

EBBING - GAMMON

General
Chemistry
ELEVENTH EDITION

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. Energy is a property of matter not material

➤ **Kinetic Energy**

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

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

$$\text{kg}\cdot\text{m}^2/\text{s}^2 = \text{joule}$$

$$\text{Watt} = \text{joule}/\text{s}$$

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 = 9.11×10^{-31} kg) is accelerated by a positive charge to a speed of 5.0×10^6 m/s.

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

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

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

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

➤ **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)

h = height

➤ **Internal Energy (U)**

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

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

➤ **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

✓ 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)

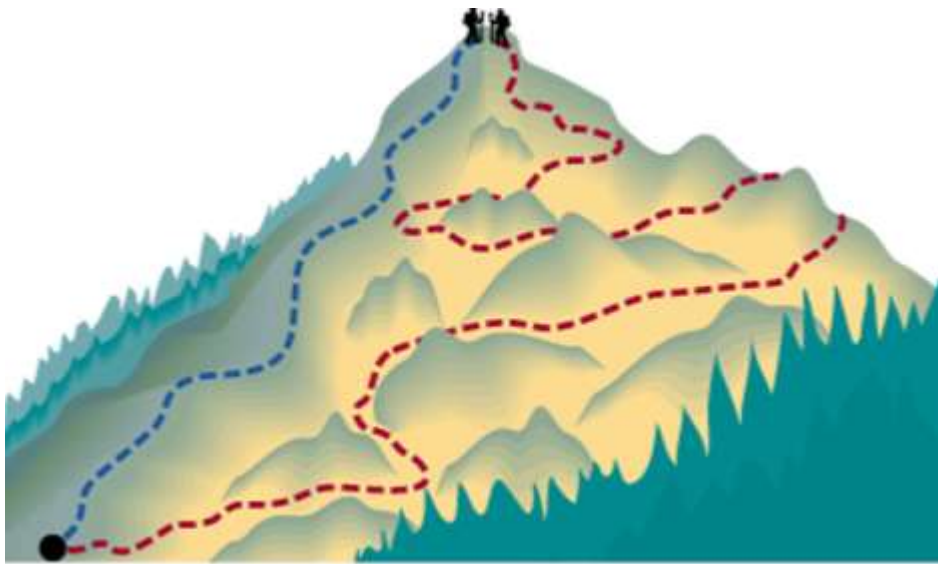
+

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.*



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

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

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

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

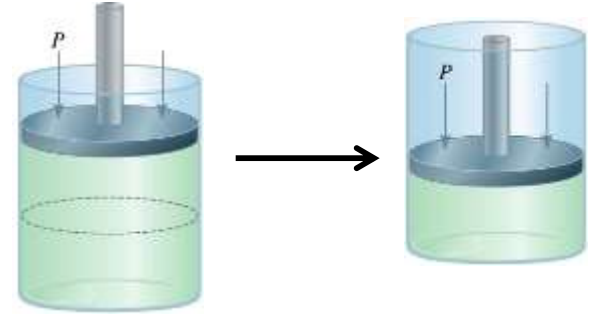
$$\Delta T = T_{final} - T_{initial}$$

➤ 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.

$$\begin{aligned}\Delta U &= q + w \\ &= -128 \text{ J} + 462 \text{ J} = 334 \text{ J}\end{aligned}$$



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 $q = -82 \text{ J}$

system contracts so $w = +29 \text{ J}$.

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

6.3 Heat of Reaction; Enthalpy of Reaction

➤ Heat of Reaction

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

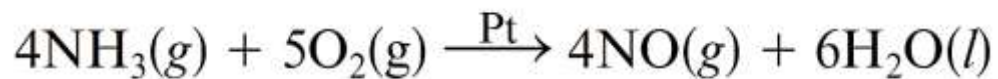
is a chemical reaction or a physical change in which heat is evolved or is released from the system.

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

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

<i>Type of Reaction</i>	<i>Experimental Effect Noted</i>	<i>Result on System</i>	<i>Sign of q</i>
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 NH₃ is burned and evolves +170 kJ of heat. Is the reaction endothermic or exothermic? What is the value of q ?



Heat is evolved \rightarrow 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 .



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 ΔU for the change indicated by the chemical equation.

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

$$\Delta V = \frac{(1\text{ mol} - 3\text{ mol})(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(350\text{ K})}{1.00\text{ atm}} = -57.44\text{ L}$$

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

$$w = -P \times \Delta V$$

$$= -(1.0\text{ atm}) \times (-57.44\text{ L}) = 57.44\text{ atm}\cdot\text{L}$$

$$57.44\text{ atm}\cdot\text{L} \times 101.3 = +5818\text{ J} = +5.8\text{ kJ}$$

$$1\text{ atm}\cdot\text{L} = 101.3\text{ J}$$

$$\Delta U = q + w \quad \rightarrow \Delta U = -885.5\text{ kJ} + 5.8\text{ kJ} = -879.7\text{ kJ}$$

➤ Enthalpy (H) and Enthalpy of Reaction

$$H = U + PV$$

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

$$\Delta U = q + w$$

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

$$w = -P\Delta V$$

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

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

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

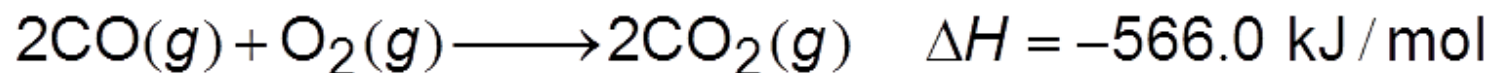
$$q = \Delta H \text{ (At fixed pressure and a given temperature)}$$

➤ 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 CO₂ at 1 atm. and 25°C.




$$\Delta U = q - RT\Delta n$$

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

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

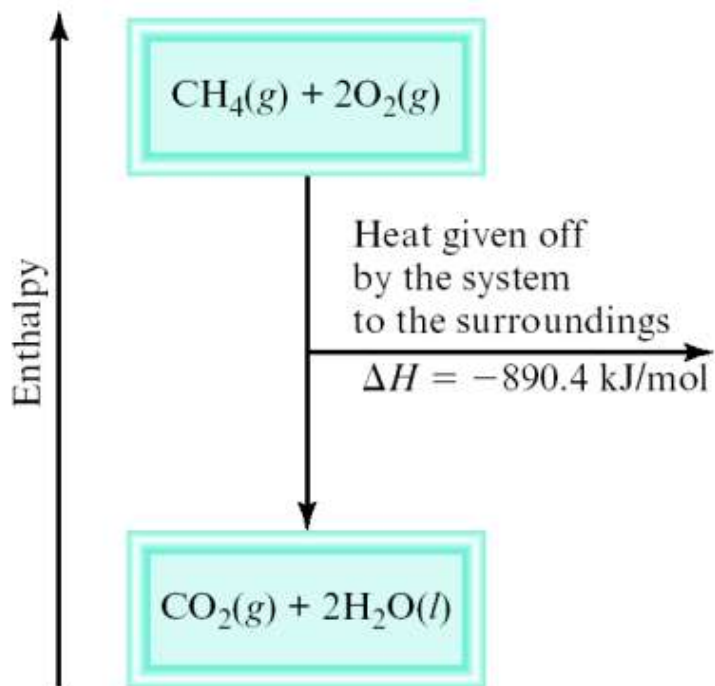
$$R = 8.314 \text{ J/K} \cdot \text{mol} \quad \text{and} \quad T = 298 \text{ K}$$

$$\Delta U = \Delta H - RT\Delta n$$

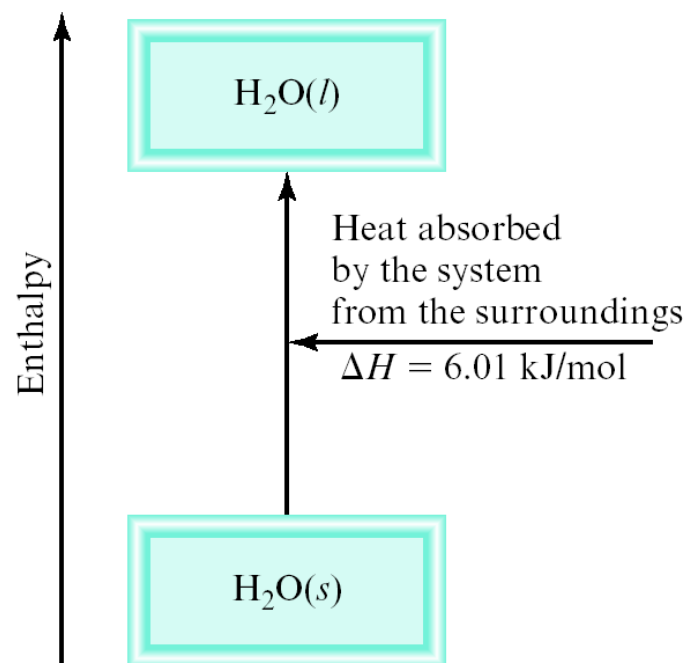
$$= -566.0 \text{ kJ/mol} - (8.314 \text{ J/K} \cdot \text{mol}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) (298 \text{ K})(-1)$$


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

6.4 Thermochemical Equations

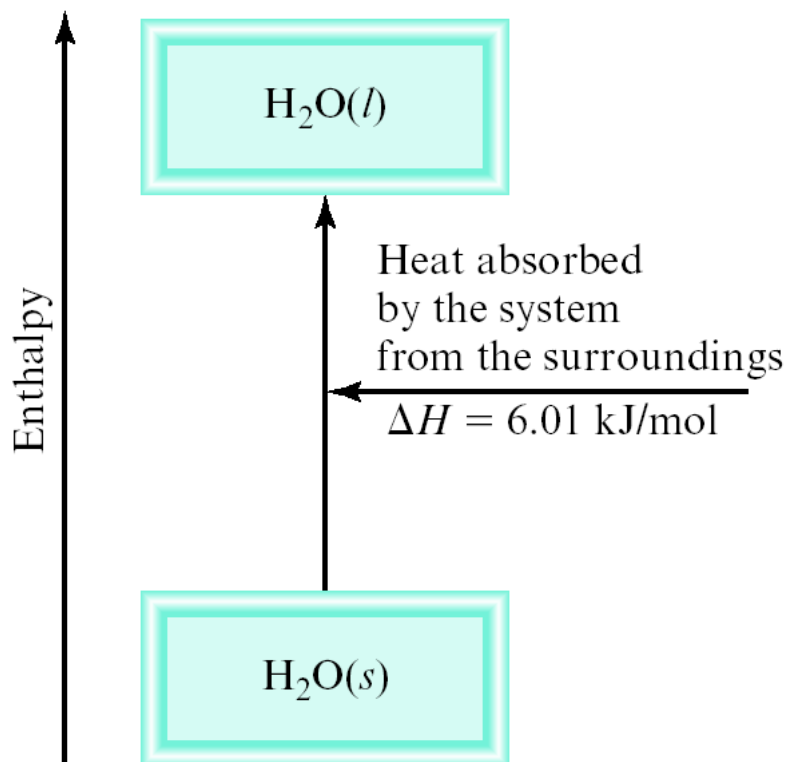


$$H_{\text{products}} < H_{\text{reactants}}$$
$$\Delta H < 0$$



$$H_{\text{products}} > H_{\text{reactants}}$$
$$\Delta H > 0$$

Thermochemical Equations



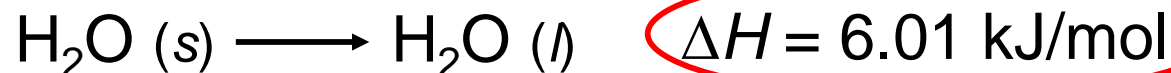
Is ΔH negative or positive?

System absorbs heat

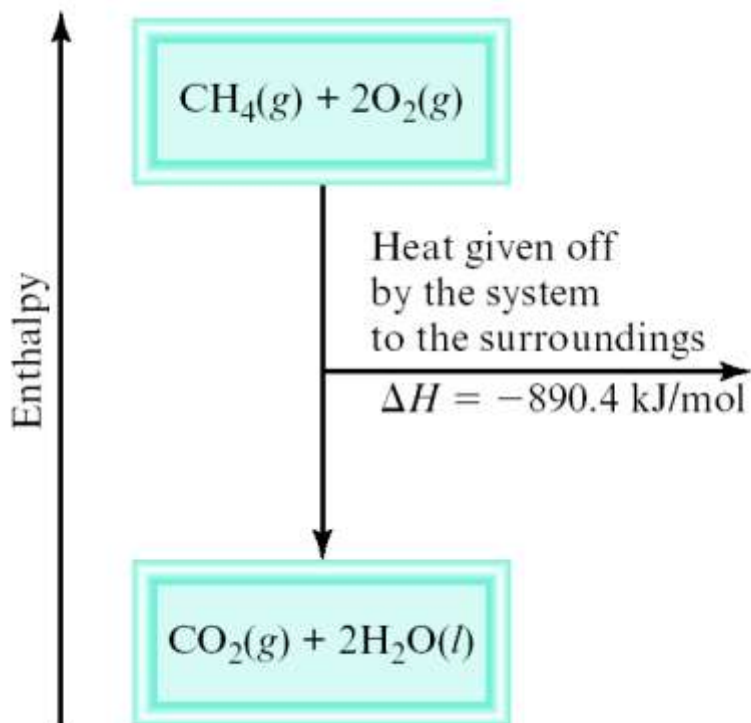
Endothermic

$\Delta H > 0$

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



Thermochemical Equations



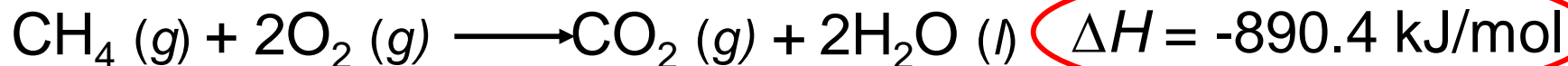
Is ΔH negative or positive?

System gives off heat

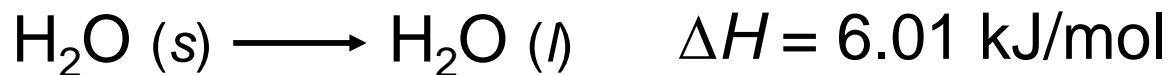
Exothermic

$\Delta H < 0$

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



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



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



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



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



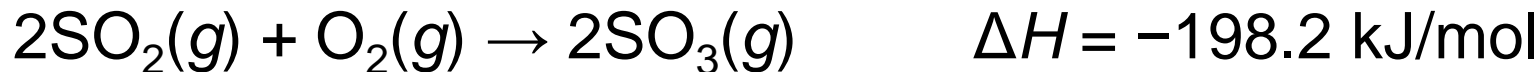
6.5 Applying Stoichiometry to Heats of Reaction

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



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

(Q) Given the thermochemical equation



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 \longrightarrow moles of SO_2 \longrightarrow kilojoules of heat generated

$$\begin{aligned} \Delta H &= 87.9 \text{ g } \cancel{\text{SO}_2} \times \frac{1 \text{ mol } \cancel{\text{SO}_2}}{64.07 \text{ g } \cancel{\text{SO}_2}} \times \frac{-198.2 \text{ kJ}}{2 \text{ mol } \cancel{\text{SO}_2}} \\ &= -136 \text{ kJ} \end{aligned}$$

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** (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*.

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

$$C = m \times s$$

(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).

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

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

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

➤ 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** → $q_{\text{system}} = 0$

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

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

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

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

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

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

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

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, ΔH , for the reaction: assume that the specific heat and the density of the final solution in the cup are those of water $\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$

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

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

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

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

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

➤ **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:



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.

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

$$\begin{aligned} q_{\text{rxn}} &= -C_{\text{cal}}\Delta t = -20.7 \text{ kJ/}^\circ\text{C} \times (25.89^\circ\text{C} - 25.00^\circ\text{C}) \\ &= -20.7 \text{ kJ/}^\circ\text{C} \times 0.89^\circ\text{C} = -18.4 \text{ kJ} \end{aligned}$$

0.562 g \rightarrow ? Mole C



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 $1071 \text{ J}/^\circ\text{C}$, what is the enthalpy change when 1 mol. of NaNO_3 dissolves in water? The solution process is

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



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

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

The amount of heat absorbed by 15.3 g of $\text{NaNO}_3 = 3684.2 \text{ J}$

The amount of heat absorbed by 1 mol 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

$$q_{\text{cal}} = C\Delta t$$
$$= 2.47 \text{ kJ/}^\circ\text{C} \times 2.14 \text{ }^\circ\text{C} = 5.286 \text{ kJ}$$

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

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

(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?

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

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

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

$$\begin{aligned} q_{\text{H}_2\text{O}} &= (100.0 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(23.17^\circ\text{C} - 22.50^\circ\text{C}) \\ &= 280.3 \text{ J} \quad \rightarrow \quad q_{\text{Pb}} = -280.3 \text{ J} \end{aligned}$$

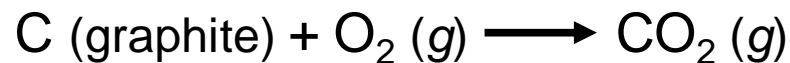
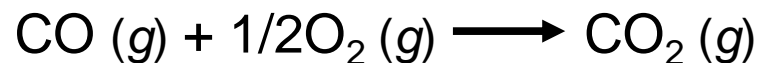
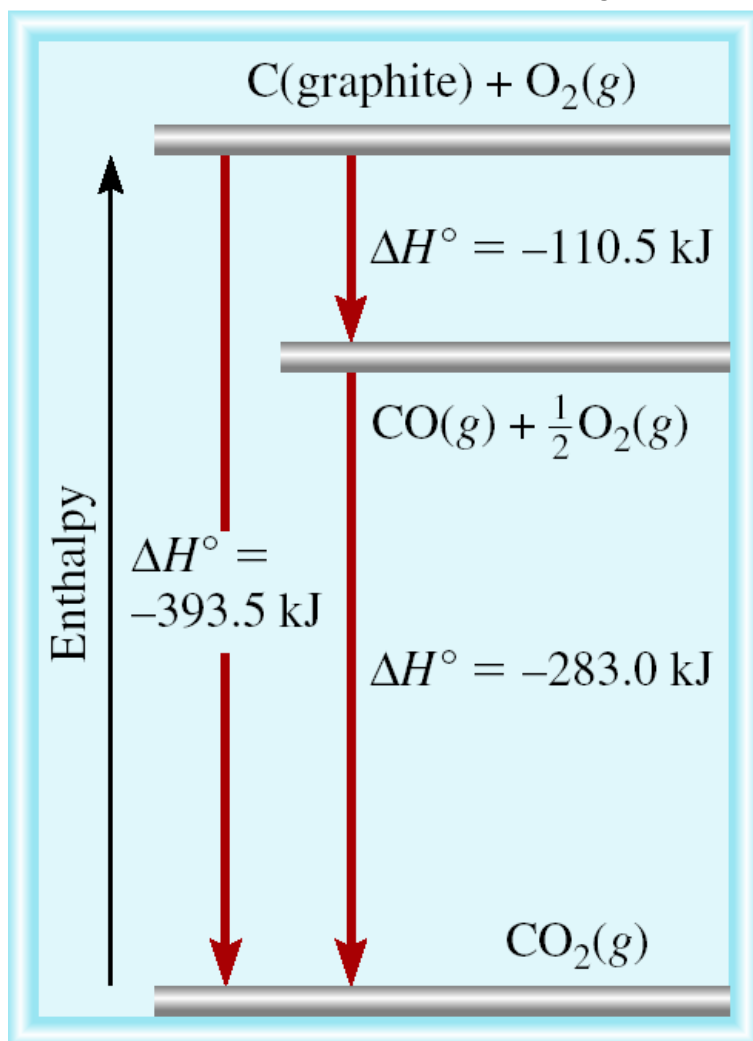
$$q_{\text{Pb}} = ms\Delta t$$

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

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

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”



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



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



What is ΔH for this reaction? Use the following data:



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).

ΔH° 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. (O₂ and O₃), (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 O₂(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

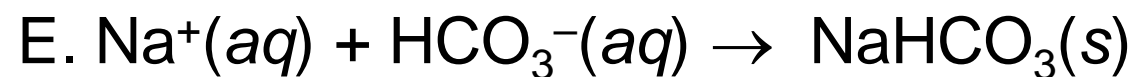
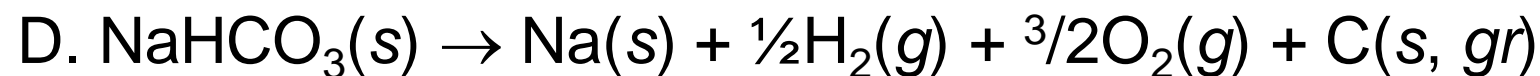
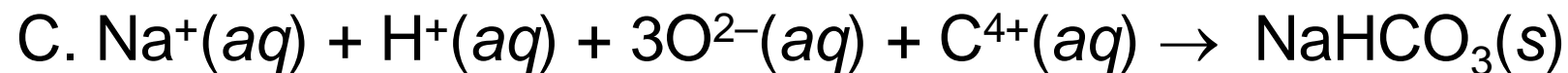
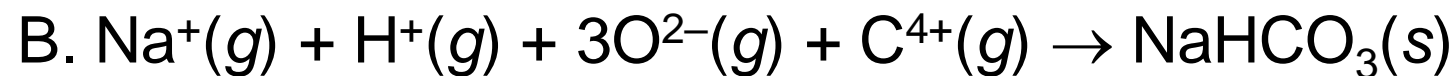
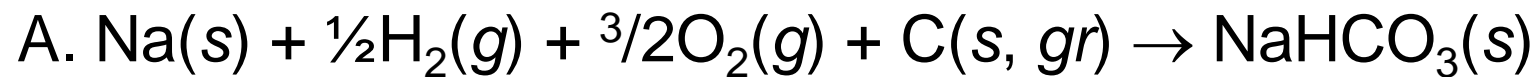
Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
Ag(s)	0	H ₂ O ₂ (l)	-187.6
AgCl(s)	-127.04	Hg(l)	0
Al(s)	0	I ₂ (s)	0
Al ₂ O ₃ (s)	-1669.8	HI(g)	25.94
Br ₂ (l)	0	Mg(s)	0
HBr(g)	-36.2	MgO(s)	-601.8
C(graphite)	0	MgCO ₃ (s)	-1112.9
C(diamond)	1.90	N ₂ (g)	0
CO(g)	-110.5	NH ₃ (g)	-46.3
CO ₂ (g)	-393.5	NO(g)	90.4
Ca(s)	0	NO ₂ (g)	33.85
CaO(s)	-635.6	N ₂ O ₄ (g)	9.66
CaCO ₃ (s)	-1206.9	N ₂ O(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 ₂ S(g)	-20.15
H ₂ O(g)	-241.8	ZnO(s)	-347.98
H ₂ O(l)	-285.8	ZnS(s)	-202.9

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

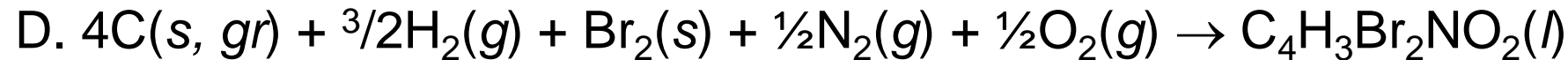
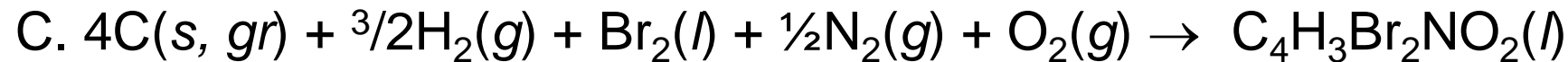
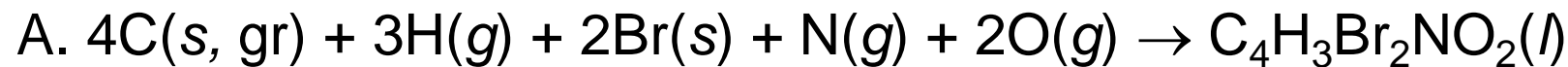
Substance or Ion	ΔH_f° (kJ/mol)	Substance or Ion	ΔH_f° (kJ/mol)	Substance or Ion	ΔH_f° (kJ/mol)
$e^-(g)$	0	$\text{CH}_3\text{CHO}(g)$	-166.1	$\text{NH}_3(g)$	-45.90
Bromine		$\text{CH}_3\text{CHO}(l)$	-191.8	$\text{NH}_4^+(aq)$	-132.5
$\text{Br}(g)$	111.9	Chlorine		$\text{NO}(g)$	90.29
$\text{Br}^-(aq)$	-121.5	$\text{Cl}(g)$	121.3	$\text{NO}_2(g)$	33.10
$\text{Br}^-(g)$	-219.0	$\text{Cl}^-(aq)$	-167.2	$\text{HNO}_3(aq)$	-207.4
$\text{Br}_2(g)$	30.91	$\text{Cl}^-(g)$	-234.0	Oxygen	
$\text{Br}_2(l)$	0	$\text{Cl}_2(g)$	0	$\text{O}(g)$	249.2
$\text{HBr}(g)$	-36.44	$\text{HCl}(g)$	-92.31	$\text{O}_2(g)$	0
Calcium		Fluorine		$\text{O}_3(g)$	142.7
$\text{Ca}(s)$	0	$\text{F}(g)$	79.39	Silicon	
$\text{Ca}^{2+}(aq)$	-542.8	$\text{F}^-(g)$	-255.1	$\text{Si}(s)$	0
$\text{CaCO}_3(s, \text{calcite})$	-1206.9	$\text{F}^-(aq)$	-332.6	$\text{SiCl}_4(l)$	-687.0
$\text{CaO}(s)$	-635.1	$\text{F}_2(g)$	0	$\text{SiF}_4(g)$	-1614.9
Carbon		$\text{HF}(g)$	-272.5	$\text{SiO}_2(s, \text{quartz})$	-910.9
$\text{C}(g)$	716.7	Hydrogen		Silver	
$\text{C}(s, \text{diamond})$	1.897	$\text{H}(g)$	218.0	$\text{Ag}(s)$	0
$\text{C}(s, \text{graphite})$	0	$\text{H}^+(aq)$	0	$\text{Ag}^+(aq)$	105.6
$\text{CCl}_4(g)$	-95.98	$\text{H}^+(g)$	1536.2	$\text{AgBr}(s)$	-100.4
$\text{CCl}_4(l)$	-135.4	$\text{H}_2(g)$	0	$\text{AgCl}(s)$	-127.1
$\text{CO}(g)$	-110.5	$\text{H}_2\text{O}(g)$	-241.8	$\text{AgF}(s)$	-204.6
$\text{CO}_2(g)$	-393.5	$\text{H}_2\text{O}(l)$	-285.8	$\text{AgI}(s)$	-61.84
$\text{CO}_3^{2-}(aq)$	-677.1	$\text{OH}^-(aq)$	-230.0	Sodium	
$\text{CS}_2(g)$	116.9	Iodine		$\text{Na}(g)$	107.3
$\text{CS}_2(l)$	89.70	$\text{I}(g)$	106.8	$\text{Na}(s)$	0
$\text{HCN}(g)$	135.1	$\text{I}^-(aq)$	-55.19	$\text{Na}^+(aq)$	-240.1
$\text{HCN}(l)$	108.9	$\text{I}^-(g)$	-194.6	$\text{Na}^+(g)$	609.3
$\text{HCO}_3^-(aq)$	-692.0	$\text{I}_2(s)$	0	$\text{Na}_2\text{CO}_3(s)$	-1130.8
Hydrocarbons		$\text{HI}(g)$	26.36	$\text{NaCl}(s)$	-411.1
$\text{CH}_4(g)$	-74.87	Lead		$\text{NaHCO}_3(s)$	-950.8
$\text{C}_2\text{H}_4(g)$	52.47	$\text{Pb}(s)$	0	Sulfur	
$\text{C}_2\text{H}_6(g)$	-84.68	$\text{Pb}^{2+}(aq)$	-1.7	$\text{S}(g)$	277.0
$\text{C}_6\text{H}_6(l)$	49.0	$\text{PbO}(s)$	-219.4	$\text{S}(s, \text{monoclinic})$	0.360
Alcohols		$\text{PbS}(s)$	-98.32	$\text{S}(s, \text{rhombic})$	0
$\text{CH}_3\text{OH}(l)$	-238.7	Nitrogen		$\text{S}_2(g)$	128.6
$\text{C}_2\text{H}_5\text{OH}(l)$	-277.7	$\text{N}(g)$	472.7	$\text{SO}_2(g)$	-296.8
Aldehydes		$\text{N}_2(g)$	0	$\text{H}_2\text{S}(g)$	-20.50
$\text{HCHO}(g)$	-117				

*See Appendix C for additional values

(Q) Which reaction corresponds to the standard enthalpy of formation of $\text{NaHCO}_3(\text{s})$, $\Delta H_f^\circ = -947.7 \text{ kJ/mol}$?



(Q) Which reaction corresponds to the standard enthalpy of formation of $\text{C}_4\text{H}_3\text{Br}_2\text{NO}_2(\text{l})$?



(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?

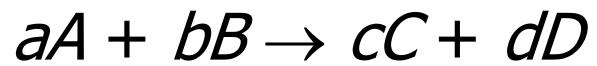
($\text{SO}_2 = 64.07 \text{ g/mol}$)

- A. 74.28 kJ
- B. -296.9 kJ
- C. $-4,759 \text{ kJ}$
- D. -74.28 kJ
- E. 593.6 kJ

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

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

Consider the reaction:



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

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

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

$\Delta H^\circ_{\text{rxn}}$ has units of kJ ΔH°_f has units of kJ/mol

Ex. 11: Calculate $\Delta H^\circ_{\text{rxn}}$ Using ΔH_f°

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



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

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

ΔH_f° has units of kJ/mol

$$\Delta H^\circ_{\text{rxn}} = \Delta H_f^\circ (\text{SO}_2(g)) + \frac{1}{2} \Delta H_f^\circ (\text{O}_2(g)) - \Delta H_f^\circ (\text{SO}_3(g))$$

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

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

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

$$4\text{NH}_3(g) + 7\text{O}_2(g) \rightarrow 4\text{NO}_2(g) + 6\text{H}_2\text{O}(l)$$

$$\Delta H^\circ_{\text{rxn}} = 4\Delta H_f^\circ \text{NO}_2(g) + 6\Delta H_f^\circ \text{H}_2\text{O}(l) - 4\Delta H_f^\circ \text{NH}_3(g) - 7\Delta H_f^\circ \text{O}_2(g)$$

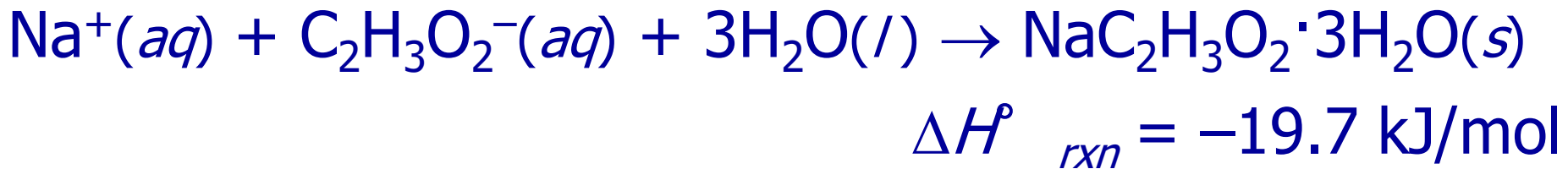
$$\Delta H^\circ_{\text{rxn}} = 4 \text{ mol} (34 \text{ kJ/mol}) + 6 \text{ mol} (-285.9 \text{ kJ/mol}) - 4 \text{ mol} (-46.0 \text{ kJ/mol}) - 7 \text{ mol} (0 \text{ kJ/mol})$$

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

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

- 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 ($\text{C}_2\text{H}_3\text{O}_2^{-}$, *aq*)?



$$\Delta H^{\circ}_{rxn} = \Delta H_f^{\circ} (\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}, s) - \Delta H_f^{\circ} (\text{Na}^+, aq) - \Delta H_f^{\circ} (\text{C}_2\text{H}_3\text{O}_2^-, aq) - 3\Delta H_f^{\circ} (\text{H}_2\text{O}, l)$$

Rearranging

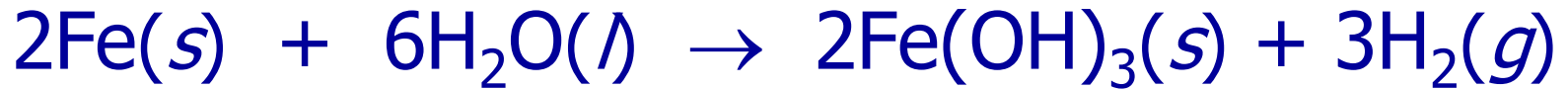
$$\Delta H_f^{\circ} (\text{C}_2\text{H}_3\text{O}_2^-, aq) = \Delta H_f^{\circ} (\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}, s) - \Delta H_f^{\circ} (\text{Na}^+, aq) - \Delta H^{\circ}_{rxn} - 3\Delta H_f^{\circ} (\text{H}_2\text{O}, l)$$

$$\Delta H_f^{\circ} (\text{C}_2\text{H}_3\text{O}_2^-, aq) =$$

$$\begin{aligned} & -710.4 \text{ kJ/mol} - (-239.7 \text{ kJ/mol}) - (-19.7 \\ & \text{kJ/mol}) - 3(-285.9 \text{ kJ/mol}) \end{aligned}$$

$$= +406.7 \text{ kJ/mol (Fix answer = 122.1 kJ/mol)}$$

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



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

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

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

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

$$\Delta H^\circ_{\text{rxn}} = \mathbf{321.8 \text{ kJ}}$$

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



$$\Delta H_f^\circ \quad -393.5 \quad -285.8 \quad 0 \quad -74.8$$

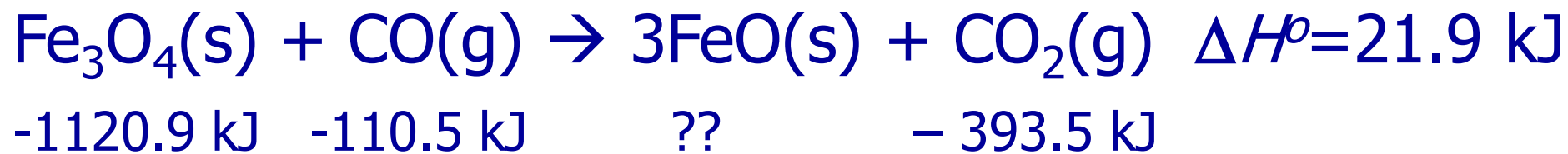
$$\Delta H^\circ_{\text{rxn}} = 2 \times \Delta H_f^\circ (\text{O}_2, g) + \Delta H_f^\circ (\text{CH}_4, g) - \Delta H_f^\circ (\text{CO}_2, g) - 2 \times \Delta H_f^\circ (\text{H}_2\text{O}, l)$$

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

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

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

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



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

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

Important



$$\Delta H_{\text{rxn}}^{\circ} = [3\Delta H_f^{\circ} (\text{FeO}, s) + \Delta H_f^{\circ} (\text{CO}_2, g)] - [\Delta H_f^{\circ} (\text{Fe}_3\text{O}_4, s) + \Delta H_f^{\circ} (\text{CO}, g)]$$

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

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

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

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

(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.

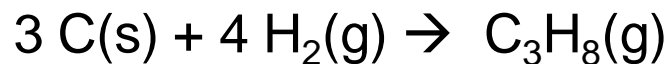
Warm up.

Condense.

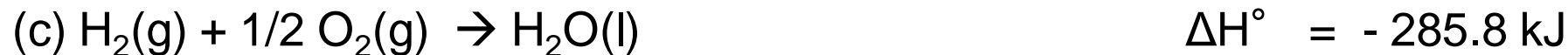
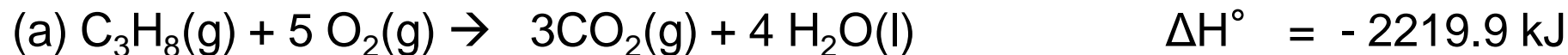
Decrease in temperature.

Expand.

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

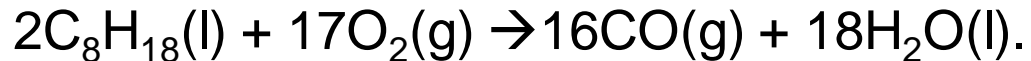


Use the following information:

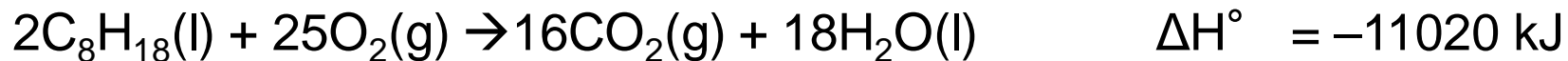


Answer: - 104 kJ

Calculate the standard enthalpy change for the reaction:

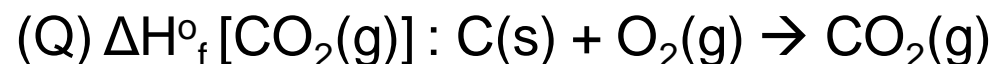
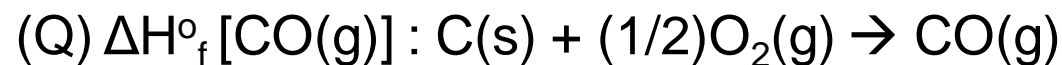
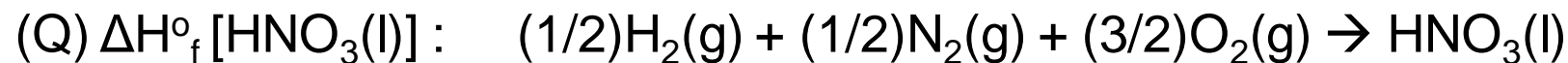
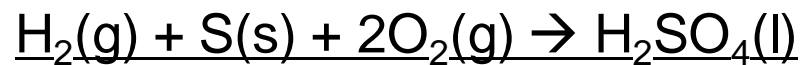
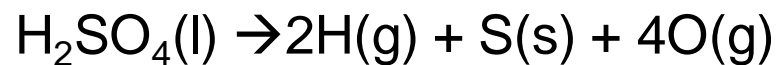
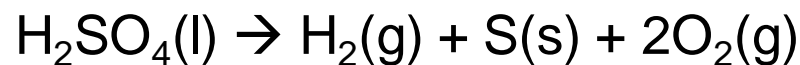


Given:



Answer= **-6492 kJ**

(Q) To which one of the following reactions occurring at 25° C does the symbol $\Delta H^\circ_f [\text{H}_2\text{SO}_4(\text{l})]$ refer?



6.55 What is ΔU when 1.00 mol of liquid water vaporizes at 100°C ? The heat of vaporization, $\Delta H^\circ_{\text{vap}}$, 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, $\Delta H^\circ_{\text{vap}}$, of water at 100°C is 40.66 kJ/mol.