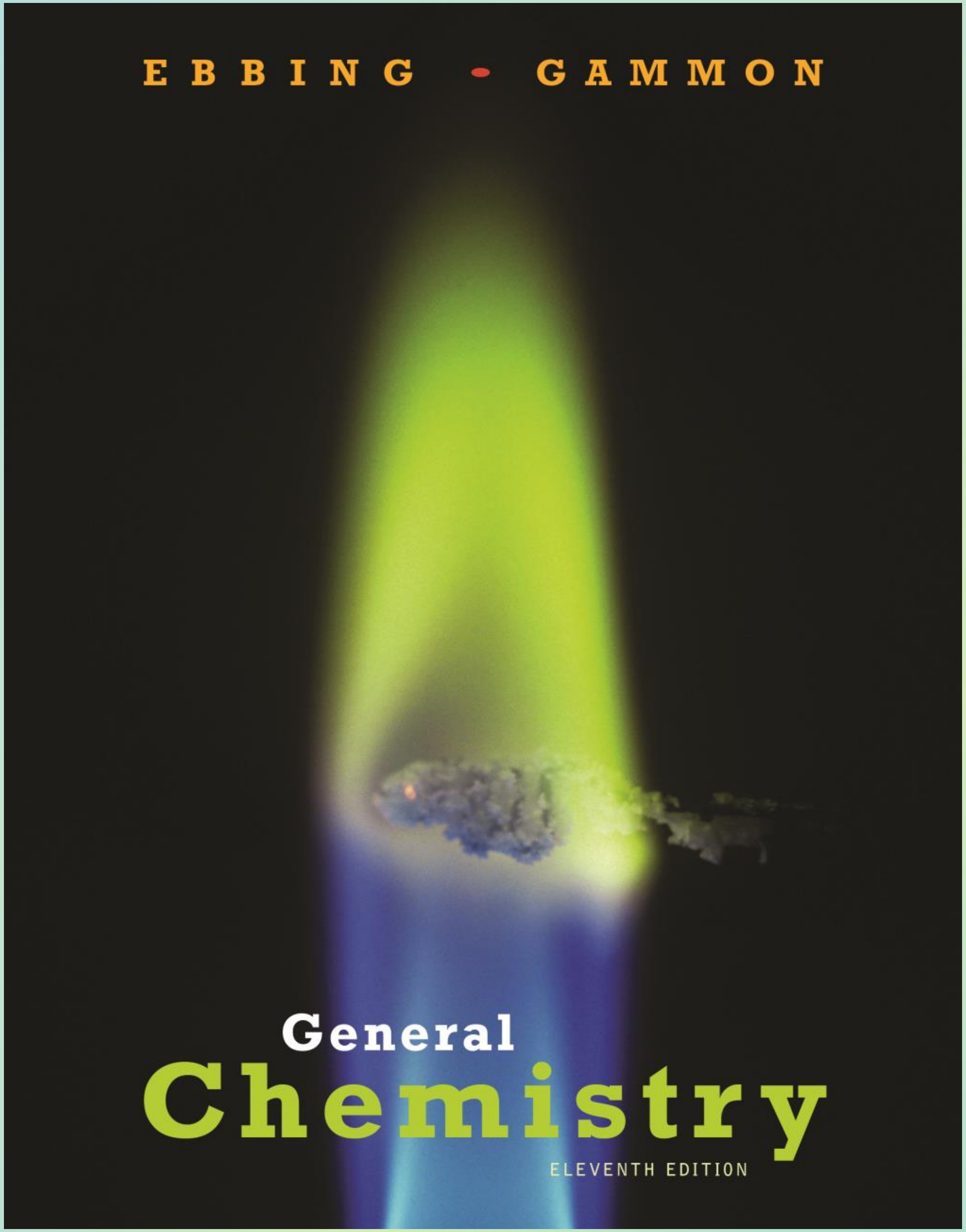


Thermochemistry

Understanding Heats of Reaction

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

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.

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

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

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

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?

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

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

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

- **Potential Energy** $E_p = mgh$

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

m= *mass (gram)*, *g* = constant acceleration of gravity = 9.807 m/s^2

h = height

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

U = internal energy

- ➢ **Internal Energy**

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

- ➢ **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.*

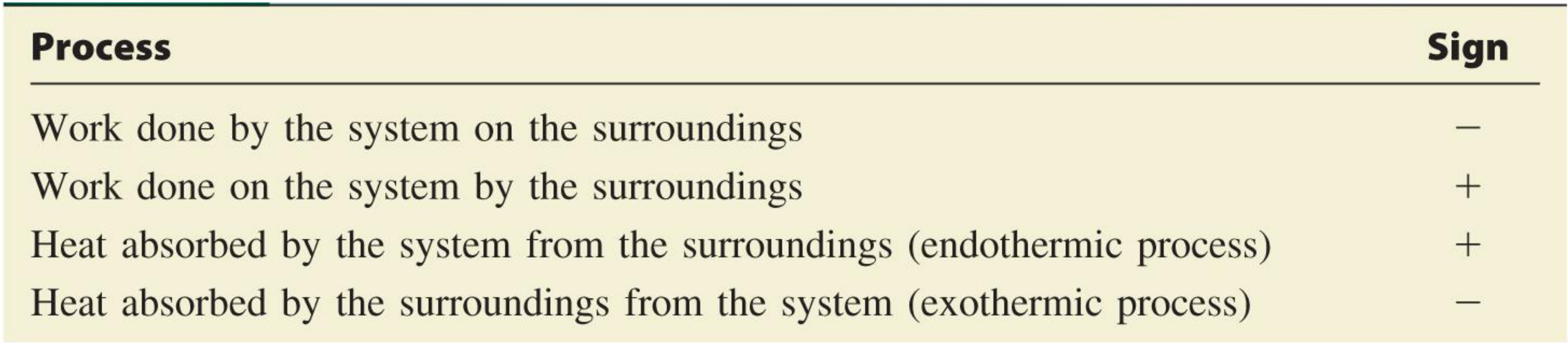
6.2 First Law of Thermodynamics; Work and Heat

- ✓ Definition of Work (w):

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.*

- ✓ Definition of Heat (q):

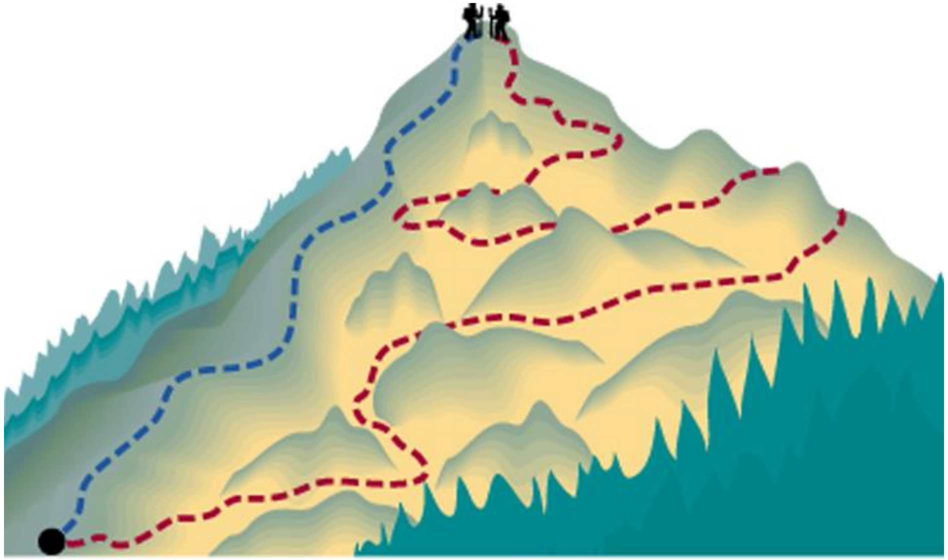
Heat is *an energy transfer (energy flow) into or out of a thermodynamic system that results from a temperature difference between the system and its surroundings.*



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

- ➢ **Change of Internal Energy** $\Delta U = U_f - U_i$

- ✓ 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.

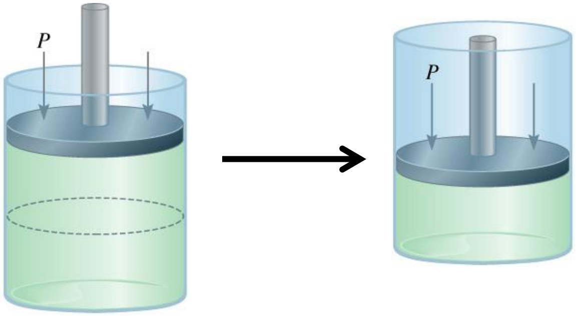
- **First Law of Thermodynamics**

$$\Delta U = q + w$$

(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.

$\Delta U = q + w$

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



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.

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

6.3 Heat of Reaction; Enthalpy of Reaction

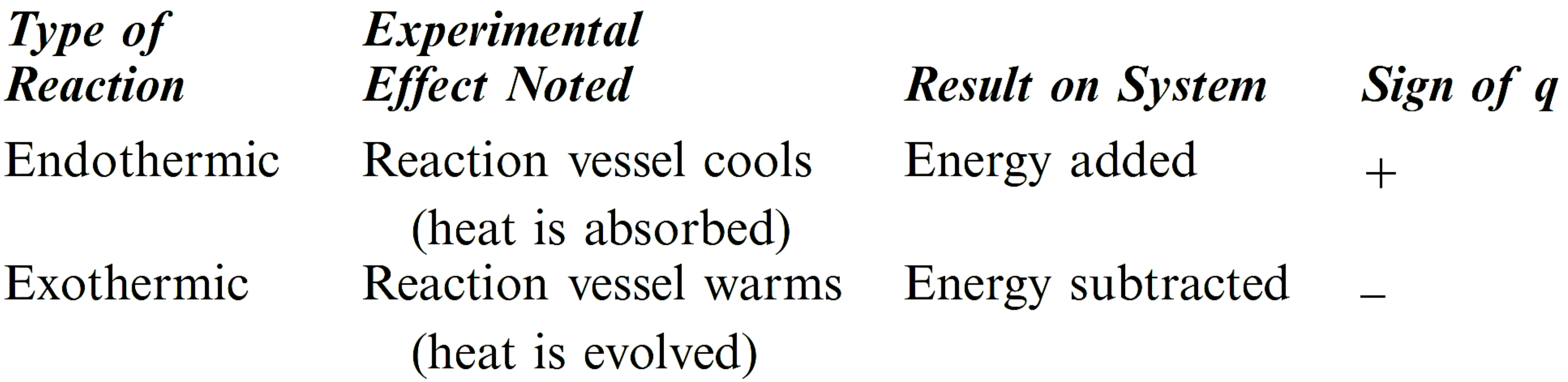
➢ Heat of Reaction

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

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

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

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



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*?

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

Heat is evolved → reaction is exothermic.
The value of *q* is −170 kJ.

➢ Pressure-Volume Work

$$w = -P\Delta V$$

Exercise 6.4 Consider the combustion of CH_4.

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

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

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

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

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)

$w = -P \times \Delta V$
$= -(1.0\ \text{atm}) \times (-57.44\ \text{L}) = 57.44$ atm.L
57.44 atm.L x 101.3 = + 5818 J = + 5.8 kJ

1 atm.L = 101.3 J

➢ Enthalpy (H) and Enthalpy of Reaction

$$H = U + PV$$

✓ Because *U*, *P*, and *V* are state functions, *H* is also a state function. $\Delta H = H_f - H_i$

$$\Delta U = q + w = q - P\Delta V = q - RT\Delta n$$

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

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

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

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

➢ Enthalpy of reaction

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

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

(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.

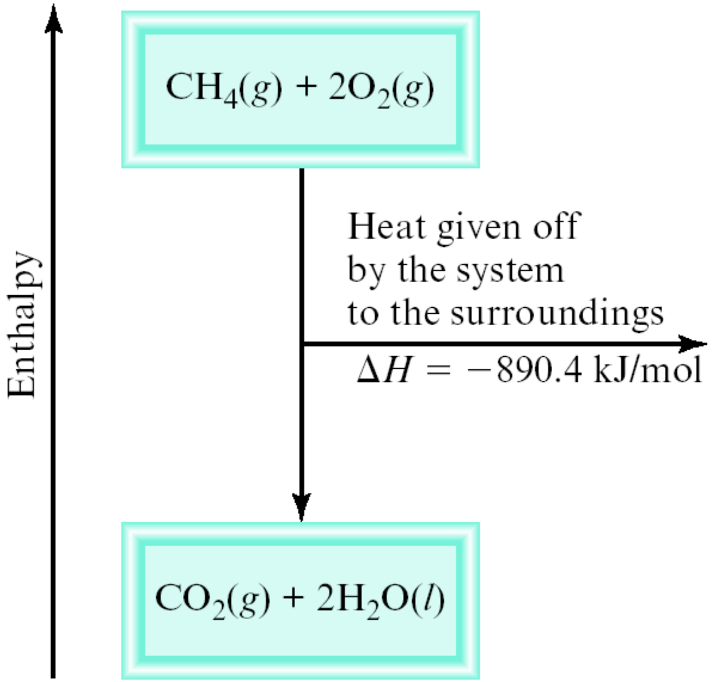
$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H = -566.0 \text{ kJ/mol}$$

$$\begin{aligned}\Delta n &= \text{number of moles of product gas} - \text{number of moles of reactant gases} \\ &= 2 - 3 \\ &= -1\end{aligned}$$

R = 8.314 J/K · mol and T = 298 K

$$\begin{aligned}\Delta U &= \Delta H - RT\Delta n \\ &= -566.0 \text{ kJ/mol} - (8.314 \text{ J/K} \cdot \text{mol})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(298 \text{ K})(-1) \\ &= -563.5 \text{ kJ/mol}\end{aligned}$$

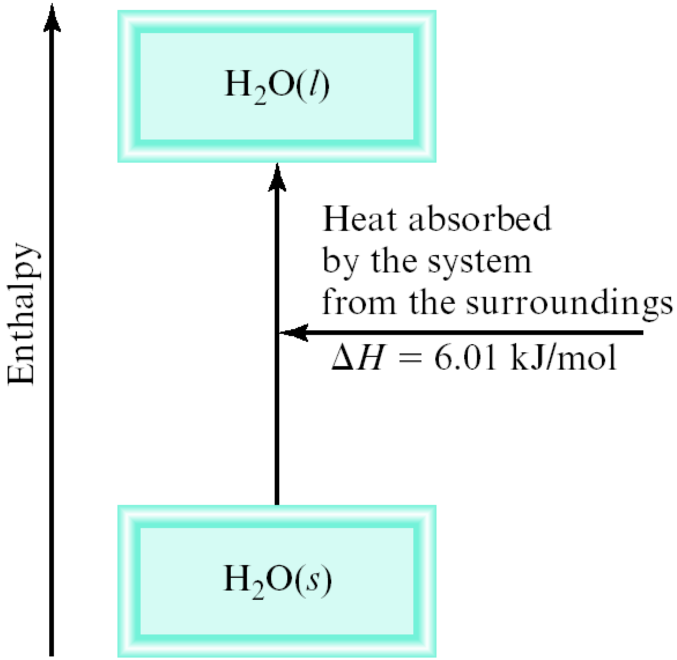
6.4 Thermochemical Equations


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

Heat given off
by the system
to the surroundings

$\Delta H = -890.4$ kJ/mol

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


$H_2O(l)$

Heat absorbed
by the system
from the surroundings

$\Delta H = 6.01$ kJ/mol

$H_2O(s)$

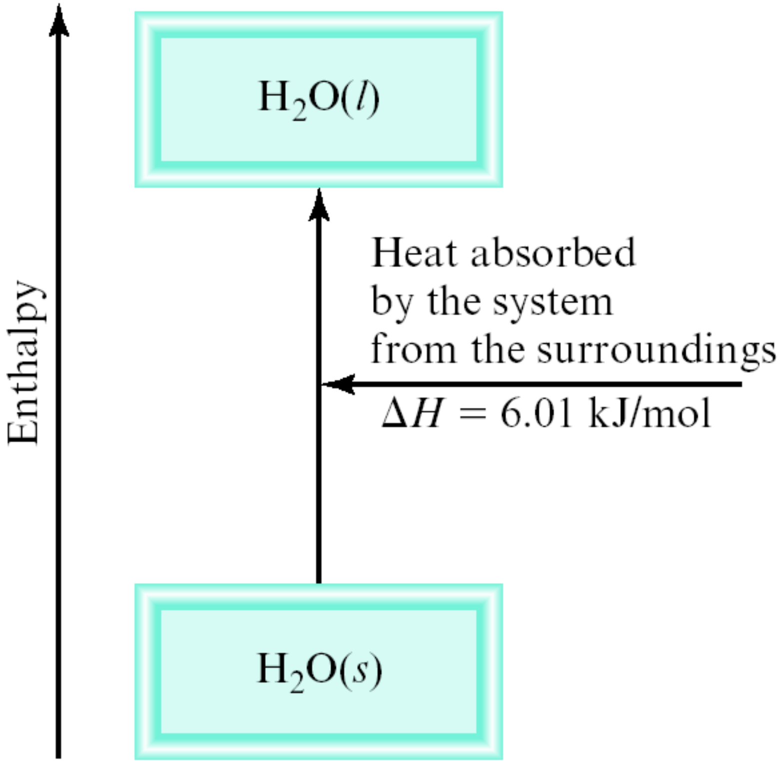
$H_{\text{products}} < H_{\text{reactants}}$

$\Delta H < 0$

$H_{\text{products}} > H_{\text{reactants}}$

$\Delta H > 0$

Thermochemical Equations



Is ΔH negative or positive?

System absorbs heat

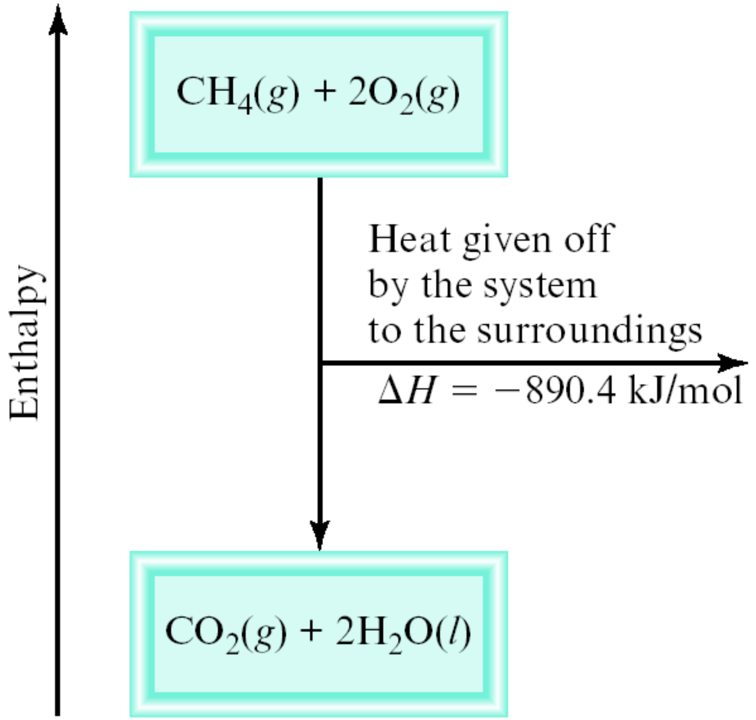
Endothermic

$\Delta H > 0$

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

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

Thermochemical Equations



Is ΔH negative or positive?

System gives off heat

Exothermic

$\Delta H < 0$

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

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

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

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

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

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

- 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.

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

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

6.5 Applying Stoichiometry to Heats of Reaction

(Q) How much heat is evolved when 9.07 . 105 g of ammonia is produced according to the following equation?

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

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

(Q) Given the thermochemical equation

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

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

$$\text{grams of SO}_2 \longrightarrow \text{moles of SO}_2 \longrightarrow \text{kilojoules of heat generated}$$

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

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

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).*

$$q = C\Delta t$$

✓ The **specific heat capacity** (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.*

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

$C = m \times s$

(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).

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

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

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

➢ 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.*
- ✓ *Calorimeters are considered isolated systems* → $q_{\text{system}} = 0$

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

$$q_{\text{sys}} = 0$$

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

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

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

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

$\Delta H = q_{\text{rxn}}$

<u>Exercise 6.9 </u>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 heat capacity and the density of the final solution in the cup are those of water

$$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$$

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

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

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

$$\Delta H = \frac{-2\underline{1}33.8\ \text{J}}{0.039\underline{6}\ \text{mol}} = -53884\ \text{J/mol} = -54\ \text{kJ/mol}$$

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

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:

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

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.

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

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

0.562 g → ? Mole C

$$\textbf{C(graphite)} + \textbf{O}_2(g) \longrightarrow \textbf{CO}_2(g);\ \Delta H = -3.9 \times 10^2\ \textbf{kJ}$$

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 heat capacity and the density of the final solution in the cup are those of water

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

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

mol HCl = 1.20 mol/L × 0.033 L = 0.0396 mol

$$\Delta H = \frac{-2\underline{1}33.8\ \mathrm{J}}{0.03\underline{9}6\ \mathrm{mol}} = -53884\ \mathrm{J/mol} = -54\ \mathrm{kJ/mol}$$

Expressing this result as a thermochemical equation →

$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l) \qquad \Delta H = -54\ \mathrm{kJ}$

6.73 When 15.3 g of $NaNO_3$ 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

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

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

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

The amount of heat absorbed by 15.3 g of $NaNO_3$ = 3684.2 J
The amount of heat absorbed by 1mol of $NaNO_3$ is ?

(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.

A. –5.29 kJ/mol

B. 5.29 kJ/mol

C. –148 kJ/mol

D. –1410 kJ/mol

E. 1410 kJ/mol

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

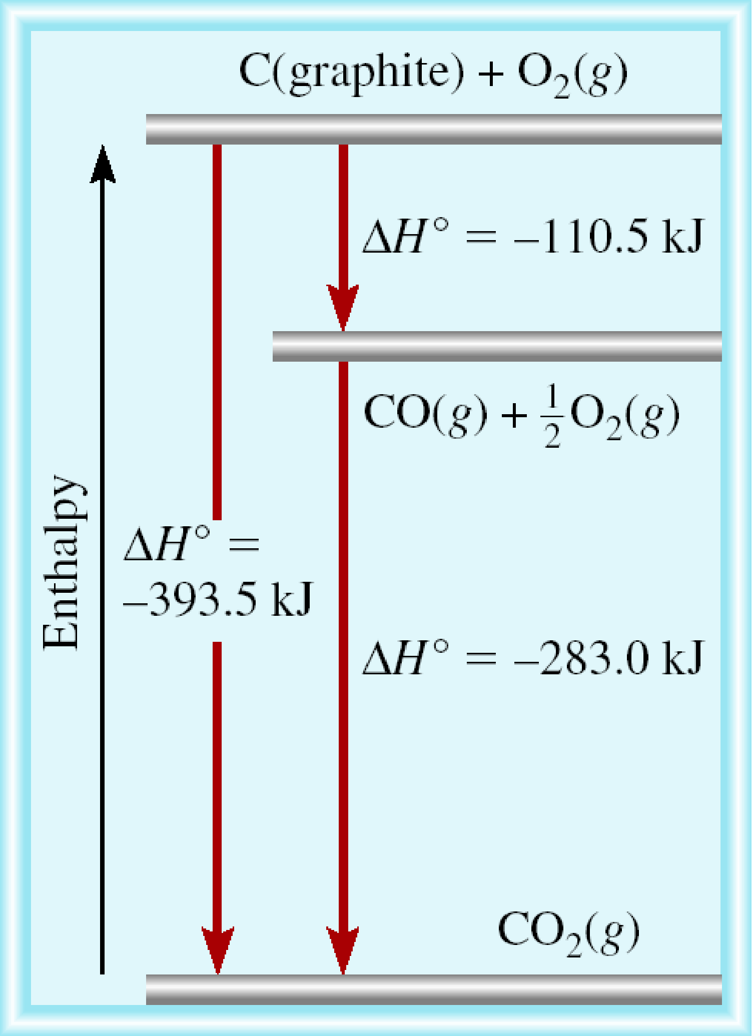
$$= 2.47\ \text{kJ}/\cancel{^\circ\text{C}} \times 2.14\ \cancel{^\circ\text{C}} = 5.286\ \text{kJ}$$

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

$$\Delta H_{\text{rxn}} = -5.286\ \text{kJ}/3.74\ \text{x}10^{-3}\ \text{mol}$$
$$= -1410\ \text{kJ/mol}$$

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"



$$\frac{\begin{array}{l} \text{C (graphite)} + 1/2O_2\,(g) \longrightarrow \text{CO}\,(g) \\ \text{CO}\,(g) + 1/2O_2\,(g) \longrightarrow CO_2\,(g) \end{array}}{\text{C (graphite)} + O_2\,(g) \longrightarrow CO_2\,(g)}$$

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

$$W(s) + C(\text{graphite}) \longrightarrow WC(s)$$

$$2W(s) + 3O_2(g) \longrightarrow 2WO_3(s);\ \Delta H = -1685.8\ \text{kJ} \qquad \textbf{(1)}$$

$$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -393.5\ \text{kJ} \qquad \textbf{(2)}$$

$$2WC(s) + 5O_2(g) \longrightarrow 2WO_3(s) + 2CO_2(g);\ \Delta H = -2391.8\ \text{kJ} \qquad \textbf{(3)}$$

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

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

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

$$2\mathrm{Al}(s) + \tfrac{3}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{Al_2O_3}(s);\ \Delta H = -1676\ \mathrm{kJ}$$

$$\mathrm{Mn}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{MnO_2}(s);\ \Delta H = -520\ \mathrm{kJ}$$

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 $\Delta H_f°$, 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.*

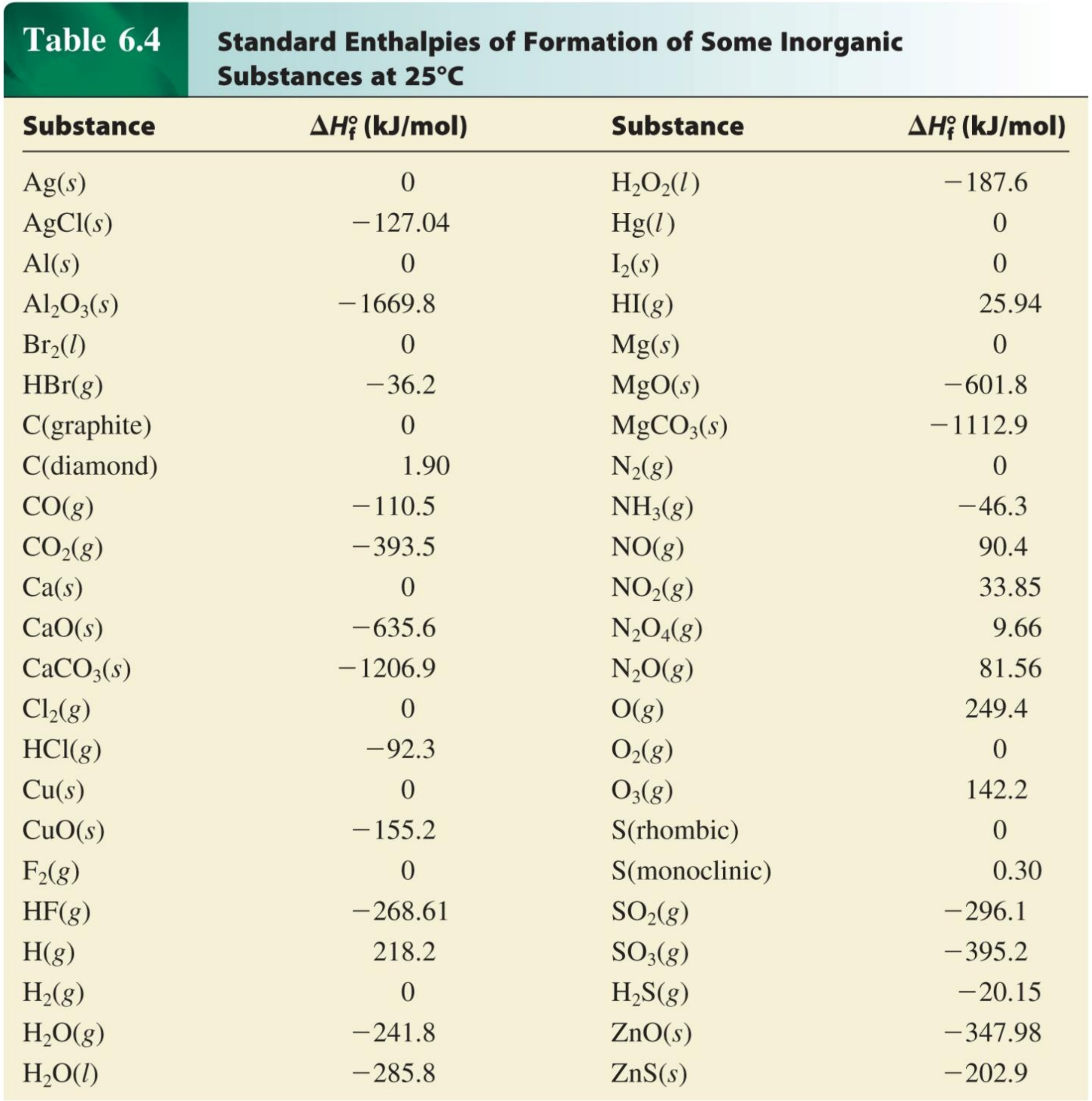


Table 6.4 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

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

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

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 is -296.9 kJ. What is Δ*H* for the formation of 16.03 g of sulfur dioxide in its standard state from its elements in their standard states?

A. 148.4 kJ

B. - 296.9 kJ

C. - 4,759 kJ

D. -148.4 kJ

E. 593.6 kJ

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

= −148.4 kJ

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

$$\Delta H^\circ_{\text{reaction}} = \left(\begin{array}{l}\text{Sum of all } \Delta H^\circ_{\text{f}} \\ \text{of all of the} \\ \text{products}\end{array}\right) - \left(\begin{array}{l}\text{Sum of all} \\ \Delta H^\circ_{\text{f}} \text{ of all of} \\ \text{the reactants}\end{array}\right)$$

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 mol × kJ/mol

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

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

$\Delta H^\circ_{\text{rxn}}$ 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

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

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

ΔH°_{rxn} has units of kJ

ΔH°_{f} has units of kJ/mol

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

$$DH^\circ_{rxn} = -\,297\text{ kJ/mol} + \tfrac{1}{2}(0\text{ kJ/mol}) \; - \; (-\,396\text{ kJ/mol})$$

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

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

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

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

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

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

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

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

- 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

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

Rearranging

ΔH_f° ($C_2H_3O_2^-$, *aq*) = ΔH_f° ($NaC_2H_3O_2{\cdot}3H_2O$, *s*) – ΔH_f° (Na^+, *aq*) – ΔH°_{rxn} – $3\Delta H_f^\circ$ (H_2O, *l*)

ΔH_f° ($C_2H_3O_2^-$, *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.

$$2\mathrm{Fe}(s) + 6\mathrm{H_2O}(l) \rightarrow 2\mathrm{Fe(OH)_3}(s) + 3\mathrm{H_2}(g)$$

	$2\mathrm{Fe}(s)$	$6\mathrm{H_2O}(l)$	$2\mathrm{Fe(OH)_3}(s)$	$3\mathrm{H_2}(g)$
$\boldsymbol{\Delta H_f^\circ}$	$\underline{\mathbf{0}}$	-285.8	-696.5	$\underline{\mathbf{0}}$

$$\Delta H^\circ_{\mathrm{rxn}} = 2 \times \Delta H_f^\circ\,(\mathrm{Fe(OH)_3}, s) + 3 \times \Delta H_f^\circ\,(\mathrm{H_2}, g) - 2 \times \Delta H_f^\circ\,(\mathrm{Fe}, s) - 6 \times \Delta H_f^\circ\,(\mathrm{H_2O}, l)$$

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

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

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

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

	$CO_2(g)$	$+\ 2H_2O(l)$	$\rightarrow\ 2O_2(g)$	$+\ CH_4(g)$
ΔH_f°	−393.5	−285.8	0	− 74.8

$$\Delta H^\circ_{\text{rxn}} = 2\times\Delta H_f^\circ\ (O_2, g) + \Delta H_f^\circ\ (CH_4, g)$$
$$-\Delta H_f^\circ\ (CO_2\cancel{, g)}) - 2\times\ \Delta H_f^\circ\ (\cancel{H_2O}, l)$$

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

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

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

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

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

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

Important

↓

$$\sum\left[DH^{o}_{f}\left(\text{reactants}\right)\times\left(\text{moles of reactant}\right)\right]$$

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

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

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

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

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

(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) → C_3H_8(g)

Use the following information:

(a) C_3H_8(g) + 5 O_2(g) → 3CO_2(g) + 4 H_2O(l) ΔH° = - 2219.9 kJ

(b) C(s) + O_2(g) → CO_2(g) ΔH° = - 393.5 kJ

(c) H_2(g) + 1/2 O_2(g) → H_2O(l) ΔH° = - 285.8 kJ

Answer: - 104 kJ

Calculate the standard enthalpy change for the reaction:

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

Given:

$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$ $\Delta H^\circ = -11020\ \text{kJ}$

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ $\Delta H^\circ = -566.0\ \text{kJ}$

Answer= **–6492 kJ**

(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) $\Delta H^o{}_f\,[CO_2(g)]$: $C(s) + O_2(g) \rightarrow CO_2(g)$