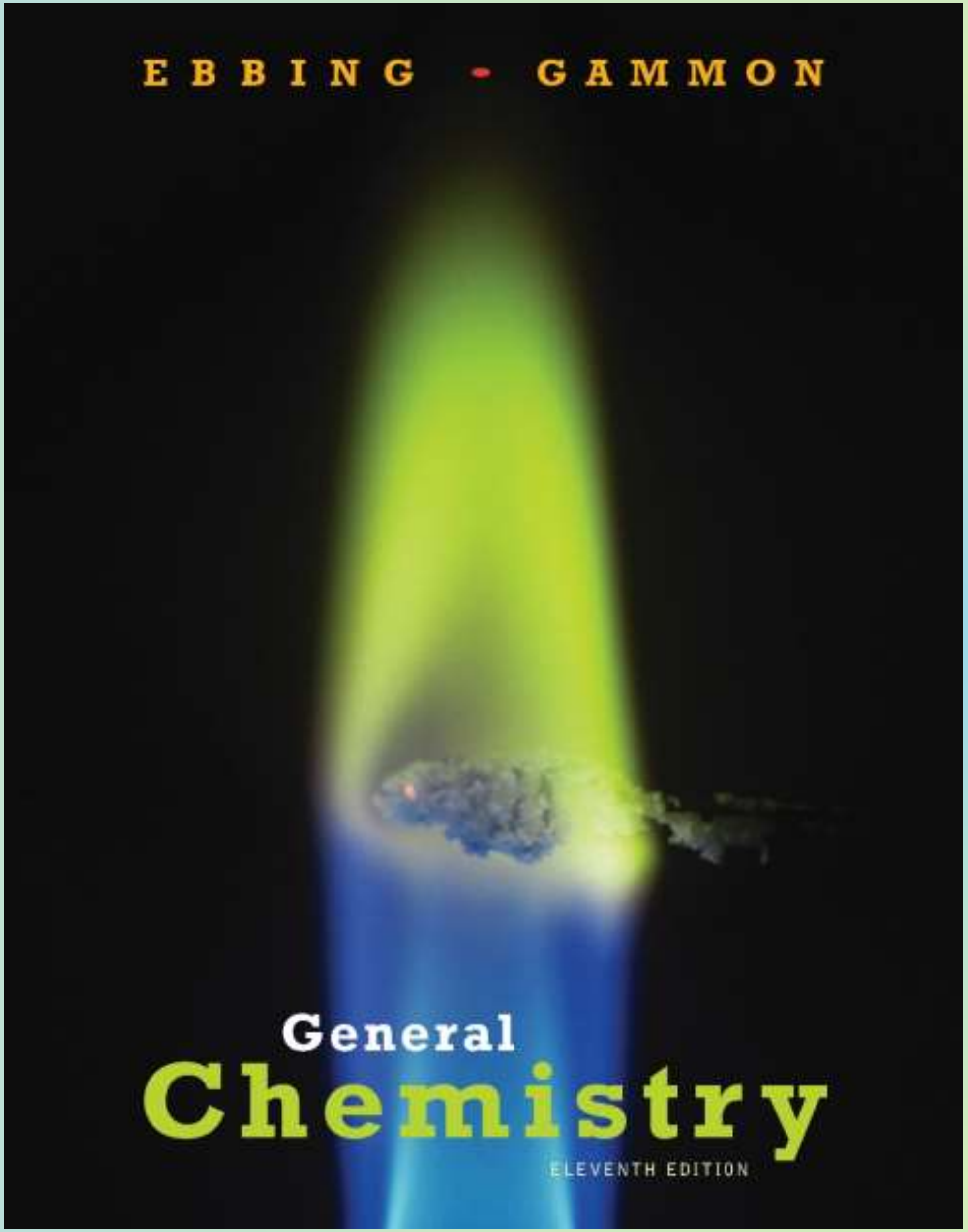


اللهم صلّ وسلّم على نبينا محمد وعلى آله وصحبه أجمعين

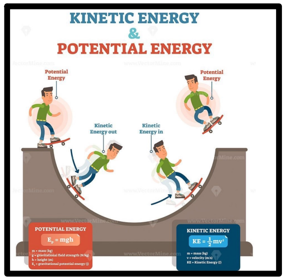
Thermochemistry

➢ Understanding Heats of Reaction

- ✓ *Thermodynamics* is the science of the relationships between heat and other forms of energy. Heat is a form energy
- ✓ *Thermochemistry* is one area of thermodynamics. It concerns the study of the quantity of heat absorbed or evolved (given off) by chemical reactions.

تم اطلاقها

تم امتصاصها



➢ 6.1 Energy and Its Units :

- ✓ **Energy** is *the potential or capacity to move matter*.
- ✓ Energy can exist in different forms, including heat, light, and electrical energy, and these different forms can be interconverted. Energy is a property of matter not material

①

➢ Kinetic Energy

is *the energy associated with an object by virtue of its motion.*

$$E_k = \frac{1}{2}mv^2$$ *

$kg.m^2/s^2$ = joule *

Watt = joule/s *

A 100-watt bulb uses 100 joules of energy every second

Second

✓ **calorie (cal)** (*non-SI unit*) *the amount of energy required to raise the temperature of one gram of water by one degree Celsius*

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

✓ Exercise 6.1

An electron (mass = 9.11 x10^{-31} kg) is accelerated by a positive charge to a speed of 5.0 x 10^{6} m/s.

What is the kinetic energy of the electron in joules? in calories?

$$\boxed{E_k = \tfrac{1}{2}mv^2}$$

$$E_k = \tfrac{1}{2} \times 9.11 \times 10^{-31}\ \text{kg} \times (5.0 \times 10^{6}\ \text{m/s})^2 = 1.13 \times 10^{-17}\ \underline{\text{kg.m}^2/\text{s}^2 \text{ or J}}$$

$$1.13 \times 10^{-17}\ \text{J} \times \frac{1\ \text{cal}}{4.184\ \text{J}} \underline{= 2.7 \times 10^{-18}\ \text{cal}}$$

- **Potential Energy** ② $$\boxed{E_p = mgh}$$

the energy an object has by virtue of its position in a field of force.

m= *mass (gram)*, *g* = constant acceleration of gravity)

h = height

- **Internal Energy (U)** ③

Is the sum of the kinetic and potential energies of the particles making up a substance.

$$\boxed{E_{tot} = E_k + E_p + U}$$

- **Law of Conservation of Energy** *(first law of thermodynamics)*

✓ (*Energy may be converted from one form to another, but the total quantity of energy remains constant.*)

6.2 First Law of Thermodynamics; Work and Heat 8

✓ Definition of Work (w): → J

Work is *an energy transfer (or energy flow) into or out of a thermodynamic system* ***whose effect*** *on the surroundings is equivalent to moving an object through a field of force.* ← Path.

✓ Definition of Heat (q): → J

Heat is *an energy transfer (energy flow) into or out of a thermodynamic system* **that results** *from a temperature difference between the system and its surroundings.*

path

Example 6.1

- A good pitcher can throw a baseball so that it travels between 60 and 90 miles per hour (although speeds in excess of 100 miles per hour have been recorded). A regulation baseball weighing 143 g (0.143 kg) travels 75 miles per hour (33.5 m/s). What is the kinetic energy of this baseball in joules? in calories??

* $KE = \frac{1}{2} m (v)^2 = \frac{1}{2} \times 0.143 \text{ Kg} \times (33.5)^2 \Rightarrow$

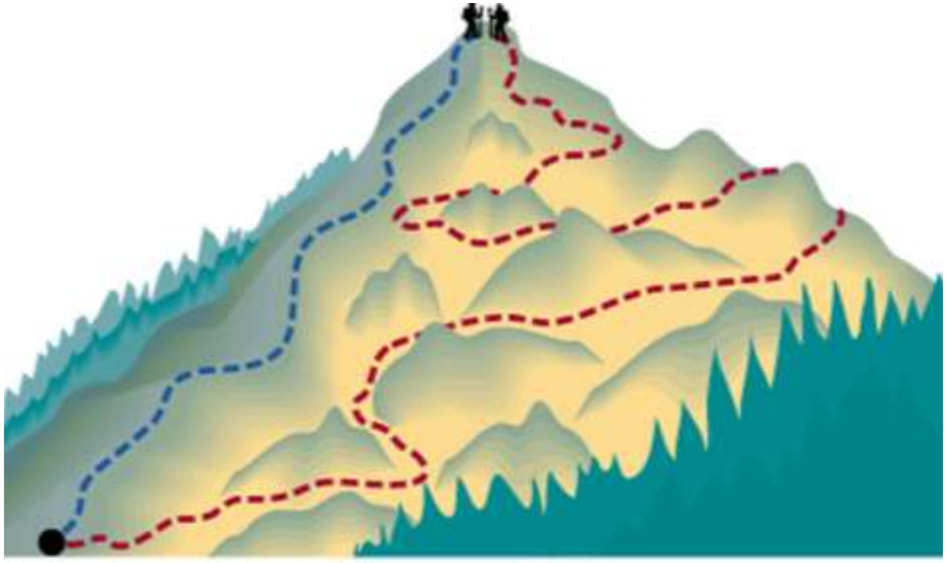
80.2 Joule

* $J \longrightarrow Cal = 80.2 J \times \frac{1 Ca}{4.184 J} \Rightarrow 19.2$ Cal

Process		**Sign**
Work done by the system on the surroundings	The system lose	−
Work done on the system by the surroundings	The system gain	+
Heat absorbed by the system from the surroundings (endothermic process)	gain	+
Heat absorbed by the surroundings from the system (exothermic process)	lose	−

➢ **Change of Internal Energy** : $\boxed{\Delta U = U_f - U_i}$ Extensive

- ✓ Internal energy is an ***extensive property***, that is, it depends on the amount of substances in the system.
- ✓ Other examples of extensive properties are mass and volume.
- ✓ **Intensive property** does not depend on the amount of substance (color, density)
- ✓ Internal energy is also a state function.
- ✓ **A state function** is *a property of a system that depends only on initial and final states.*
- ✓ *Such as temperature and pressure.*



$$\Delta U = U_{final} - U_{initial}$$

$$\Delta P = P_{final} - P_{initial}$$

$$\Delta V = V_{final} - V_{initial}$$

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

Potential energy of hiker 1 and hiker 2 is the same even though they took different paths.

- **First Law of Thermodynamics**

$$\Delta U = q + w$$

The energy change\ Internal energy = heat + work

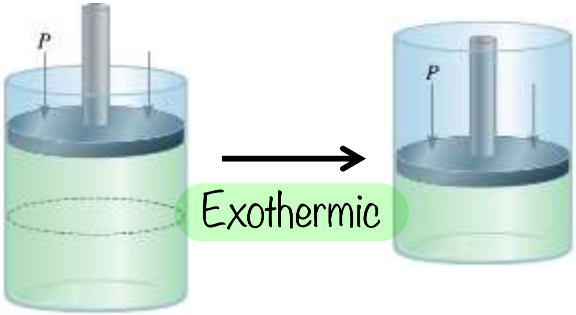
(Q) The work done when a gas is compressed in a cylinder is 462 J. During this process, there is a heat transfer of 128 J from the gas to the surroundings. Calculate the energy change for this process.

$\boxed{\Delta U = q + w}$

$= -128\text{ J} + 462\text{ J} \quad = 334\text{ J}$

Work done by the surrounding on the system = gas

Heat absorbed by the surrounding from the system



6.49 A gas is cooled and loses 82 J of heat. The gas contracts as it cools, and work done on the system equal to 29 J is exchanged with the surroundings. Calculate ΔU ?

system loses heat so q = - 82 J

system contracts so w = + 29 J.

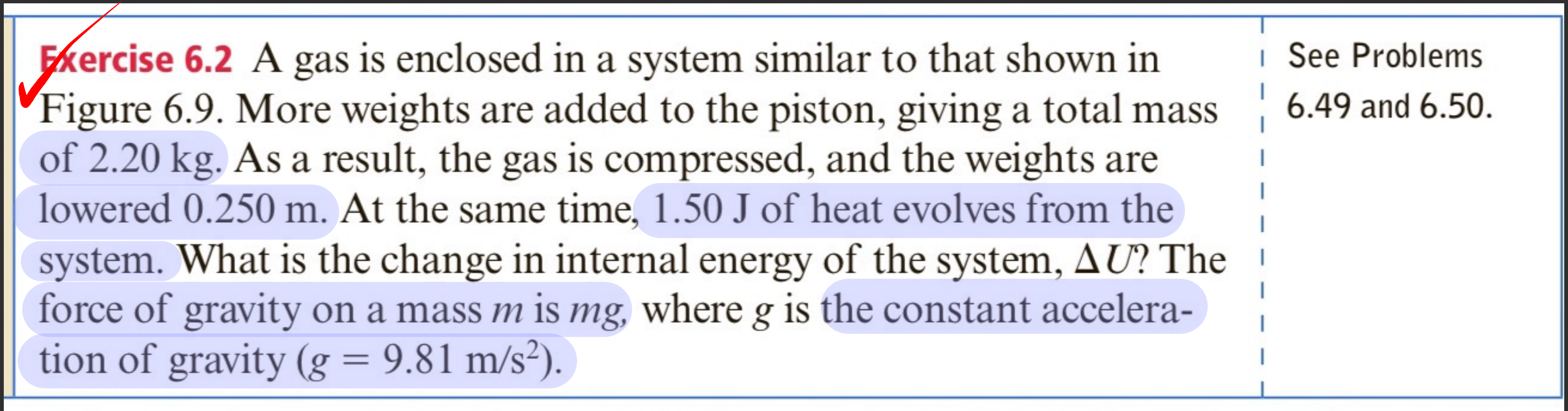
$\boxed{\Delta U = q + w} = -82\text{ J} + 29\text{ J} = -53\text{ J}$

Work done by the surrounding on the system

Heat absorbed by the surrounding from the system

Exothermic

- Gas is compressed. Work done from the surrounding on the system. w+
- Gas expand work done from the system on the surrounding. w-



Exercise 6.2 A gas is enclosed in a system similar to that shown in Figure 6.9. More weights are added to the piston, giving a total mass of 2.20 kg. As a result, the gas is compressed, and the weights are lowered 0.250 m. At the same time, 1.50 J of heat evolves from the system. What is the change in internal energy of the system, ΔU? The force of gravity on a mass m is mg, where g is the constant acceleration of gravity ($g = 9.81\ \text{m/s}^2$).

See Problems 6.49 and 6.50.

→ The change in the internal energy ; The energy change.

* $\Delta U = q + w$

Internal energy = heat + Work → (mgh)

$\ominus 1.50 + (2.2 \times 9.8 \times (.25)) = 3.89\text{J}$

heat (evolves) from the System → (exothermic) → the System lose Heat.

→ get off

6.3 Heat of Reaction; Enthalpy of Reaction

Heat of Reaction

lose

✓ **exothermic process** (*q is negative*)

is a chemical reaction or a physical change in which heat is evolved or is released from the system. The system lose heat

gain

✓ **endothermic process** (*q is positive*)

is a chemical reaction or a physical change in which heat is absorbed by the system. The system gain heat

Type of Reaction	*Experimental Effect Noted*	*Result on System*	*Sign of q*
Endothermic	Reaction vessel cools (heat is absorbed)	Energy added	+
Exothermic	Reaction vessel warms (heat is evolved)	Energy subtracted	−

Exercise 6.3 Ammonia burns in the presence of a platinum catalyst to give nitric oxide, NO. In an experiment, 4 mol NH_3 is burned and evolves +170 kJ of heat. Is the reaction endothermic or exothermic? What is the value of *q*?

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt} 4NO(g) + 6H_2O(l)$$

Produce / get off / release

Heat is evolved → reaction is exothermic.

The value of *q* is −170 kJ.

Combustion = lose heat

➢ Pressure-Volume Work

$$\boxed{w = -P\Delta V}$$

$$\boxed{PV = nRT}$$

The ideal gas law

Exercise 6.4 Consider the combustion of CH_4.

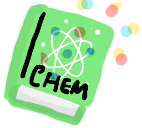
The system → compressed

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

The heat of reaction at 77°C and 1.00 atm is – 885.5 kJ. → Release/Exothermic

What is the change in volume when 1.00 mol CH_4 reacts with 2.00 mol O_2? (You can ignore the volume of liquid water). What is *w* for this change?

Calculate Δ*U* for the change indicated by the chemical equation.



$$\Delta V = V_{final} - V_{initial} = \left(\left(\frac{n_{final}RT}{P} - \frac{n_{initial}RT}{P}\right)\right) = \frac{(n_{final} - n_{initial})RT}{P} \quad *$$

Product - reactant

$$\Delta V = \frac{(1\text{ mol} - 3\text{ mol})(0.08206\,\frac{\text{L•atm}}{\text{mol•K}})(35\underline{0}\text{ K})}{1.0\underline{0}\text{ atm}} = \boxed{-57.\underline{4}4\text{ L}}$$

Because the change is from 3 moles of gas to 1 mole of gas, this represents a compression being performed on the system → work is done on the system (+ve)

$$\boxed{w = -P \times \Delta V} \quad *$$

= −(1.0 atm) × (−57.44 L) = $\boxed{57.44 \text{ atm.L}}$

57.44 atm.L x 101.3 = + 5818 J = $\boxed{+ 5.8 \text{ kJ}}$

*

1 atm.L = 101.3 J

$$\boxed{\Delta U = q + w} \quad *$$

→ Δ*U* = -885.5 kJ + 5.8 kJ = $\boxed{-\ 879.7 \text{ kJ}}$

➢ Enthalpy (H) and Enthalpy of Reaction

$$\boxed{H = U + PV}$$

✓ Because U, P and V are state functions, H is also a state function.

$$\Delta H = H_f - H_i$$

$$\boxed{\Delta U = q + w}$$

$$\boxed{w = -P\Delta V}$$

$$\boxed{\Delta U = q + w} = q - \underline{\underline{P\Delta V}} = q \underline{\underline{- RT\Delta n}}$$

Δn = number of moles of product gas – number of moles of reactant gases

$$q = \Delta U + P\Delta V = (U_f - U_i) + P(V_f - V_i) = U_f - U_i + PV_f - PV_i$$

$$q = (U_f + PV_f) - (U_i + PV_i) = H_f - H_i$$

$$\boxed{\boxed{q = \Delta H}\ \text{(At }\underline{\underline{\text{fixed pressure}}}\text{ and a }\underline{\underline{\text{given temperature}}}\text{)}}$$

$$\Delta H \neq 0$$

➢ Enthalpy of reaction

The change in enthalpy, ΔH, for a reaction at a given temperature and fixed pressure

$$\boxed{\Delta H = H\ (\text{products}) - H\ (\text{reactants})}$$

(Q) Calculate the change in internal energy when 2 moles of CO are converted to 2 moles of CO_2 at 1 atm. and 25°C.

Reminder!

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H = -566.0 \text{ kJ/mol}$$

$$\boxed{\Delta U = q - RT\Delta n}$$

$q = \Delta H$ (At fixed pressure and a given temperature)

$$\Delta n = \text{number of moles of product gas} - \text{number of moles of reactant gases}$$

$$= 2 - 3$$

$$= -1$$

If the thermochemical equation is a limiting reactant reaction, take the ratio between the L.R & ΔH

R = 8.314 J/K · mol and T = 298 K

R = 0.0821 atm.L/mol.K

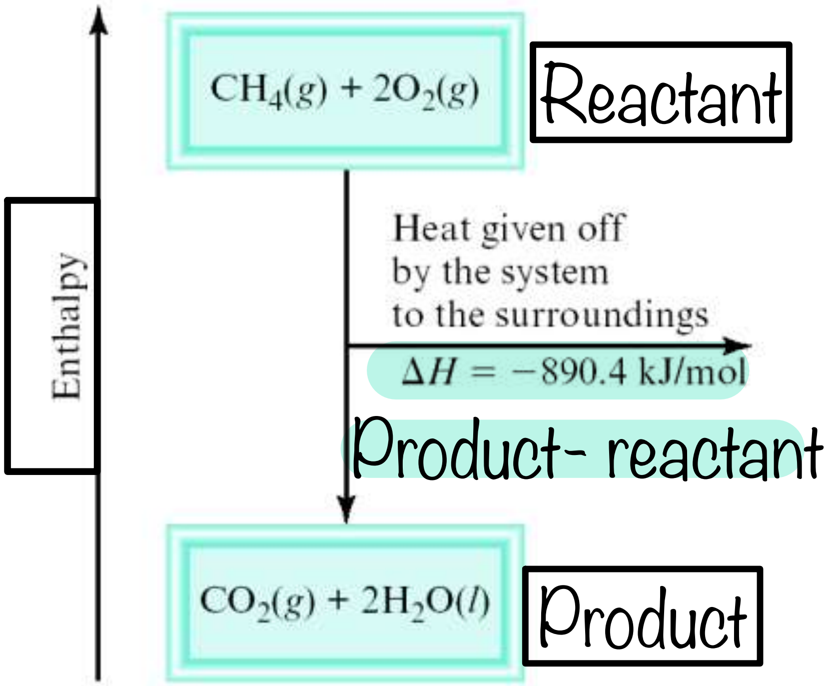
$$\boxed{\Delta U = \Delta H - RT\Delta n}$$

$$= -566.0 \text{ kJ/mol} - (8.314 \text{ J/K} \cdot \text{mol})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(298 \text{ K})(-1)$$

$$= -563.5 \text{ kJ/mol}$$

If he ask for ΔH in KJ/mol — devide the answer by number of moles

6.4 Thermochemical Equations



Enthalpy

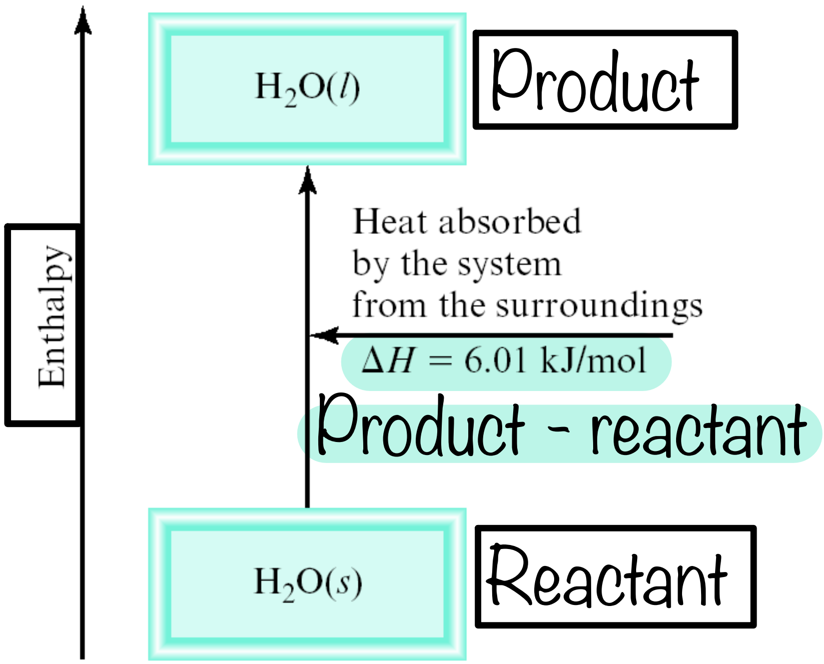
$CH_4(g) + 2O_2(g)$ Reactant

Heat given off by the system to the surroundings

$\Delta H = -890.4$ kJ/mol

Product- reactant

$CO_2(g) + 2H_2O(l)$ Product



Enthalpy

$H_2O(l)$ Product

Heat absorbed by the system from the surroundings

$\Delta H = 6.01$ kJ/mol

Product - reactant

$H_2O(s)$ Reactant

$$\boxed{\begin{array}{c} H_{\text{products}} < H_{\text{reactants}} \\ \Delta H < 0 \end{array}}$$

Exothermic

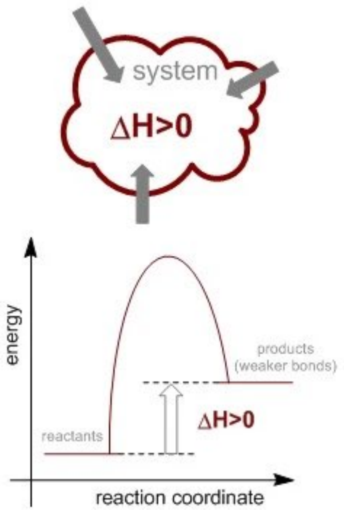
Combustion

$$\boxed{\begin{array}{c} H_{\text{products}} > H_{\text{reactants}} \\ \Delta H > 0 \end{array}}$$

Endothermic

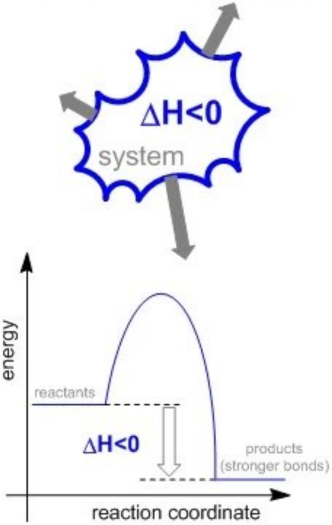
ENDO-THERMIC

Q<0 (surrounding heat)



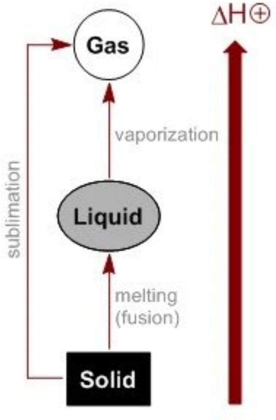
EXO-THERMIC

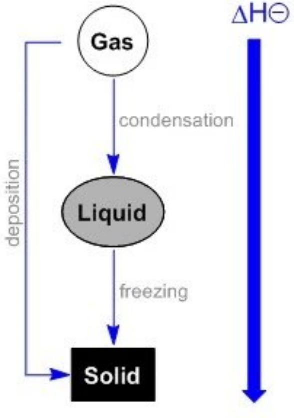
Q>0 (surrounding heat)



$$\Delta H_{rxn} = \Sigma\Delta H_{(bonds\ broken)} - \Sigma\Delta H_{(bonds\ formed)}$$

$$\Delta H_r = \Sigma\Delta H_f\,(\text{products}) - \Sigma\Delta H_f\,(\text{reactants})$$





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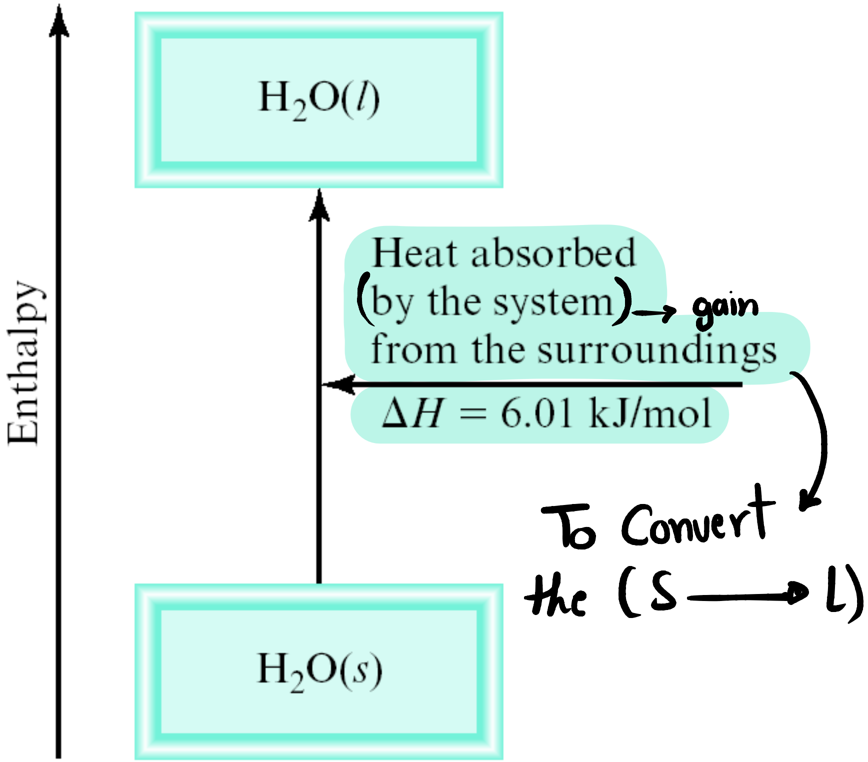
Thermochemical Equations



Enthalpy

$H_2O(l)$

Heat absorbed (by the system) → gain from the surroundings

$\Delta H = 6.01$ kJ/mol

To Convert the ($s \longrightarrow l$)

$H_2O(s)$

Is ΔH negative or positive?

System absorbs heat

Endothermic

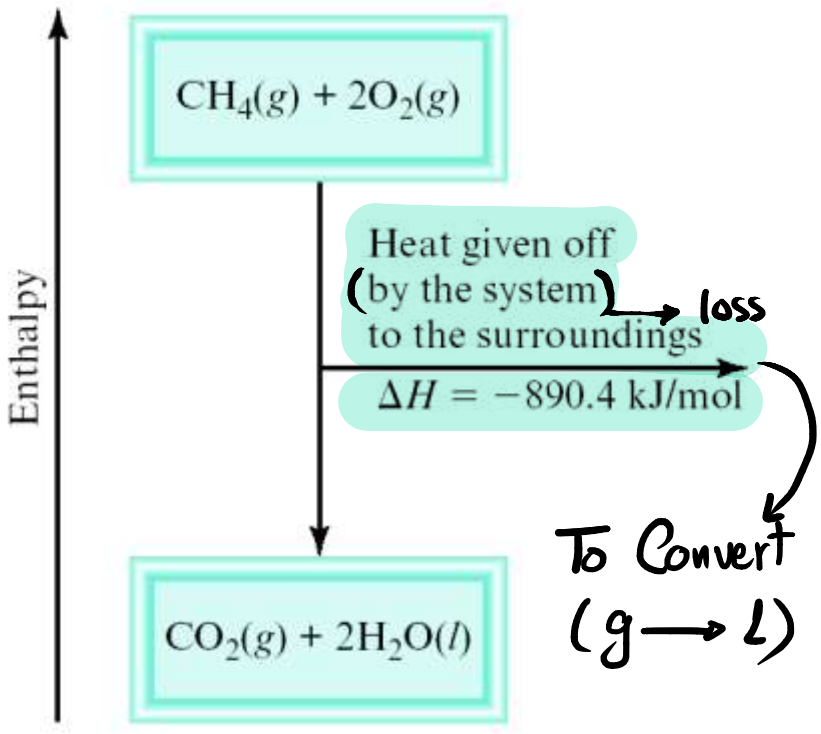
$\Delta H > 0$

6.01 kJ are absorbed for every 1 mole of ice that melts at 0^0C and 1 atm.

(Depend on the number of moles)

$$1\,H_2O\ (s) \longrightarrow H_2O\ (l) \qquad \Delta H = 6.01 \text{ kJ/mol}$$

Thermochemical Equations



Is ΔH negative or positive?

System gives off heat

Exothermic

$\Delta H < 0$

Evolved

890.4 kJ are released for every 1 mole of methane that is combusted at 25^0C and 1 atm.

1 $CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (l)$ $\quad \Delta H = -890.4$ kJ/mol

- The stoichiometric coefficients always refer to the number of moles of a substance → Reactant

$$1H_2O\,(s) \longrightarrow H_2O\,(l) \qquad \Delta H = 6.01\ \text{kJ/mol}$$

- If you reverse a reaction, the sign of ΔH changes

$$1H_2O\,(l) \longrightarrow H_2O\,(s) \qquad \Delta H = -6.01\ \text{kJ/mol}$$

- If you multiply both sides of the equation by a factor n, then ΔH must change by the same factor n.

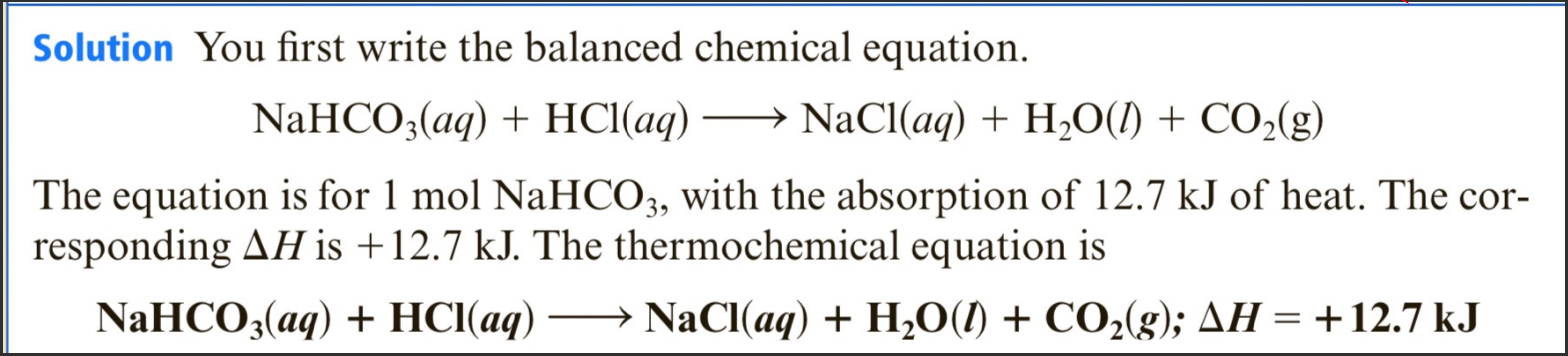
$$2H_2O\,(s) \longrightarrow 2H_2O\,(l) \qquad \Delta H = 2 \times 6.01 = 12.0\ \text{kJ}$$

- The physical states of all reactants and products must be specified in thermochemical equations.

$$H_2O\,(s) \longrightarrow H_2O\,(l) \qquad \Delta H = 6.01\ \text{kJ/mol}$$

$$H_2O\,(l) \longrightarrow H_2O\,(g) \qquad \Delta H = 44.0\ \text{kJ/mol}$$

Aqueous sodium hydrogen carbonate solution (baking soda solution) reacts with hydrochloric acid to produce aqueous sodium chloride, water, and carbon dioxide gas. The reaction absorbs 12.7 kJ of heat at constant pressure for each mole of sodium hydrogen carbonate. Write the thermochemical equation for the reaction. (Example . 6:2)



Solution You first write the balanced chemical equation.

$$NaHCO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

The equation is for 1 mol $NaHCO_3$, with the absorption of 12.7 kJ of heat. The corresponding ΔH is +12.7 kJ. The thermochemical equation is

$$\mathbf{NaHCO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l) + CO_2(g);\ \Delta H = +12.7\ kJ}$$

A propellant for rockets is obtained by mixing the liquids hydrazine, N2H4, and dinitrogen tetroxide, N2O4. These compounds react to give gaseous nitrogen, N2, and water vapor, evolving 1049 kJ of heat at constant pressure when 1 mol N2O4 reacts. Write the thermochemical equation for this reaction. Exercise .6:5

$$2N_2H_{4(l)} + N_2O_{4(l)} \longrightarrow 3N_{2(g)} + 4H_2O_{(g)} \quad \Delta H = +1049\ kJ$$

Example 63:

When 2 mol H2 (g) and 1 mol O2 (g) react to give liquid water, 572 kJ of heat evolves.

$((2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(l) + \Delta H = -572\ kJ))$

Write this equation for 1 mol of liquid water. Give the reverse equation, in which 1 mol of liquid water dissociates into hydrogen and oxygen.

$$\frac{1}{2} \times \left(2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}\right) = -572\ KJ$$

A) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O_{(l)} = -286\ KJ$

Reserve equation ⟶ $\Delta H = \times(-1)$

B) $H_2O_{(l)} \longrightarrow H_{2(g)} + \frac{1}{2}O_2 = 286\ KJ$

a) Write the thermochemical equation for the reaction described in Exercise 6.5 for the case involving 1 mol N2H4. Exercise 6.6:

b) Write the thermochemical equation for the reverse of the reaction described in Exercise 6.5.

$\Delta H = +1049\,KJ$

A. $2N_2H_{4\,(l)} + N_2O_{4\,(l)} \longrightarrow 3N_{2\,(g)} + 4H_2O_{(g)}$ $\times \frac{1}{2}$

$N_2H_4 + \frac{1}{2}N_2O_4 \longrightarrow \frac{3}{2}N_2 + 2H_2O =$

$\Delta H = 524.5$

B. $3N_2 + 4H_2O \longrightarrow N_2H_4 + 2N_2O_4 = \Delta H = -1049\,KJ$

Exercise 6.7 How much heat evolves when 10.0 g of hydrazine reacts according to the reaction described in Exercise 6.5?

$10\,g \times \frac{1}{32.05} \times \frac{+1049\,\Delta H}{2\,mol} = -164\,KJ$

Evolves

6.5 Applying Stoichiometry to Heats of Reaction

(Q) How much heat is evolved when 9.07 x 10^5 g of ammonia is produced according to the following equation?

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g);\ \Delta H = -91.8\ \text{kJ}$$

$$9.07 \times 10^5\ \cancel{\text{g NH}_3} \times \frac{1\ \cancel{\text{mol NH}_3}}{17.0\ \cancel{\text{g NH}_3}} \times \frac{-91.8\ \text{kJ}}{2\ \cancel{\text{mol NH}_3}} = \boxed{-2.45 \times 10^6\ \text{kJ}}$$

(Q) Given the thermochemical equation Combustion- exothermic

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) \qquad \Delta H = -198.2\ \text{kJ/mol}$$

calculate the heat evolved when 87.9 g of SO_2 (molar mass = 64.07 g/mol) is converted to SO_3.

grams of SO_2 ⟶ moles of SO_2 ⟶ kilojoules of heat generated

$$\Delta H = 87.9\ \cancel{\text{g SO}_2} \times \frac{1\ \cancel{\text{mol SO}_2}}{64.07\ \cancel{\text{g SO}_2}} \times \frac{-198.2\ \text{kJ}}{2\ \cancel{\text{mol SO}_2}}$$

$$\boxed{= -136\ \text{kJ}}$$

6.6 Measuring Heats of Reaction

➢ Heat Capacity and Specific Heat

✓ The **heat capacity** (C) of a sample of substance is *the quantity of heat needed to raise the temperature of the sample of substance one degree Celsius (or one kelvin).* J/C°

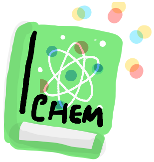
$$\boxed{q = C\Delta t}$$

✓ The **specific heat capacity** (*S*) (or simply **specific heat**) is *the quantity of heat required to raise the temperature of one gram of a substance by one degree Celsius (or one kelvin) at constant pressure.* J/(g.c)

$$\boxed{q = s \times m \times \Delta t} \qquad \boxed{C = m \times s}$$

Example 6.5

✓(Q) Calculate the heat absorbed by 15.0 g of water to raise its temperature from 20.0°C to 50.0°C (at constant pressure). The specific heat of water is 4.18 J/(g ·°C).



$$\boxed{q = s \times m \times \Delta t}$$

$$\Delta t = t_f - t_i = 50.0°\text{C} - 20.0°\text{C} = +30.0°\text{C}$$

$$q = 4.18\ \text{J/(g} \cdot °\text{C)} \times 15.0\ \text{g} \times (+30.0°\text{C}) = \mathbf{1.88} \times \mathbf{10^3}\ \text{J}$$

K

➢ Measurement of Heat of Reaction

✓ Heat of a reaction is measured in a **calorimeter,** *a device used to measure the heat absorbed or evolved during a physical or chemical change.*

Isolated system

✓ ***Calorimeters are considered isolated systems*** → $\boxed{q_{system} = 0}$

Solution

$q_{sys} = q_{water} + q_{cal} + q_{rxn}$ → Reaction

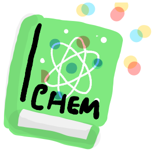
$q_{sys} = 0$

$q_{rxn} = -(q_{water} + q_{cal})$

$q_{water} = m \times s \times \Delta t$

$q_{cal} = C_{cal} \times \Delta t$

Exercise 6.8 Iron metal has a specific heat of 0.449 J/(g·°C). How much heat is transferred to a 5.00-g piece of iron, initially at 20.0°C, when it is placed in a pot of boiling water? Assume that the temperature of the water is 100.0°C and that the water remains at this temperature, which is the final temperature of the iron.	See Problems 6.69 and 6.70.



$q_{System} = S \times m \times \Delta t = 0.449 \times 5.00g \times (100-20) = 180 J$

System = Iron = absorbed heat

➢ **Constant-pressure calorimeter** coffee-cup calorimeter

$\boxed{\Delta H = q_{rxn}}$ At fixed pressure

Molarity

Neutralization = exothermic

Exercise 6.9 Suppose 33 mL of 1.20 *M* HCl is added to 42 mL of a solution containing excess sodium hydroxide, NaOH, in a coffee-cup calorimeter. The solution temperature, originally 25.0°C, rises to 31.8°C. Give the enthalpy change, Δ*H*, for the reaction: assume that the specific heat and the density of the final solution in the cup are those of water $\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$

$$\boxed{q_{sys} = q_{water} + q_{cal} + q_{rxn}}$$

q cal is Negleshiable

↑ D water ⇒ $1 = \frac{m}{V(33+42) = 75.}$

$$q_{solution} = s \times m \times \Delta t = \underset{\sim\sim\sim}{4.184\ \mathrm{J/(g.°C)}} \times 75\ \mathrm{g} \times (31.8°\mathrm{C} - 25.0°\mathrm{C})$$
$$= 2133.8\ \mathrm{J}$$

$$q_{sys} = q_{soln} + q_{rxn} = \boxed{0 \rightarrow q_{rxn} = -q_{soln}} \rightarrow q_{rxn} = -\ 2133.8\ \mathrm{J}$$

$$\text{mol HCl} = 1.20\ \mathrm{mol/L} \times 0.033\ \mathrm{L} = 0.0396\ \mathrm{mol}$$

$$\Delta H = \frac{-2133.8\ \mathrm{J}}{0.0396\ \mathrm{mol}} = -53884\ \mathrm{J/mol} = -54\ \mathrm{kJ/mol}$$

Strong Acid + Strong Base

(−54 → −56)

↳ because they have the Same Ionic equation

➢ Constant-volume calorimeter (Bomb calorimeter) $\boxed{\Delta H \sim q_{rxn}}$

Suppose 0.562 g of graphite is placed in a bomb calorimeter with an excess of oxygen at 25.0°C and 1 atm. pressure. The graphite is ignited, and it burns according to the equation: Example 6.6

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

On reaction, the calorimeter temperature rises from 25.0°C to 25.89°C. The heat capacity of the calorimeter and its contents was determined in a separate experiment to be 20.7 kJ/°C. What is the heat of reaction? Express the answer as a thermochemical equation.

$$\boxed{q_{sys} = q_{water} + q_{cal} + q_{rxn}}$$

$$\boxed{q_{rxn} = -C_{cal}\Delta t} = -20.7\ \text{kJ/°C} \times (25.89\text{°C} - 5.00\text{°C})$$

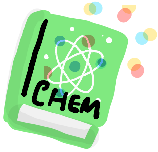
$$= -20.7\text{kJ/°C} \times 0.89\text{°C} = -18.4\ \text{kJ}$$ Exothermic

0.562 g → ? Mole C $\rightarrow 0.562\,g\,C \times \frac{1}{12.001} = 0.0468 =$

$$\Delta H = \frac{-18.4}{0.0468}$$

$$C(graphite) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -3.9 \times 10^2\ \text{kJ}$$

6.73 When 15.3 g of $NaNO_3$ (85.0 g/mol) was dissolved in water in a constant-pressure calorimeter, the temperature fell from 25.00°C to 21.56°C. If the heat capacity of the solution and the calorimeter is 1071 J/°C, what is the enthalpy change when 1 mol. of $NaNO_3$ dissolves in water? The solution process is



$$\boxed{q_{sys} = q_{water} + q_{cal} + q_{rxn}}$$

$$NaNO_3(s) \longrightarrow Na^+(aq) + NO_3^-(aq);\ \Delta H = ?$$

$q_{calorimeter}$ = C_{cal} x $\Delta T = (1071 J/°C)(21.56°C - 25.00°C) = -3684.2$ J

$q_{calorimeter} = \boxed{-q_{rxn} \rightarrow q_{rxn}} = 3684.2$ J Endothermic

The amount of heat absorbed by 15.3 g of $NaNO_3$ $\overset{+}{=}$ 3684.2 J

The amount of heat absorbed by 1mol of $NaNO_3$ is ?

$$\text{Moles} = \frac{15.3}{85} = 0.18 \rightarrow \Delta H = \frac{3684.24}{0.18} = 20.5\,kJ$$

(Q) ✓ A bomb calorimeter has a heat capacity of 2.47 kJ/°C. When a 3.74×10^{-3} mol sample of ethylene was burned in this calorimeter, the temperature increased by 2.14 °C. Calculate the energy of combustion for one mole of ethylene. Exothermic

A. –5.29 kJ/mol

B. 5.29 kJ/mol

C. –148 kJ/mol

D. –1410 kJ/mol

E. 1410 kJ/mol

$$q_{cal} = C\Delta t$$

$$= 2.47\ \text{kJ}/\cancel{°\text{C}} \times 2.14\ \cancel{°\text{C}} = 5.286\ \text{kJ}$$

$$q_{rxn} = -\,q_{cal} = -\,5.286\ \text{kJ}$$

Combustion → exothermic

$$\Delta H_{rxn} = -5.286\ \text{kJ}/3.74\times10^{-3}\ \text{mol}$$
$$= -1410\ \text{kJ/mol}$$

(Q) ✓ A lead (Pb) pellet having a mass of 26.47 g at 89.98°C was placed in a constant-pressure calorimeter of negligible heat capacity containing 100.0 mL of water.

The water temperature rose from 22.50°C to 23.17°C.

What is the specific heat of the lead pellet?

$$q_{\text{Pb}} + q_{\text{H}_2\text{O}} = 0$$

$$q_{\text{H}_2\text{O}} = ms\Delta t$$

$$q_{\text{Pb}} = -q_{\text{H}_2\text{O}}$$

$$q_{\text{H}_2\text{O}} = (100.0\text{ g})(4.184\text{ J/g}\cdot{}^\circ\text{C})\,(23.17^\circ\text{C} - 22.50^\circ\text{C})$$

$$= 280.3\text{ J} \quad \rightarrow q_{\text{Pb}} = -280.3\text{ J}$$

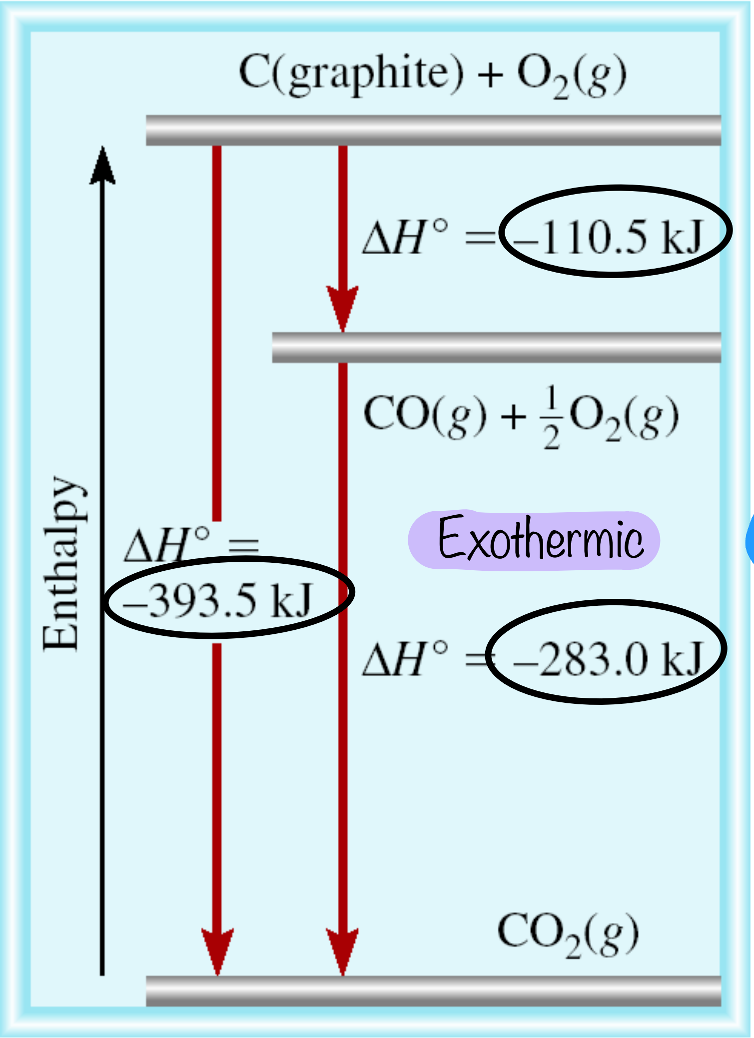
$$q_{\text{Pb}} = ms\Delta t$$

$$-280.3\text{ J} = (26.47\text{ g})(s)(23.17^\circ\text{C} - 89.98^\circ\text{C})$$

$$s = +0.158\text{ J/g}\cdot{}^\circ\text{C}$$

6.7 Hess's Law

"for a chemical equation that can be written as the sum of two or more steps, (the enthalpy change for the overall equation equals the sum of the enthalpy changes for the individual steps")



$\text{C (graphite)} + 1/2\text{O}_2\ (g) \longrightarrow \text{CO}\ (g)$ ΔH_1

$\text{CO}\ (g) + 1/2\text{O}_2\ (g) \longrightarrow \text{CO}_2\ (g)$ ΔH_2

$\text{C (graphite)} + \text{O}_2\ (g) \longrightarrow \text{CO}_2\ (g)$ ΔH_3

intermediate

✓ (Q) What is the enthalpy of reaction, Δ*H*, for the formation of tungsten carbide, WC, from the elements? Example: 6.7

$$W(s) + C(graphite) \longrightarrow WC(s)$$

$$2W(s) + 3O_2(g) \longrightarrow 2WO_3(s);\ \Delta H = -1685.8\ kJ \quad (1)$$

$$C(graphite) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -393.5\ kJ \quad (2)$$

$$2WC(s) + 5O_2(g) \longrightarrow 2WO_3(s) + 2CO_2(g);\ \Delta H = -2391.8\ kJ \quad (3)$$

$$\left(\tfrac{1}{2}\right)\quad W_{(s)} + \tfrac{3}{2}\cancel{O_2}_{(g)} \longrightarrow \cancel{WO_3}_{(s)}\ ,\ \Delta H = \underbrace{-842.9\ kJ}$$

+

$$C + \cancel{O_2} \longrightarrow \cancel{CO_2}\ ,\ \Delta H = \underbrace{-393.5\ kJ}$$

+

$$\left(\tfrac{1}{2}\right)\quad \cancel{WO_3}_{(s)} + \cancel{CO_2} \longrightarrow WC + \tfrac{5}{2}\cancel{O_2}\ ,\ \Delta H = \underbrace{+1159.9\ kJ}$$

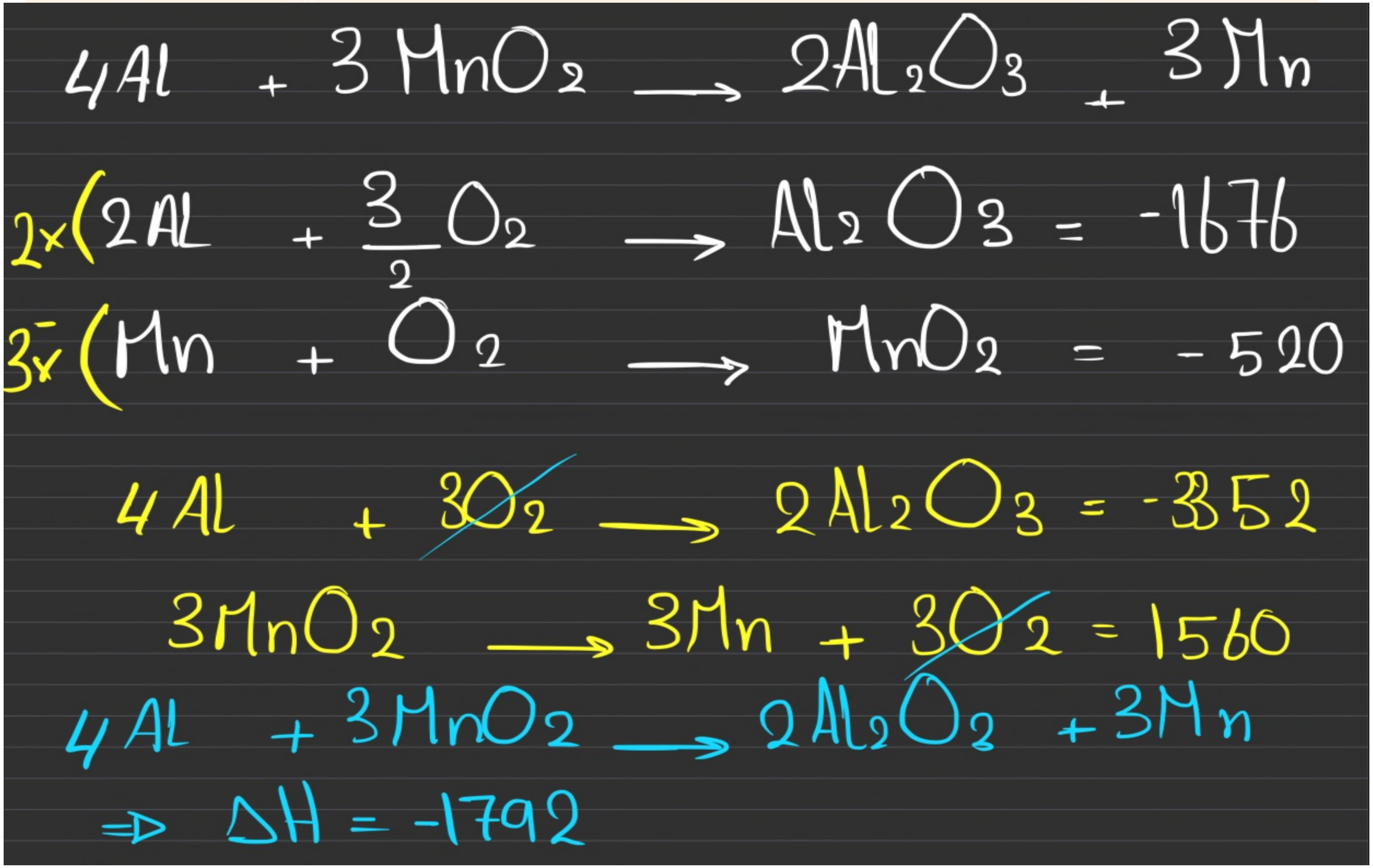
Reverse

$$W + C \longrightarrow WC \Rightarrow \Delta H = -76.5$$

Exercise 6.10 Manganese metal can be obtained by reaction of manganese dioxide with aluminum.

$$4Al(s) + 3MnO_2(s) \longrightarrow 2Al_2O_3(s) + 3Mn(s)$$

What is Δ*H* for this reaction? Use the following data:



$4Al + 3MnO_2 \longrightarrow 2Al_2O_3 + 3Mn$

$2\times(2Al + \frac{3}{2}O_2 \longrightarrow Al_2O_3 = -1676$

$3\times(Mn + O_2 \longrightarrow MnO_2 = -520$

$4Al + 3\cancel{O_2} \longrightarrow 2Al_2O_3 = -3352$

$3MnO_2 \longrightarrow 3Mn + 3\cancel{O_2} = 1560$

$4Al + 3MnO_2 \longrightarrow 2Al_2O_3 + 3Mn$

$\Rightarrow \Delta H = -1792$

6.8 Standard Enthalpies of Formation

- ✓ The term **standard state** refers to the standard thermodynamic conditions chosen for substances when listing or comparing thermodynamic data: 1 atm pressure and the specified temperature (usually 25°C).

  $\Delta H°$ is called the *standard enthalpy of reaction*

- ✓ An **allotrope** is *one of two or more distinct forms of an element in the same physical state. (O_2 and O_3), (C: graphite and diamond)*

- ✓ The **reference form** of an element for the purpose of specifying the formation reaction is usually *the most stable form of the element under standard thermodynamic conditions.*

- ✓ The reference form of oxygen at 25°C is $O_2(g)$; the reference form of carbon at 25°C is graphite ($C_{graphite}$)

The **standard enthalpy of formation** (also called the **standard heat of formation**) of a substance, denoted ΔH_f°,

is the enthalpy change for the formation of one mole of the substance in its standard state from its elements in their reference form and in their standard states.

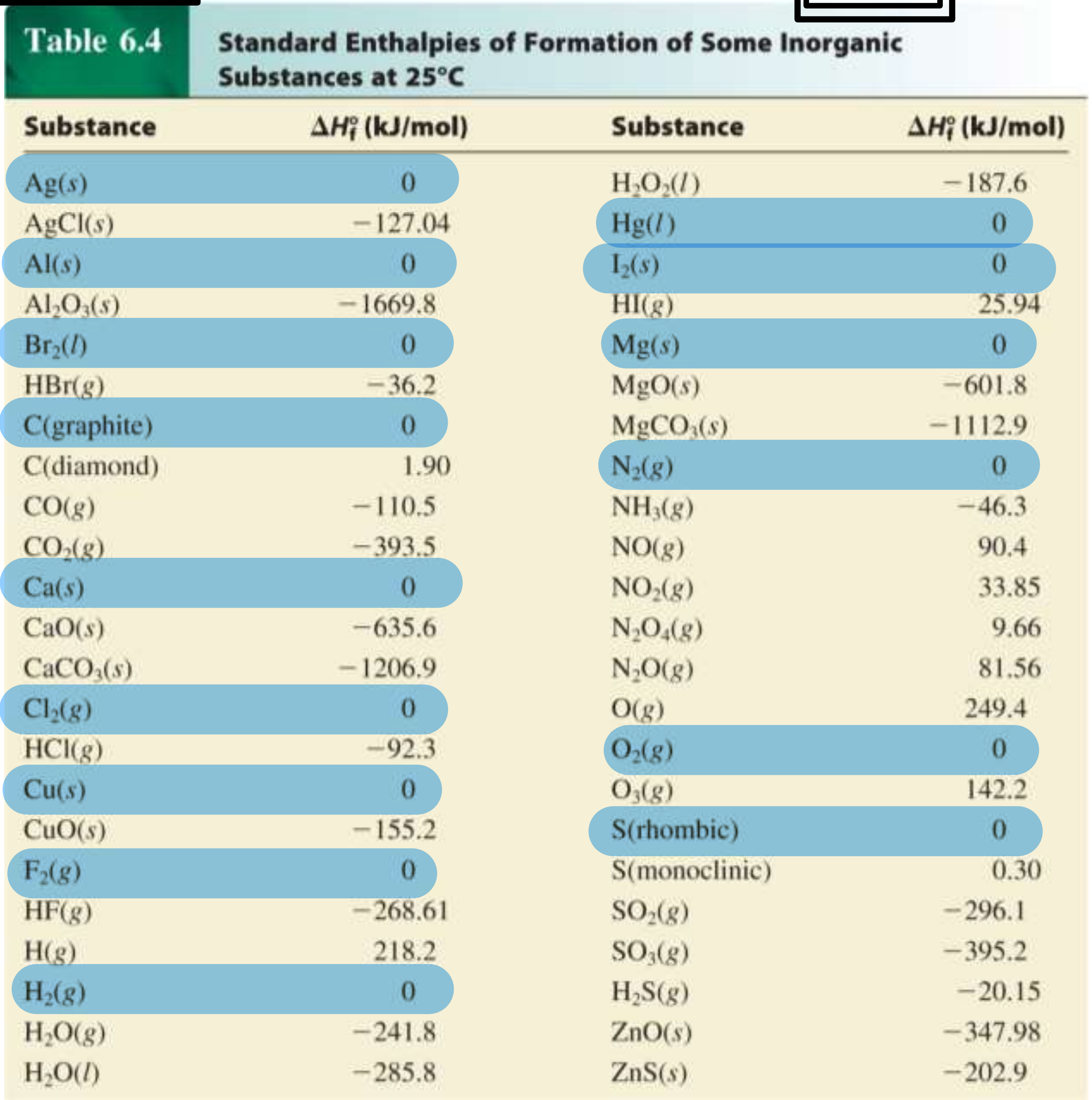


Table 6.4 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
$Ag(s)$	0	$H_2O_2(l)$	−187.6
$AgCl(s)$	−127.04	$Hg(l)$	0
$Al(s)$	0	$I_2(s)$	0
$Al_2O_3(s)$	−1669.8	$HI(g)$	25.94
$Br_2(l)$	0	$Mg(s)$	0
$HBr(g)$	−36.2	$MgO(s)$	−601.8
C(graphite)	0	$MgCO_3(s)$	−1112.9
C(diamond)	1.90	$N_2(g)$	0
$CO(g)$	−110.5	$NH_3(g)$	−46.3
$CO_2(g)$	−393.5	$NO(g)$	90.4
$Ca(s)$	0	$NO_2(g)$	33.85
$CaO(s)$	−635.6	$N_2O_4(g)$	9.66
$CaCO_3(s)$	−1206.9	$N_2O(g)$	81.56
$Cl_2(g)$	0	$O(g)$	249.4
$HCl(g)$	−92.3	$O_2(g)$	0
$Cu(s)$	0	$O_3(g)$	142.2
$CuO(s)$	−155.2	S(rhombic)	0
$F_2(g)$	0	S(monoclinic)	0.30
$HF(g)$	−268.61	$SO_2(g)$	−296.1
$H(g)$	218.2	$SO_3(g)$	−395.2
$H_2(g)$	0	$H_2S(g)$	−20.15
$H_2O(g)$	−241.8	$ZnO(s)$	−347.98
$H_2O(l)$	−285.8	$ZnS(s)$	−202.9

* كل الفلزات صلبة ما عدا
((Hg))
Nobel gas ((g)) *

$\Delta H^\circ = 0$

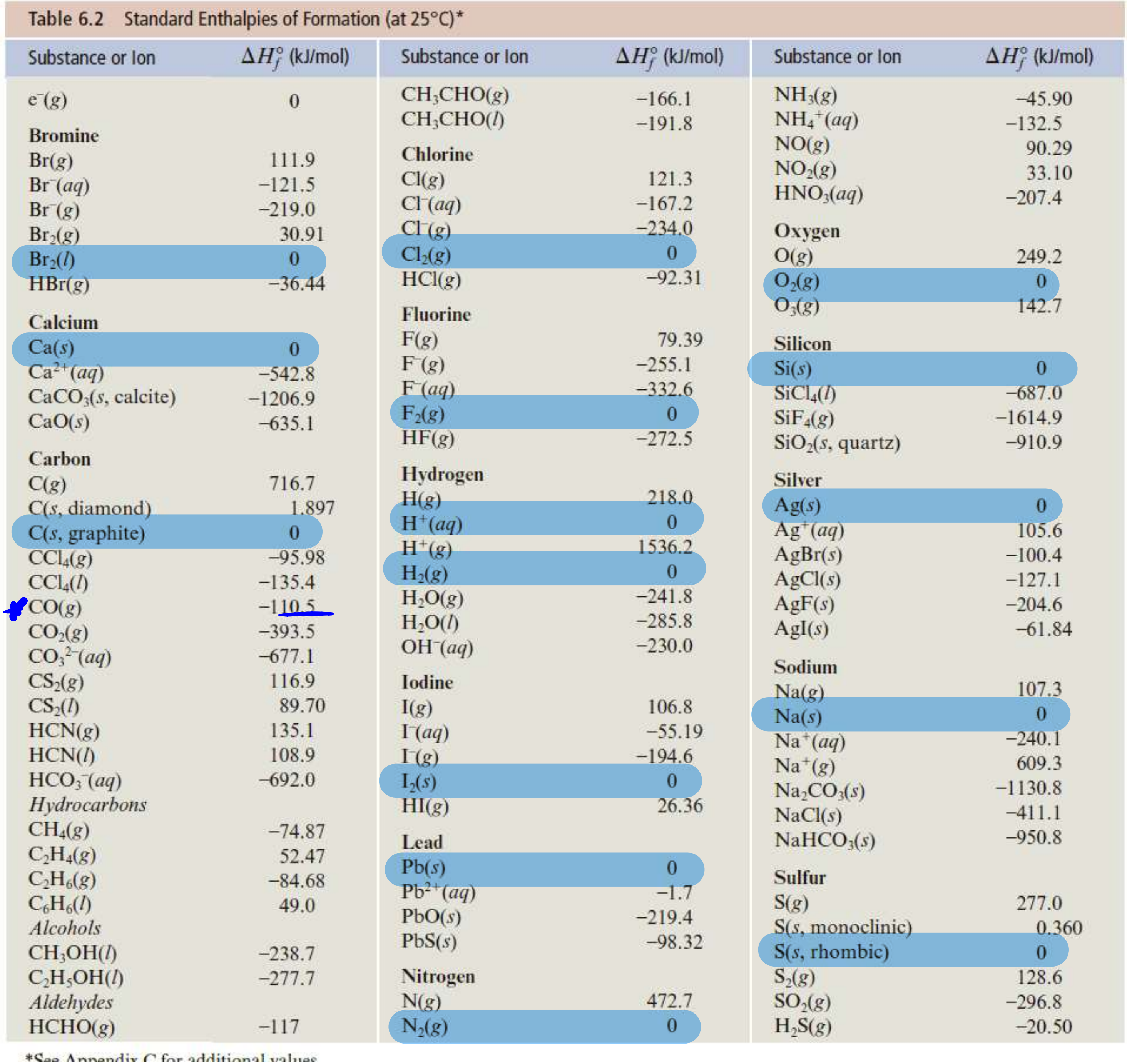


Table 6.2 Standard Enthalpies of Formation (at 25°C)*

Substance or Ion	ΔH_f° (kJ/mol)
$e^-(g)$	0
Bromine	
$Br(g)$	111.9
$Br^-(aq)$	−121.5
$Br^-(g)$	−219.0
$Br_2(g)$	30.91
$Br_2(l)$	0
$HBr(g)$	−36.44
Calcium	
$Ca(s)$	0
$Ca^{2+}(aq)$	−542.8
$CaCO_3(s$, calcite)	−1206.9
$CaO(s)$	−635.1
Carbon	
$C(g)$	716.7
$C(s$, diamond)	1.897
$C(s$, graphite)	0
$CCl_4(g)$	−95.98
$CCl_4(l)$	−135.4
$CO(g)$	−110.5
$CO_2(g)$	−393.5
$CO_3^{2-}(aq)$	−677.1
$CS_2(g)$	116.9
$CS_2(l)$	89.70
$HCN(g)$	135.1
$HCN(l)$	108.9
$HCO_3^-(aq)$	−692.0
Hydrocarbons	
$CH_4(g)$	−74.87
$C_2H_4(g)$	52.47
$C_2H_6(g)$	−84.68
$C_6H_6(l)$	49.0
Alcohols	
$CH_3OH(l)$	−238.7
$C_2H_5OH(l)$	−277.7
Aldehydes	
$HCHO(g)$	−117
$CH_3CHO(g)$	−166.1
$CH_3CHO(l)$	−191.8
Chlorine	
$Cl(g)$	121.3
$Cl^-(aq)$	−167.2
$Cl^-(g)$	−234.0
$Cl_2(g)$	0
$HCl(g)$	−92.31
Fluorine	
$F(g)$	79.39
$F^-(g)$	−255.1
$F^-(aq)$	−332.6
$F_2(g)$	0
$HF(g)$	−272.5
Hydrogen	
$H(g)$	218.0
$H^+(aq)$	0
$H^+(g)$	1536.2
$H_2(g)$	0
$H_2O(g)$	−241.8
$H_2O(l)$	−285.8
$OH^-(aq)$	−230.0
Iodine	
$I(g)$	106.8
$I^-(aq)$	−55.19
$I^-(g)$	−194.6
$I_2(s)$	0
$HI(g)$	26.36
Lead	
$Pb(s)$	0
$Pb^{2+}(aq)$	−1.7
$PbO(s)$	−219.4
$PbS(s)$	−98.32
Nitrogen	
$N(g)$	472.7
$N_2(g)$	0
$NH_3(g)$	−45.90
$NH_4^+(aq)$	−132.5
$NO(g)$	90.29
$NO_2(g)$	33.10
$HNO_3(aq)$	−207.4
Oxygen	
$O(g)$	249.2
$O_2(g)$	0
$O_3(g)$	142.7
Silicon	
$Si(s)$	0
$SiCl_4(l)$	−687.0
$SiF_4(g)$	−1614.9
$SiO_2(s$, quartz)	−910.9
Silver	
$Ag(s)$	0
$Ag^+(aq)$	105.6
$AgBr(s)$	−100.4
$AgCl(s)$	−127.1
$AgF(s)$	−204.6
$AgI(s)$	−61.84
Sodium	
$Na(g)$	107.3
$Na(s)$	0
$Na^+(aq)$	−240.1
$Na^+(g)$	609.3
$Na_2CO_3(s)$	−1130.8
$NaCl(s)$	−411.1
$NaHCO_3(s)$	−950.8
Sulfur	
$S(g)$	277.0
$S(s$, monoclinic)	0.360
$S(s$, rhombic)	0
$S_2(g)$	128.6
$SO_2(g)$	−296.8
$H_2S(g)$	−20.50

*See Appendix C for additional values.

(Q) Which reaction corresponds to the standard enthalpy of formation of $NaHCO_3(s)$, $\Delta H_f° = -947.7$ kJ/mol?

A. $Na(s) + ½H_2(g) + {}^3/2O_2(g) + C(s, gr) \rightarrow NaHCO_3(s)$

B. $Na^+(g) + H^+(g) + 3O^{2-}(g) + C^{4+}(g) \rightarrow NaHCO_3(s)$

C. $Na^+(aq) + H^+(aq) + 3O^{2-}(aq) + C^{4+}(aq) \rightarrow NaHCO_3(s)$

D. $NaHCO_3(s) \rightarrow Na(s) + ½H_2(g) + {}^3/2O_2(g) + C(s, gr)$

E. $Na^+(aq) + HCO_3^-(aq) \rightarrow NaHCO_3(s)$

(Q) Which reaction corresponds to the standard enthalpy of formation of $C_4H_3Br_2NO_2(l)$?

A. $4C(s, gr) + 3H(g) + 2Br(s) + N(g) + 2O(g) \rightarrow C_4H_3Br_2NO_2(l)$

B. $8C(s, gr) + 3H_2(g) + 2Br_2(g) + N_2(g) + 2O_2(g) \rightarrow 2C_4H_3Br_2NO_2(l)$

C. $4C(s, gr) + {}^3/2H_2(g) + Br_2(l) + ½N_2(g) + O_2(g) \rightarrow 1C_4H_3Br_2NO_2(l)$

D. $4C(s, gr) + {}^3/2H_2(g) + Br_2(s) + ½N_2(g) + ½O_2(g) \rightarrow C_4H_3Br_2NO_2(l)$

✓(Q)The standard enthalpy of formation of sulfur dioxide (SO_2) is -296.9 kJ. What is ΔH for the formation of 16.03 g of sulfur dioxide in its standard state from its elements in their standard states?

(SO_2 = 64.07 g/mol)

A. 74.28 kJ

B. - 296.9 kJ

C. - 4,759 kJ

D. -74.28 kJ

E. 593.6 kJ

Combustion reaction

$$16.03\,\cancel{\text{g}\,\text{SO}_2} \times \frac{\cancel{\text{mol}\,\text{SO}_2}}{\underset{64.07}{\cancel{32.07}}\,\cancel{\text{g}\,\text{SO}_2}} \times \frac{-296.9\ \text{kJ}}{\cancel{\text{mol}\,\text{SO}_2}}$$

$$= \underline{-148.4}\ \text{kJ}$$

-74 kJ

2. Way to apply Hess's Law without needing to manipulate thermochemical equations

$$\Delta H^\circ_{\text{reaction}} = \left[\text{Sum of all } \Delta H^\circ_{\text{f}} \text{ of all of the products}\right] - \left[\text{Sum of all } \Delta H^\circ_{\text{f}} \text{ of all of the reactants}\right]$$

Consider the reaction:

$$aA + bB \rightarrow cC + dD$$

$$\Delta H^\circ_{\text{reaction}} = c \times \Delta H^\circ_{\text{f}}(C) + d \times \Delta H^\circ_{\text{f}}(D) - \{a \times \Delta H^\circ_{\text{f}}(A) + b \times \Delta H^\circ_{\text{f}}(B)\}$$

- $\Delta H^\circ_{\text{rxn}}$ has units of kJ because
- Coefficients × heats of formation have units of $(\cancel{\text{mol}} \times \text{kJ}/\cancel{\text{mol}})$

$$\Delta H^\circ_{\text{rxn}} = \sum\left[\Delta H^\circ_{\text{f}}(\text{products}) \times (\text{moles of product})\right] - \sum\left[\Delta H^\circ_{\text{f}}(\text{reactants}) \times (\text{moles of reactant})\right]$$

$\Delta H^\circ_{\text{rxn}}$ has units of kJ

$\Delta H^\circ_{\text{f}}$ has units of kJ/mol

Ex. 11: Calculate ΔH°_{rxn} Using ΔH_f°

Calculate ΔH°_{rxn} using ΔH_f° data for the reaction

$$SO_3(g) \longrightarrow SO_2(g) + \tfrac{1}{2}O_2(g)$$

$$\Delta H^o_{rxn} = \sum\left[\Delta H^o_f(\text{products}) \times (\text{moles of product})\right] - \sum\left[\Delta H^o_f(\text{reactants}) \times (\text{moles of reactant})\right]$$

ΔH°_{rxn} has units of kJ

ΔH°_f has units of kJ/mol

$$\Delta H^\circ_{rxn} = \Delta H^\circ_f(SO_2(g)) + \tfrac{1}{2}\Delta H^\circ_f(O_2(g)) - \Delta H^\circ_f(SO_3(g))$$

$$\Delta H^{\blacksquare}_{rxn} = -297\ \text{kJ/mol} + \tfrac{1}{2}(0\ \text{kJ/mol}) - (-396\ \text{kJ/mol})$$

$$\Delta H^o_{rxn} = 99\ \text{kJ}$$

Example 6.9

(Q) Calculate $\Delta H^{\circ}_{\text{rxn}}$ using ΔH_f° for the reaction

$$4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(l)$$

$$\Delta H^{\blacksquare}_{\text{rxn}} = 4\Delta H^{\blacksquare}_{\text{f }NO_2(g)} + 6\Delta H^{\blacksquare}_{\text{f }H_2O(l)} - 4\Delta H^{\blacksquare}_{\text{f }NH_3(g)} - 7\Delta H^{\blacksquare}_{\text{f }O_2(g)}$$

$$\Delta H^{\blacksquare}_{\text{rxn}} = 4\ \cancel{\text{mol}}(34\ \text{kJ}/\cancel{\text{mol}}) + 6\ \cancel{\text{mol}}(-285.9\ \text{kJ}/\cancel{\text{mol}})$$

$$- 4\ \cancel{\text{mol}}(-46.0\ \text{kJ}/\cancel{\text{mol}}) - 7\ \cancel{\text{mol}}(0\ \text{kJ}/\cancel{\text{mol}})$$

$$\Delta H^{\circ}_{\text{rxn}} = [136 - 1715.4 + 184]\ \text{kJ}$$

$$\boldsymbol{\Delta H^{\circ}_{\text{rxn}} = -1395\ \text{kJ}}$$

- ✓ Don't always want to know ΔH°_{rxn}
- ✓ Can use Hess's Law and ΔH°_{rxn} to calculate ΔH_f° for compound where not known

Example: Given the following data, what is the value of ΔH_f° ($C_2H_3O_2^-$, *aq*)?

$$Na^+(aq) + C_2H_3O_2^-(aq) + 3H_2O(l) \rightarrow NaC_2H_3O_2{\cdot}3H_2O(s)$$

$$\Delta H^\circ_{rxn} = -19.7\ \text{kJ/mol}$$

$Na^+(aq)$ $\Delta H^\circ_f = -239.7$ kJ/mol

$NaC_2H_3O_2{\bullet}3H_2O(s)$ $\Delta H^\circ_f = 710.4$ kJ/mol

$H_2O(l)$ $\Delta H^\circ_f = -285.9$ kJ/mol

$\Delta H^\circ_{rxn} = \Delta H_f^\circ\ (\mathrm{NaC_2H_3O_2{\cdot}3H_2O}, s) - \Delta H_f^\circ\ (\mathrm{Na^+}, aq) - \Delta H_f^\circ\ (\mathrm{C_2H_3O_2^-}, aq) - 3\Delta H_f^\circ\ (\mathrm{H_2O}, l)$

Rearranging

$\Delta H_f^\circ\ (\mathrm{C_2H_3O_2^-}, aq) = \Delta H_f^\circ\ (\mathrm{NaC_2H_3O_2{\cdot}3H_2O}, s) - \Delta H_f^\circ\ (\mathrm{Na^+}, aq) - \Delta H^\circ_{rxn} - 3\Delta H_f^\circ\ (\mathrm{H_2O}, l)$

$\Delta H_f^\circ\ (\mathrm{C_2H_3O_2^-}, aq) =$ –710.4 kJ/mol – (–239.7kJ/mol) – (–19.7 kJ/mol) – 3(–285.9 kJ/mol)

= +406.7 kJ/mol

(Q)Calculate ΔH for this reaction using ΔH_f° data.

$$2\text{Fe}(s) + 6\text{H}_2\text{O}(l) \rightarrow 2\text{Fe(OH)}_3(s) + 3\text{H}_2(g)$$

$\boldsymbol{\Delta H_f^\circ}$ $\quad \underline{\mathbf{0}} \quad -285.8 \quad -696.5 \quad \underline{\mathbf{0}}$

$$\Delta H^\circ_{\text{rxn}} = 2 \times \Delta H_f^\circ(\text{Fe(OH)}_3, s) + 3 \times \Delta H_f^\circ(\text{H}_2, g) - 2 \times \Delta H_f^\circ(\text{Fe}, s) - 6 \times \Delta H_f^\circ(\text{H}_2\text{O}, l)$$

$$\Delta H^\circ_{\text{rxn}} = \cancel{2\text{ mol}} \times (-696.5\ \cancel{\text{kJ/mol}}) + 3 \times 0 - 2 \times 0 - 6\ \cancel{\text{mol}} \times (-285.8\ \text{kJ}\cancel{/\text{mol}})$$

$$\Delta H^\circ_{\text{rxn}} = -1393\ \text{kJ} + 1714.8\ \text{kJ}$$

$$\boldsymbol{\Delta H^\circ_{\textbf{rxn}} = 321.8\ \textbf{kJ}}$$

✓(Q)Calculate $\Delta H^\circ_{\text{rxn}}$ for this reaction using ΔH_f° data.

$$\begin{array}{lcccc} & CO_2(g) \; + & 2H_2O(l) \; \rightarrow & 2O_2(g) \; + & CH_4(g) \\ \Delta H_f^\circ & -393.5 & -285.8 & 0 & -74.8 \end{array}$$

$$\Delta H^\circ_{\text{rxn}} = 2 \times \Delta H_f^\circ\,(O_2, g) + \Delta H_f^\circ\,(CH_4, g) - \Delta H_f^\circ\,(CO\cancel{_2, g}) - 2 \times \Delta H_f^\circ\,(\cancel{H_2O}, l)$$

$$\Delta H^\circ_{\text{rxn}} = 2 \times \cancel{0 +} 1\ \text{mo}\cancel{\text{l} \times} (-74.8\ \text{kJ/mol}) \cancel{- 1}\ \text{mol} \times (-393.5\ \text{kJ/mol}) - 2\ \text{mol} \times (-285.8\ \text{kJ/mol})$$

$$\Delta H^\circ_{\text{rxn}} = -74.8\ \text{kJ} + 393.5\ \text{kJ} + 571.6\ \text{kJ}$$

$\Delta H^\circ_{\text{rxn}} = 890.3\ \text{kJ}$

Calculate ΔH_f° for FeO(s) using the information below. ΔH_f° values are shown below each substance.

$Fe_3O_4(s) + CO(g) \rightarrow 3FeO(s) + CO_2(g)$ $\Delta H^\circ = 21.9$ kJ

-1120.9 kJ   -110.5 kJ   ??   – 393.5 kJ

A. 272.0 kJ
B. -816.0 kJ
C. -272.0 kJ
D. 26.00 J
E. -38.60 kJ

$$\Delta H^{o}_{rxn} = \sum\left[\Delta H^{o}_{f}\left(\text{products}\right)\times\left(\text{moles of product}\right)\right] - \sum\left[\Delta H^{o}_{f}\left(\text{reactants}\right)\times\left(\text{moles of reactant}\right)\right]$$

Important

$$\Delta H^{\circ}_{rxn} = [\overset{\downarrow}{\mathbf{3}}\Delta H^{\circ}_{f}(\text{FeO}, s) + \Delta H^{\circ}_{f}(\text{CO}_2, g)] - [\Delta H^{\circ}_{f}(\text{Fe}_3\text{O}_4, s) + \Delta H^{\circ}_{f}(\text{CO}, g)]$$

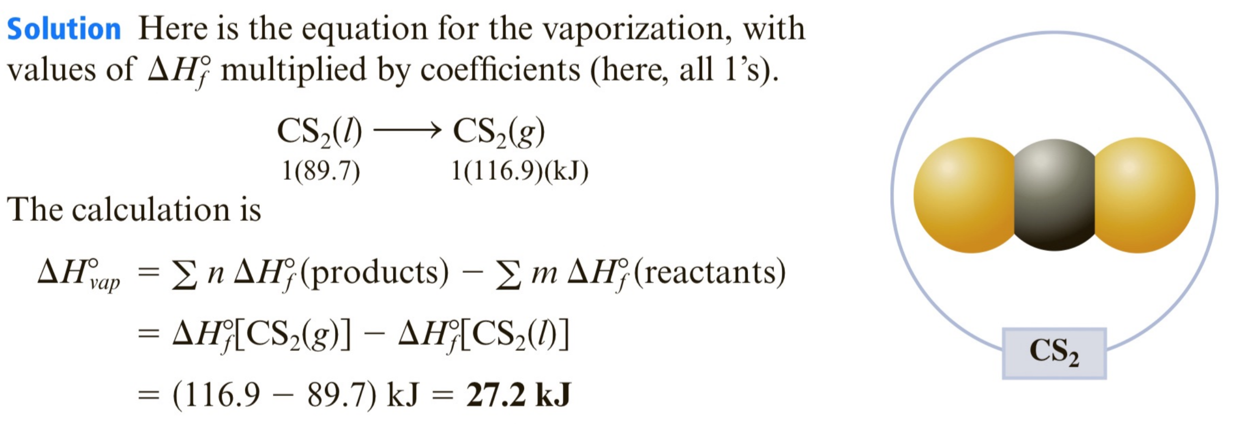
$$+21.9\text{ kJ} = [3\Delta H^{\circ}_{f}(\text{FeO}, s) + -393.5\text{ kJ})] - [-1120.9\text{ kJ} + -110.5\text{ kJ})]$$

$$+21.9\text{ kJ} = [3\Delta H^{\circ}_{f}(\text{FeO}, s) + 837.9\text{ kJ}]$$

$$-816.0\text{ kJ} = 3\Delta H^{\circ}_{f}(\text{FeO}, s)$$

$$-272.0\text{ kJ} = \Delta H^{\circ}_{f}(\text{FeO}, s)$$

Use values of ΔH, to calculate the heat of vaporization, of carbon disulfic at 25°C. The vaporization process is $CS2(l) \longrightarrow > CS2(g)$: Example 6.8

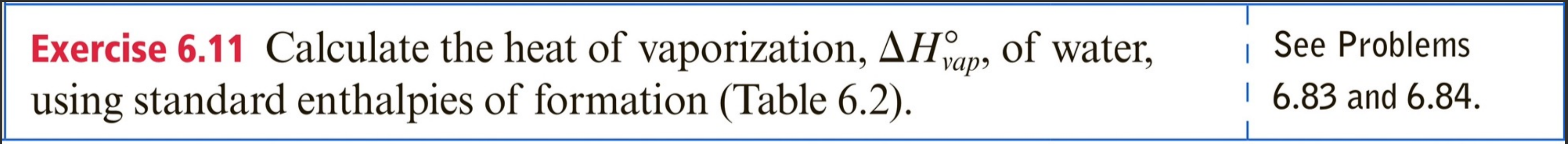

Solution Here is the equation for the vaporization, with values of ΔH_f° multiplied by coefficients (here, all 1's).

$$\underset{1(89.7)}{CS_2(l)} \longrightarrow \underset{1(116.9)(\text{kJ})}{CS_2(g)}$$

The calculation is

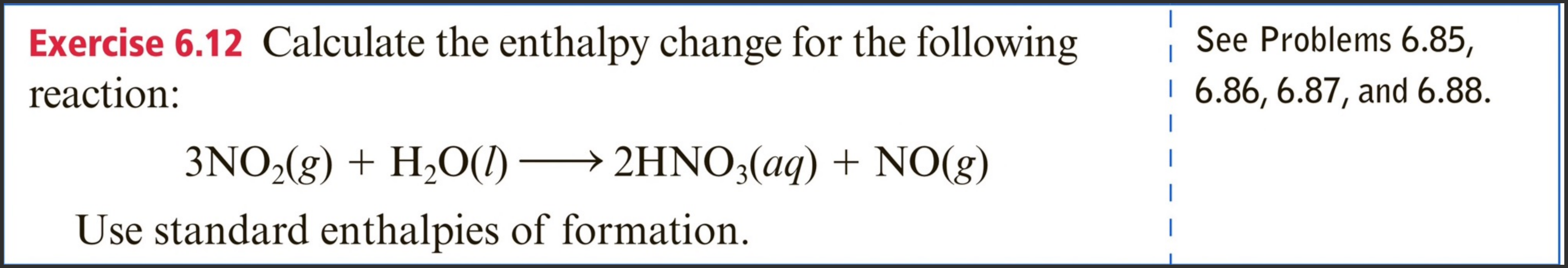
$$\begin{aligned}\Delta H^\circ_{vap} &= \sum n\,\Delta H_f^\circ(\text{products}) - \sum m\,\Delta H_f^\circ(\text{reactants}) \\ &= \Delta H_f^\circ[CS_2(g)] - \Delta H_f^\circ[CS_2(l)] \\ &= (116.9 - 89.7)\ \text{kJ} = \mathbf{27.2\ kJ}\end{aligned}$$

……


Exercise 6.11 Calculate the heat of vaporization, ΔH°_{vap}, of water, using standard enthalpies of formation (Table 6.2).

See Problems 6.83 and 6.84.

44



Exercise 6.12 Calculate the enthalpy change for the following reaction:

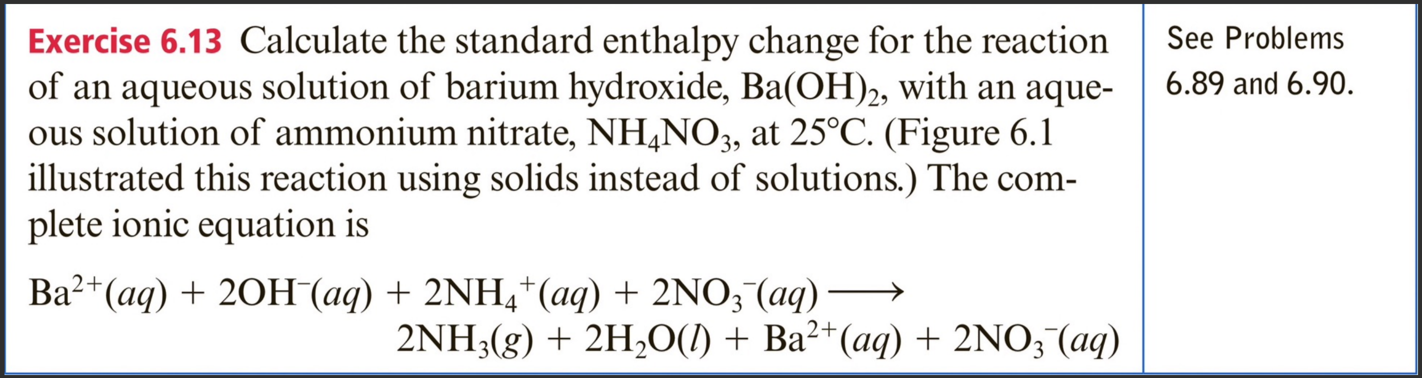
$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

Use standard enthalpies of formation.

See Problems 6.85, 6.86, 6.87, and 6.88.

-1138

……



Exercise 6.13 Calculate the standard enthalpy change for the reaction of an aqueous solution of barium hydroxide, $Ba(OH)_2$, with an aqueous solution of ammonium nitrate, NH_4NO_3, at 25°C. (Figure 6.1 illustrated this reaction using solids instead of solutions.) The complete ionic equation is

$$Ba^{2+}(aq) + 2OH^-(aq) + 2NH_4^+(aq) + 2NO_3^-(aq) \longrightarrow 2NH_3(g) + 2H_2O(l) + Ba^{2+}(aq) + 2NO_3^-(aq)$$

See Problems 6.89 and 6.90.

61.6

(Q) An endothermic reaction causes the surroundings to:

- Warm up.
- Become acidic.
- Condense.
- [✓ Decrease in temperature.]
- Expand.

(Q)An endothermic reaction causes the system to:

- Become acidic.
- [✓ Warm up.]
- Condense.
- Decrease in temperature.
- Expand.

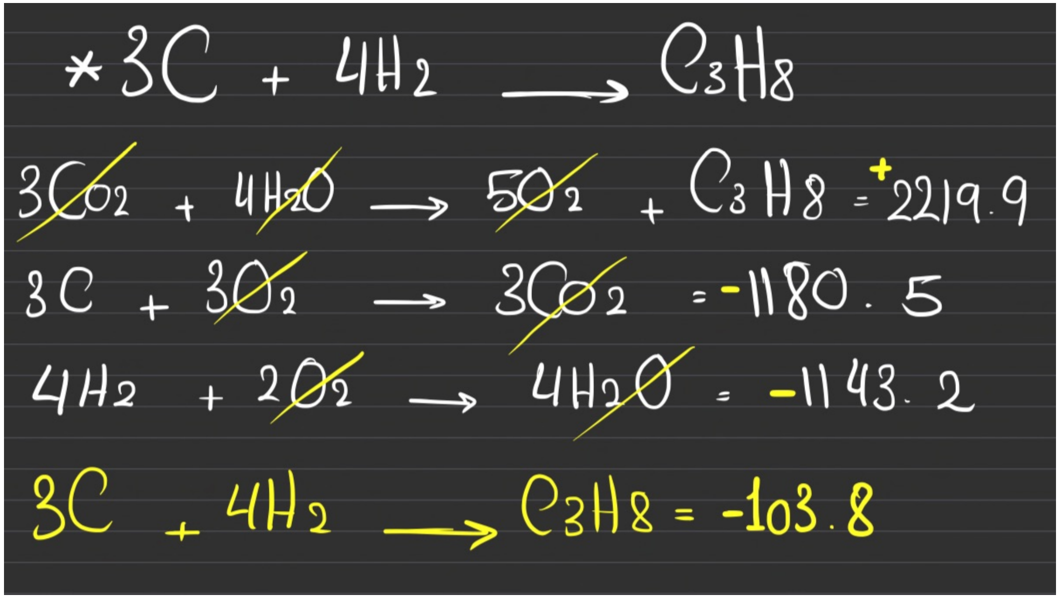
✓Use Hess’s law to determine the standard enthalpy of formation for the following reaction

$3\ C(s) + 4\ H_2(g) \rightarrow C_3H_8(g)$

Use the following information:

(a) $C_3H_8(g) + 5\ O_2(g) \rightarrow 3CO_2(g) + 4\ H_2O(l)$	$\Delta H° = -2219.9$ kJ
(b) $C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta H° = -393.5$ kJ
(c) $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$	$\Delta H° = -285.8$ kJ

Answer: - 104 kJ



$* 3C + 4H_2 \longrightarrow C_3H_8$

$\cancel{3CO_2} + \cancel{4H_2O} \longrightarrow \cancel{5O_2} + C_3H_8 = +2219.9$

$3C + \cancel{3O_2} \longrightarrow \cancel{3CO_2} = -1180.5$

$4H_2 + \cancel{2O_2} \longrightarrow \cancel{4H_2O} = -1143.2$

$3C + 4H_2 \longrightarrow C_3H_8 = -103.8$

Calculate the standard enthalpy change for the reaction:

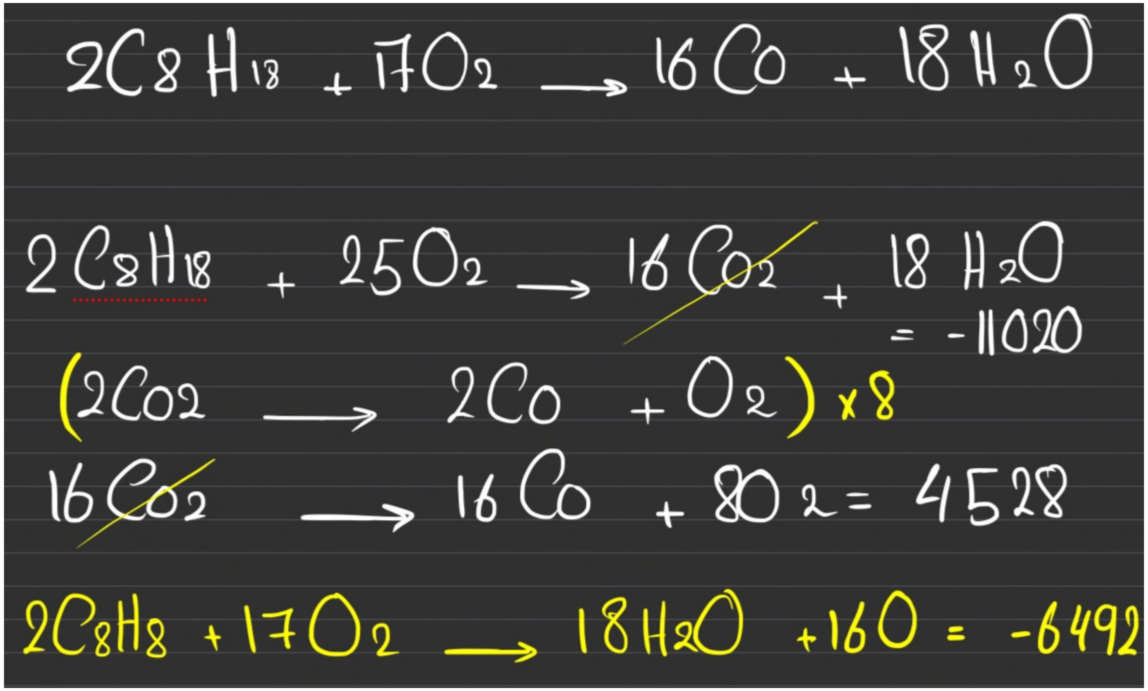
$2C_8H_{18}(l) + 17O_2(g) \rightarrow 16CO(g) + 18H_2O(l)$.

Given:

$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$ ΔH° = –11020 kJ

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ ΔH° = –566.0 kJ

Answer= **–6492 kJ**



$2C_8H_{18} + 17O_2 \longrightarrow 16CO + 18H_2O$

$2C_8H_{18} + 25O_2 \longrightarrow 16\cancel{CO_2} + 18H_2O$
$= -11020$

$(2CO_2 \longrightarrow 2CO + O_2) \times 8$

$16\cancel{CO_2} \longrightarrow 16CO + 8O_2 = 4528$

$2C_8H_8 + 17O_2 \longrightarrow 18H_2O + 16O = -6492$

(Q) To which one of the following reactions occurring at 25° C does the symbol $\Delta H^o_f\,[H_2SO_4(l)]$ refer?

$2H(g) + S(g) + 4O(g) \rightarrow H_2SO_4(l)$

$H_2(g) + S(g) + 2O_2(g) \rightarrow H_2SO_4(l)$

$H_2SO_4(l) \rightarrow H_2(g) + S(s) + 2O_2(g)$

$H_2SO_4(l) \rightarrow 2H(g) + S(s) + 4O(g)$

$\underline{H_2(g) + S(s) + 2O_2(g) \rightarrow H_2SO_4(l)}$

(Q) $\Delta H^o_f\,[HNO_3(l)]$: $(1/2)H_2(g) + (1/2)N_2(g) + (3/2)O_2(g) \rightarrow HNO_3(l)$

(Q) $\Delta H^o_f\,[CO(g)]$: $C(s) + (1/2)O_2(g) \rightarrow CO(g)$

(Q) $\Delta H^o_f\,[CO_2(g)]$: $C(s) + O_2(g) \rightarrow CO_2(g)$

6.55 What is ΔU when 1.00 mol of liquid water vaporizes at 100°C ? The heat of vaporization, DH°$_{vap}$, of water at 100°C is 40.66 kJ/mol.

What is ΔU when 9.0 g of liquid water vaporizes at 100°C ? The heat of vaporization, DH°$_{vap}$, of water at 100°C is 40.66 kJ/mol.

Learning Objectives

Important Terms

Ek → Ep

6.1 Energy and Its Units

- Define *energy, kinetic energy, potential energy,* and *internal energy.* → U
- Define the SI unit of energy, *joule,* as well as the common unit of energy, *calorie.* → watt . Joule/s
- Calculate the kinetic energy of a moving object. → $\frac{1}{2} m (V)^2$
  Example 6.1
- State the law of conservation of energy.

The energy Can be transferred from one type to another but the total amount of energy will stay Constant

- energy E
- kinetic energy Ek
- joule (J) J
- calorie (cal) Cal
- potential energy Ep
- internal energy U
- law of conservation of energy

6.2 First Law of Thermodynamics; Work and Heat

- Define a thermodynamic system and its surroundings.
- Define *work* and *heat.*
- Define the change of internal energy of a system. → ΔU
- Express the *first law of thermodynamics* verbally and mathematically.

$\Delta U = q + w$

- thermodynamic system (or system)
- surroundings
- work → mgh -(w)
- heat → mgh (q)
- state function → doesn't depend on the pathway
- first law of thermodynamics

6.3 Heat of Reaction; Enthalpy of Reaction

- Define the heat of reaction.
- Distinguish between an exothermic process and an endothermic process. → $q = (-)$ lose heat → $q = +$ gain heat
- Describe *pressure-volume work* verbally and mathematically. → $w = -P\Delta V \rightarrow -\Delta nRT$
- Define enthalpy and enthalpy of reaction. $= \Delta H = H_P - H_i$
- Relate the heat of reaction at constant pressure and the enthalpy of reaction.

$\Delta H = q \rightarrow$ constant T, P, $\Delta H \neq 0$

- heat of reaction
- exothermic process
- endothermic process
- pressure-volume work
- enthalpy
- enthalpy of reaction

6.4 Thermochemical Equations

- Define a *thermochemical equation.* $\Rightarrow \Delta H =$
- Write a thermochemical equation given pertinent information. **Example 6.2**
- Learn the two rules for manipulating (reversing and multiplying) thermochemical equations. → (-1) $\Delta H = n \rightarrow$ factor
- Manipulate a thermochemical equation using these rules. **Example 6.3**

- thermochemical equation

6.5 Applying Stoichiometry to Heats of Reaction

- Calculate the heat absorbed or evolved from a reaction given its enthalpy of reaction and the mass of a reactant or product. **Example 6.4**

mass → moles →

$\boxed{1\text{ mole} = \Delta H}$

$(C) = J/C°$ $\Delta H = (q)$

6.6 Measuring Heats of Reaction

$(S)\ J/g.C°$

- Define *heat capacity* and *specific heat.*
- Relate the heat absorbed or evolved to the specific heat, mass, and temperature change.

$q = -$

$q = +$

- Calculate the heat involved in changing the temperature of a material, given its specific heat. **Example 6.5**
- Define *calorimeter.*
- Calculate the enthalpy of reaction from calorimetric data (its temperature change and heat capacity). **Example 6.6**

heat capacity

specific heat capacity (specific heat)

calorimeter

$heat_c = C \times \Delta t$

$S.H. = m \times S \times \Delta t$

6.7 Hess's Law

- State Hess's law of heat summation.
- Apply Hess's law to obtain the enthalpy change for one reaction from the enthalpy changes of a number of other reactions. **Example 6.7**

Hess's law of heat summation

$\Delta H =$ the Sum - - -

6.8 Standard Enthalpies of Formation

- Define *standard state* and *reference form.*
- Define *standard enthalpy of formation.*
- Calculate the heat of a phase transition using standard enthalpies of formation for the different phases. **Example 6.8**
- Calculate the heat (enthalpy) of reaction from the standard enthalpies of formation of the substances in the reaction. **Example 6.9**

standard state

allotrope

reference form

standard enthalpy of formation (standard heat of formation)

6.9 Fuels—Foods, Commercial Fuels, and Rocket Fuels

- ~~Define *fuel.*~~
- ~~Describe the three needs of the body that are fulfilled by foods.~~
- ~~Give the approximate average values quoted (per gram) for the heat values (heats of combustion) for fats and for carbohydrates.~~
- ~~List the three major fossil fuels.~~
- ~~Describe the processes of coal gasification and coal liquefaction.~~
- ~~Describe some fuel–oxidizer systems used in rockets.~~

Key Equations

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

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

$\Delta U = q + w$

$w = -P\Delta V$

$H = U + PV$ *

$q = \Delta H$ (At fixed pressure and a given temperature)

$q = C\,\Delta t$

$q = s \times m \times \Delta t$

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

Done by: Joud Jaber