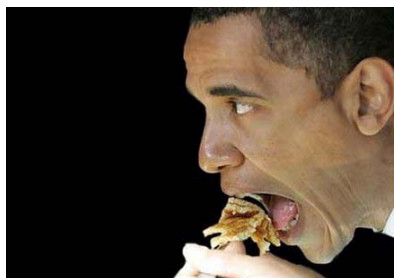# Thermochemistry
(Chapter 5)

1. **Energy.**
2. **Work and heat.**
3. **Enthalpy.**
4. **Standard enthalpies of reactions and formations.**

Our body gains internal energy by ingesting foods; dissipates the excess heat to surroundings by sweating.

1

Energy

- **The ability to do work or transfer heat.**

  ➢ **Work (*w*): Energy used to cause an object to move.**

  $$[J] \quad w = F \cdot d \quad [N\ m]$$

  where *F* is the force, and *d* is the distance over which the force is exerted.

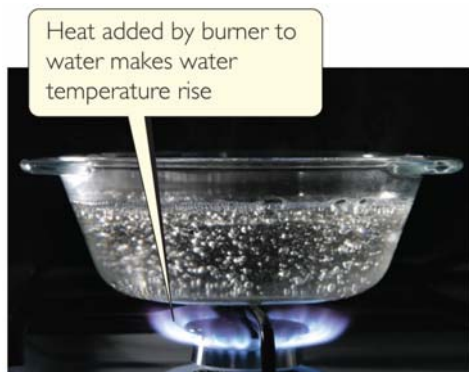Work done by pitcher on ball to make ball move

(a)

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2

Energy

➢ **Heat (*q*): Energy used to cause the temperature to rise.**

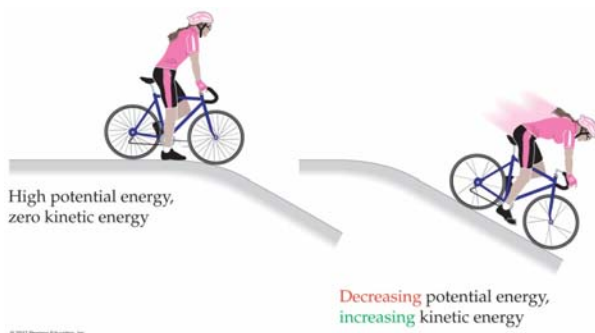➢ **Heat always flows from warmer objects to cooler objects.**

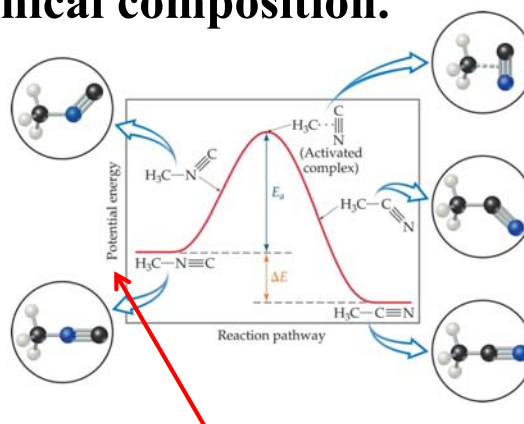Heat added by burner to water makes water temperature rise

(b)

3

Energy

➢ **Potential energy: Energy an object possesses by virtue of its position or chemical composition.**

High potential energy, zero kinetic energy

Decreasing potential energy, increasing kinetic energy

due to the interaction between atom

➢ **Kinetic energy: Energy an object possesses by virtue of its motion.**

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Unit of energy $(\equiv kg\ m^2 s^{-2})$

- The SI unit of energy is the **Joule** (J). $(\equiv N\ m)$
- An older, non-SI unit is still in widespread use: calorie (cal).

1 calories = 4.184 J

1 kWh $\equiv$ 3600 kJ
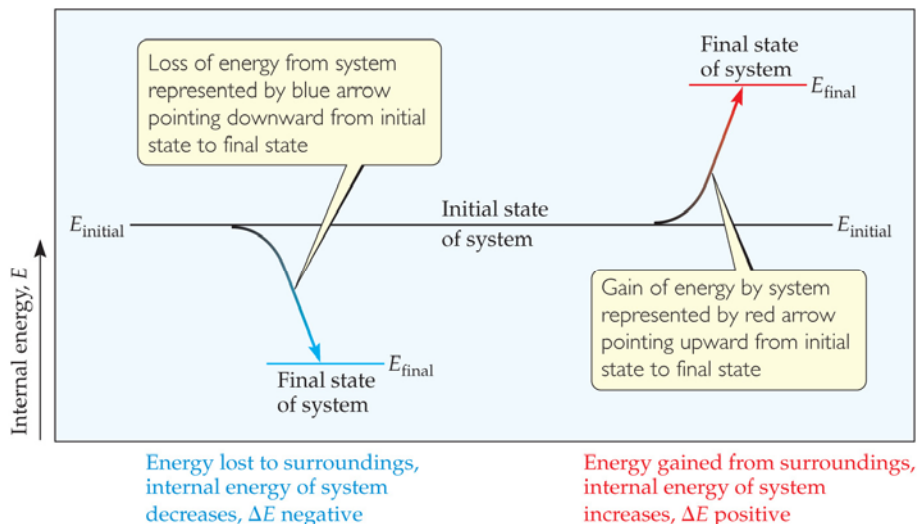

System and Surroundings

- **The system includes the gaseous molecules we want to study.**

- **The surroundings are everything else, i.e., the cylinder and piston.**

First Law of Thermodynamics

- **Energy can neither be created nor destroyed.**

- **The total energy of the universe is constant; if the system loses energy, it must be gained by the surroundings, and vice versa.**

Loss of energy from system represented by blue arrow pointing downward from initial state to final state

Final state of system E_{final}

$E_{initial}$ Initial state of system $E_{initial}$

Gain of energy by system represented by red arrow pointing upward from initial state to final state

Internal energy, E

E_{final} Final state of system

Energy lost to surroundings, internal energy of system decreases, ΔE negative

Energy gained from surroundings, internal energy of system increases, ΔE positive

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Internal Energy

- **The internal energy of a system is the sum of all kinetic and potential energies of all components of the system; we call it E.**

- **By definition, the change in internal energy, ΔE, is the difference between the final energy of the and initial energy of the system:**

$$\Delta E = E_{final} - E_{initial}$$

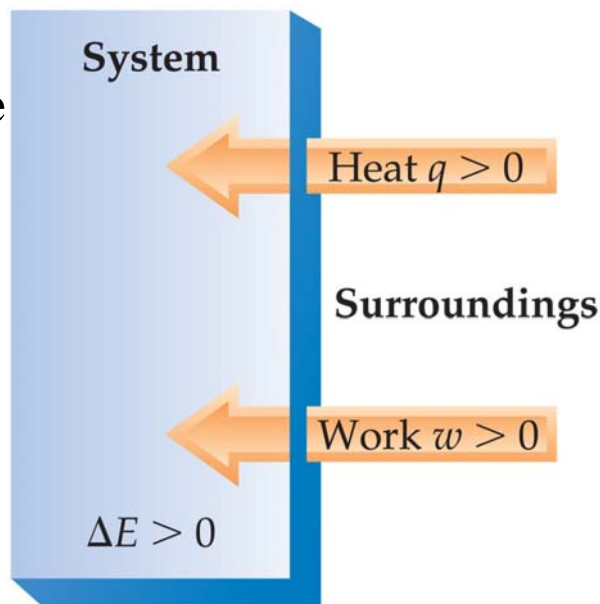- **If $\Delta E > 0, \Rightarrow$ endergonic (system absorbs energy from the surroundings).**

- **If $\Delta E < 0, \Rightarrow$ exergonic (system releases energy to the surroundings).**

Changes in Internal Energy

- **When energy is exchanged between the system and the surroundings, it is exchanged as either heat (*q*) or work (*w*).**

$$\Delta E = q + w$$

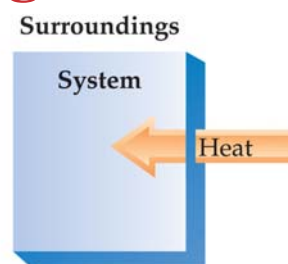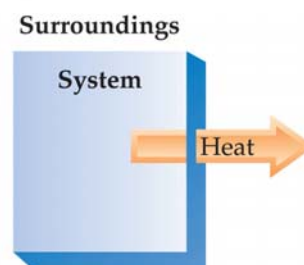| For q	+ means system *gains* heat	− means system *loses* heat
For w	+ means work done *on* system	− means work done *by* system
For ΔE	+ means *net gain* of energy by system	− means *net loss* of energy by system

Exchange of Heat between System and Surroundings

- **When heat is absorbed by the system from the surroundings, the process is endothermic.**

- **When heat is released by the system to the surroundings, the process is exothermic.**

Internal energy is a state function

- **Internal energy is a state function because it**
  - ➤ **depends only on the initial and final states of the system;**
  - ➤ **is independent of the path from the initial to final state.**

- **ΔE depends only on $E_{initial}$ and E_{final}.**

50 g
H_2O (l)
100°C

50 g
H_2O (l)
25°C

Cooling
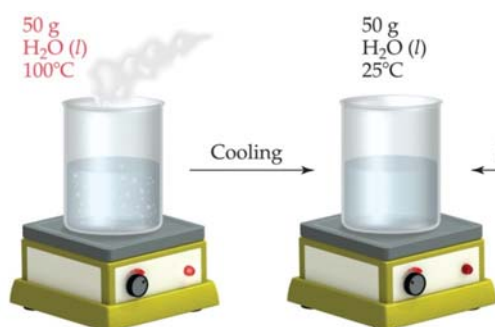
The ΔE for water to be cooled from 100 °C to 25 °C is independent of the way (or path) how we cool it.

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Work and heat are not state functions

- **However, *q* and *w* are not state functions.**
- **The changes in *q* and *w* are depended on the pathway.**

When a battery is shorted out or is discharged by running the fan, its ΔE is the same. But *q* and *w* are different.

Energy lost as both heat and work

Energy lost only as heat

(a)   (b)

Charged battery

Heat

Heat

ΔE Energy lost by battery

Work

Discharged battery
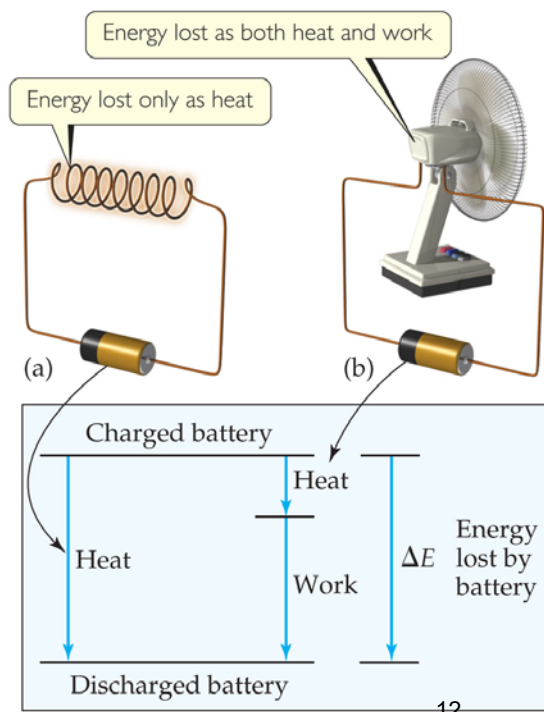
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Work done in an expansion ($P-V$ work)

- When a process occurs in an open container, the work done is change in volume of a gas pushing on the surroundings (or being pushed on by the surroundings).
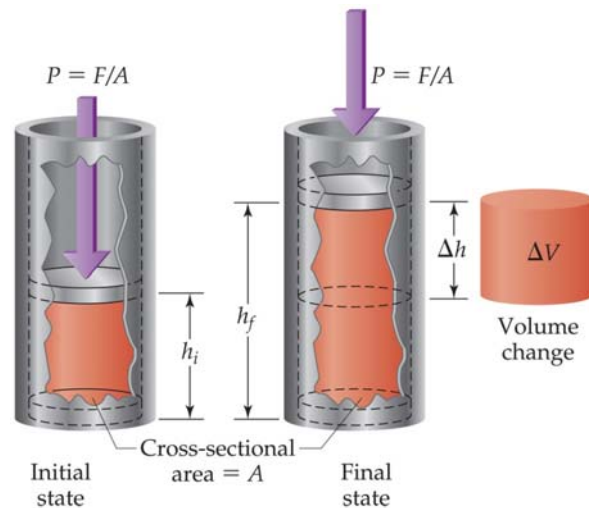
Work done in an expansion work:

$$w = -P\Delta V$$

expansion: ΔV is +ve

work is done by the system (−ve)

Enthalpy

- Enthalpy, a thermodynamic function, accounts for the heat flow in processes at **constant pressure**, when no other form of work except $P-V$ work.

- Enthalpy is the internal energy plus the $P-V$ work:

$$H = E + PV$$

$$\Delta H = \Delta(E + PV) = \Delta E + \Delta(PV) = \Delta E + V\Delta P + P\Delta V$$

$$\boxed{\Delta H = \Delta E + P\Delta V}$$

- H is a state function because E, P and V are all state functions.

Enthalpy

- **But we know that:**

$$\Delta E = q + w \quad \text{and} \quad w = -P\Delta V$$

- **Thus,**

$$\Delta H = \Delta E + P\Delta V = q + w + P\Delta V$$

$$= q - P\Delta V + P\Delta V$$

$$= q$$

- **Enthalpy is the heat change at constant pressure.**

$\Delta H > 0 \implies$ **the process is endothermic.**

$\Delta H < 0 \implies$ **the process is exothermic**

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Enthalpies of Reaction

- **The change in enthalpy, ΔH, is the enthalpy of the products minus the enthalpy of the reactants:**

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

- **Some properties of enthalpy:**
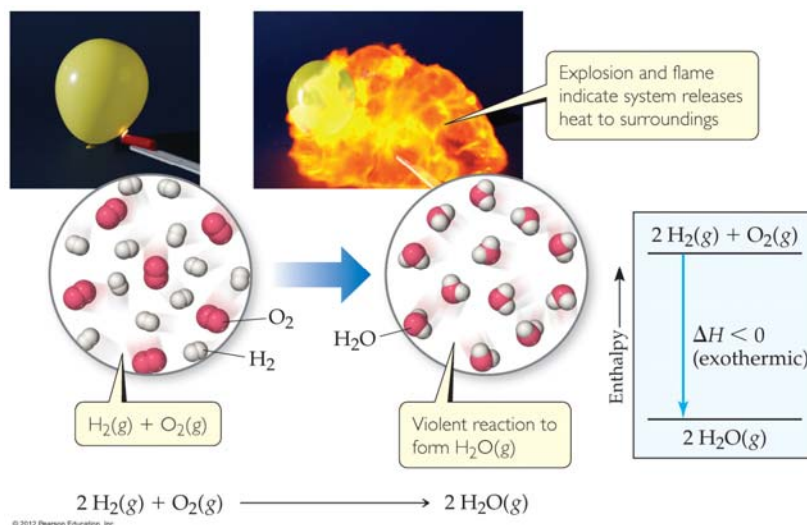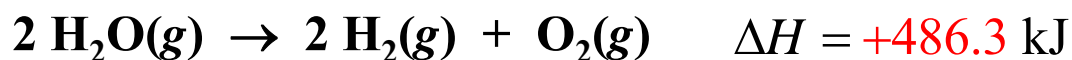
1. **Enthalpy is an extensive property − its value is proportional to the amount.**

   2 H$_2$(g) + O$_2$(g) → 2 H$_2$O(g) $\Delta H = -486.3$ kJ

   1 H$_2$(g) + ½ O$_2$(g) → 1 H$_2$O(g) $\Delta H = -243.15$ kJ

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2. ΔH for a reaction in the forward direction is equal, but opposite in sign, to ΔH for the reverse reaction.

$$2\ H_2(g)\ +\ O_2(g)\ \rightarrow\ 2\ H_2O(g) \qquad \Delta H = -486.3\ kJ$$

$$2\ H_2O(g)\ \rightarrow\ 2\ H_2(g)\ +\ O_2(g) \qquad \Delta H = +486.3\ kJ$$

Explosion and flame indicate system releases heat to surroundings

O₂

H₂

H₂O

$H_2(g) + O_2(g)$

Violent reaction to form $H_2O(g)$

$2\ H_2(g) + O_2(g)$

$\Delta H < 0$ (exothermic)

Enthalpy

$2\ H_2O(g)$

$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(g)$

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3. ΔH for a reaction depends on the **physical state** of products and reactants.

$$2\ H_2(g)\ +\ O_2(g)\ \rightarrow\ 2\ H_2O(l) \qquad \Delta H = -574.3\ kJ$$

$$2\ H_2(g)\ +\ O_2(g)\ \rightarrow\ 2\ H_2O(g) \qquad \Delta H = -486.3\ kJ$$

$$2\ H_2O(l)\ \rightarrow\ 2\ H_2O(g) \qquad \Delta H = +88\ kJ$$

Heat added by burner to water makes water temperature rise
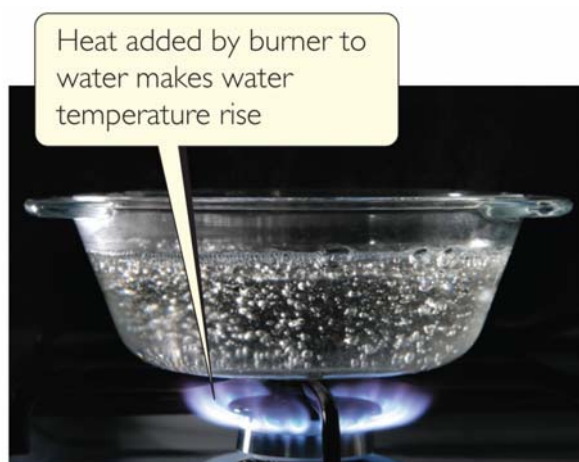
Boiling 1 mole of water into gas requires +44 kJ of energy.

Hess's Law

- **Hess's law states that "If a reaction is carried out in a series of steps, ΔH for the overall reaction will be equal to the sum of the enthalpy changes for the individual steps."**

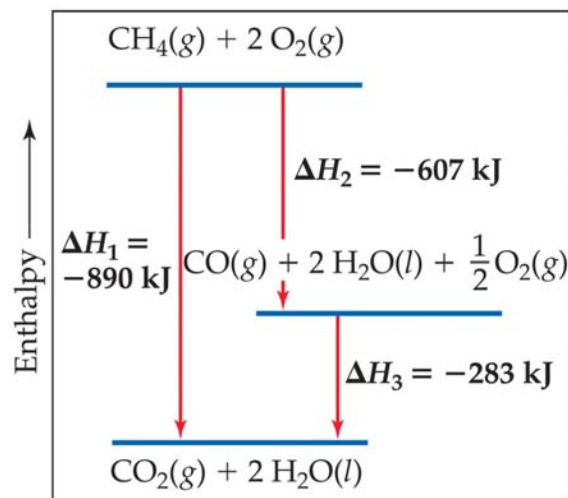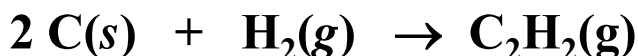- **The reaction for ΔH_1 may be broken down into two steps:**

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

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

$$\Delta H_2 = -607 \text{ kJ}$$

$$\Delta H_1 = -890 \text{ kJ} \quad CO(g) + 2\,H_2O(l) + \tfrac{1}{2}O_2(g)$$

$$\Delta H_3 = -283 \text{ kJ}$$

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

Enthalpy

Example: calculate ΔH for this reaction:
$$2\text{ C}(s) \; + \; H_2(g) \; \rightarrow \; C_2H_2(g)$$
using enthalpy changes of the following reactions:

$$C_2H_2(g) + \tfrac{5}{2}\,O_2(g) \longrightarrow 2\,CO_2(g) + H_2O(l) \qquad \Delta H_1 = -1299.6 \text{ kJ}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_2 = -393.5 \text{ kJ}$$

$$H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_3 = -285.8 \text{ kJ}$$
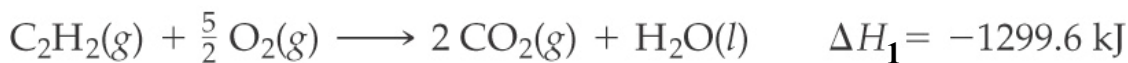
Standard Enthalpies of Formation

• **Standard enthalpy of formation** (ΔH^o_f) is defined as the heat change for the formation reaction of **one mole** of a compound from its constituent elements under standard conditions (25 °C and 1.00 atm pressure).
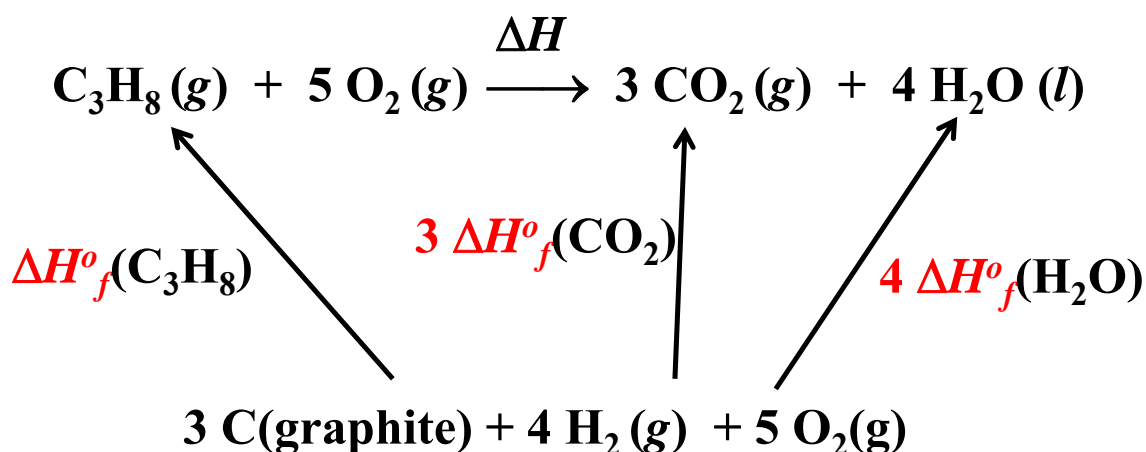
• If the element exists in more than one forms, we use the most stable one for the ΔH^o_f.

• By definition, the ΔH^o_f for the **most stable form** of any elements is **zero**.

$$\Delta H^o_f [H_2(g)], \ \Delta H^o_f [O_2(g)], \ \Delta H^o_f [C(graphite)] = 0$$

$$\Delta H^o_f [C(diamond)] \neq 0$$

Calculation of ΔH

$$C_3H_8(g) + 5\,O_2(g) \xrightarrow{\ \Delta H\ } 3\,CO_2(g) + 4\,H_2O(l)$$

$\Delta H^o_f(C_3H_8)$ $3\,\Delta H^o_f(CO_2)$ $4\,\Delta H^o_f(H_2O)$

$$3\,C(graphite) + 4\,H_2(g) + 5\,O_2(g)$$

$$\Delta H = 4\,\Delta H^o_f(H_2O) + 3\,\Delta H^o_f(CO_2) - \Delta H^o_f(C_3H_8)$$

$$= 4\,(-285.8) + 3\,(-393.5) - (-103.85)$$

$$= -2219.85 \ kJ/mol$$

Calculation of ΔH

$$\text{Reactants} \xrightarrow{\Delta H} \text{Products}$$

We can use Hess's law in this way:

$$\Delta H = \Sigma\, n\, \Delta H^o_f(\text{products}) - \Sigma\, m\, \Delta H^o_f(\text{reactants})$$

where n and m are the stoichiometric coefficients.

Substance	Formula	ΔH°_f (kJ/mol)	Substance	Formula	ΔH°_f (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	−92.30
Ammonia	$NH_3(g)$	−46.19	Hydrogen fluoride	$HF(g)$	−268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	−1207.1	Methane	$CH_4(g)$	−74.80
Calcium oxide	$CaO(s)$	−635.5	Methanol	$CH_3OH(l)$	−238.6
Carbon dioxide	$CO_2(g)$	−393.5	Propane	$C_3H_8(g)$	−103.85
Carbon monoxide	$CO(g)$	−110.5	Silver chloride	$AgCl(s)$	−127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	−947.7
Ethane	$C_2H_6(g)$	−84.68	Sodium carbonate	$Na_2CO_3(s)$ 1	− 130.9
Ethanol	$C_2H_5OH(l)$	−277.7	Sodium chloride	$NaCl(s)$	−410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	−2221
Glucose	$C_6H_{12}O_6(s)$	−1273	Water	$H_2O(l)$	−285.8
Hydrogen bromide	$HBr(g)$	−36.23	Water vapor	$H_2O(g)$	−241.8

Exercise: The ΔH for the reaction

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

is 178.1 kJ/mol. Calculate the $\Delta H^o_f[CaCO_3(s)]$.