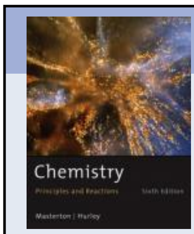

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Chapter 8
Thermochemistry

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Outline

1. Principles of heat flow
2. Measurement of heat flow; calorimetry
3. Enthalpy
4. Thermochemical equations
5. Enthalpies of formation
6. Bond enthalpy
7. The first law of thermodynamics

Heat – Some Things to Think About

- What is heat?
- How do we measure heat?
- What connection is there between heat and matter at the molecular level?

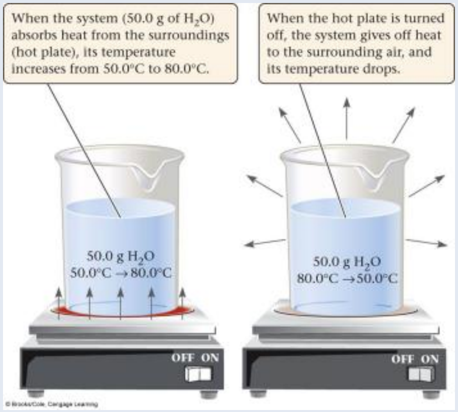
Heat

- Heat will flow from a hotter object to a colder object
  - Mix boiling water with ice
  - Temperature of the ice rises after it melts
  - Temperature of the water falls

Principles of Heat Flow

- Definitions
  - The system: that part of the universe on which attention is focused
  - The surroundings: the rest of the universe
    - Practically speaking, it is possible to consider only the surroundings that directly contact the system

Figure 6.1 – Systems and Surroundings



When the system (50.0 g of H_2O) absorbs heat from the surroundings (hot plate), its temperature increases from 50.0°C to 80.0°C.

When the hot plate is turned off, the system gives off heat to the surrounding air, and its temperature drops.

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Chemical Reactions

- When we study a chemical reaction, we consider the system to be the reactants and products
- The surroundings are the vessel (beaker, test tube, flask) in which the reaction takes place plus the air or other material in thermal contact with the reaction system

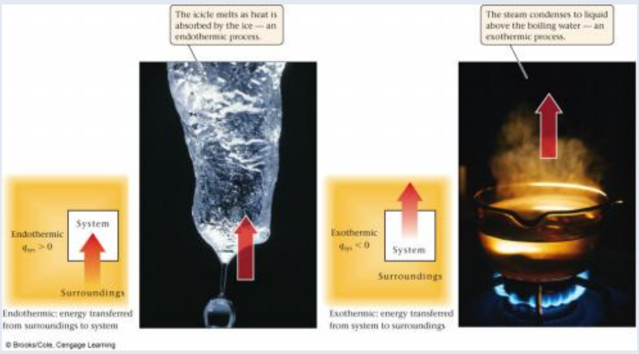
State Properties

- The state of a system is specified by enumerating:
  - Composition
  - Temperature
  - Pressure
- State properties depend only on the state of the system, not on the path the system took to reach the state
- Mathematically for a state property X:
  - ΔX is the ***change*** in X
  - $\Delta X = X_{final} – X_{initial}$

Direction and Sign of Heat Flow

- Heat is given the symbol, q
  - q is positive when heat flows into the system from the surroundings
  - q is negative when heat flows from the system into the surroundings
- Endothermic processes have positive q
  - H_2O (s) → H_2O (ℓ) $q > 0$
- Exothermic processes have negative q
  - CH_4 (g) + $2O_2$ (g) → CO_2 (g) + H_2O (ℓ) $q < 0$

Exothermic and Endothermic Processes



Endothermic: energy transferred from surroundings to system

Exothermic: energy transferred from system to surroundings

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Magnitude of Heat Flow

- In any process, we are interested in both the direction of heat flow and in its magnitude
  - q is expressed in joules (or kilojoules)
  - James Joule (1818-1889); calorimetry
  - Alternate unit: calorie
    - 1 calorie = 4.184 J
    - 1 kilocalorie = 4.184 kJ
    - Nutritional calories are kcal

The Calorimetry Equation

- $q = C \times \Delta t$
  - $\Delta t = t_{final} – t_{initial}$
  - ***C (uppercase)*** is the heat capacity of the system: it is the quantity of heat needed to raise the temperature of the system by 1 ˚C
- $q = m \times c \times \Delta t$
  - ***c (lowercase)*** is the specific heat: the quantity of heat needed to raise the temperature of one gram of a substance by 1 ˚C
- c depends on the identity and phase of the substance

Specific Heat

- The specific heat of a substance, like the density or melting point, is an intensive property that can be used to identify a substance or determine its purity
- Water
  - Water has an unusually large specific heat
  - A large quantity of heat is required to raise the temperature of water
  - Climate is moderated by the specific heat of water
    - Only two states in the US have never recorded temperatures over 100 ˚F – one is Alaska (cold North) and the other is Hawaii (moderated by water)

Table 8.1

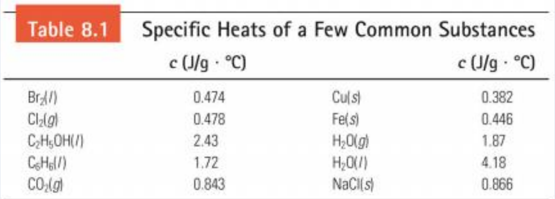
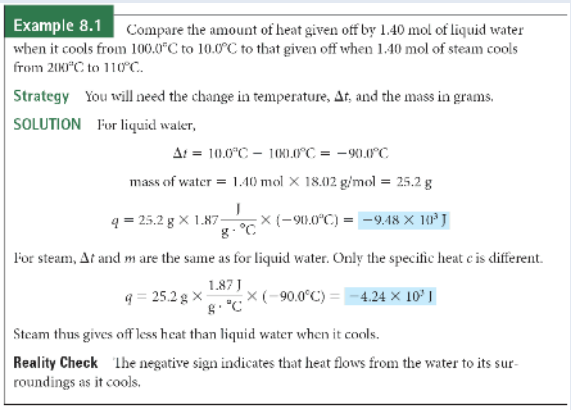


Table 8.1 Specific Heats of a Few Common Substances

	c (J/g · °C)		c (J/g · °C)
$Br_2(l)$	0.474	$Cu(s)$	0.382
$Cl_2(g)$	0.478	$Fe(s)$	0.446
$C_2H_5OH(l)$	2.43	$H_2O(g)$	1.87
$C_6H_6(l)$	1.72	$H_2O(l)$	4.18
$CO_2(g)$	0.843	$NaCl(s)$	0.866

Example 8.1



Example 8.1 Compare the amount of heat given off by 1.40 mol of liquid water when it cools from 100.0°C to 10.0°C to that given off when 1.40 mol of steam cools from 200°C to 110°C.

Strategy You will need the change in temperature, Δt, and the mass in grams.

SOLUTION For liquid water,

$$\Delta t = 10.0°C - 100.0°C = -90.0°C$$

$$\text{mass of water} = 1.40 \text{ mol} \times 18.02 \text{ g/mol} = 25.2 \text{ g}$$

$$q = 25.2 \text{ g} \times 1.87 \frac{\text{J}}{\text{g} \cdot °\text{C}} \times (-90.0°\text{C}) = -9.48 \times 10^3 \text{ J}$$

For steam, Δt and m are the same as for liquid water. Only the specific heat c is different.

$$q = 25.2 \text{ g} \times \frac{1.87 \text{ J}}{\text{g} \cdot °\text{C}} \times (-90.0°\text{C}) = -4.24 \times 10^3 \text{ J}$$

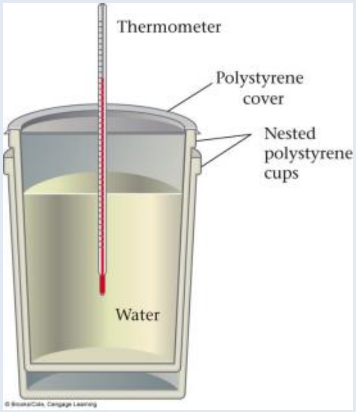
Steam thus gives off less heat than liquid water when it cools.

Reality Check The negative sign indicates that heat flows from the water to its surroundings as it cools.

Measurement of Heat Flow: Calorimetry

- A calorimeter is a device used to measure the heat flow of a reaction
  - The walls of the calorimeter are insulated to block heat flow between the reaction and the surroundings
  - The heat flow for the system is equal in magnitude and opposite in sign from the heat flow of the calorimeter
    - $q_{reaction} = - q_{calorimeter}$
    - $q_{reaction} = - C_{cal} \Delta t$

Figure 8.2

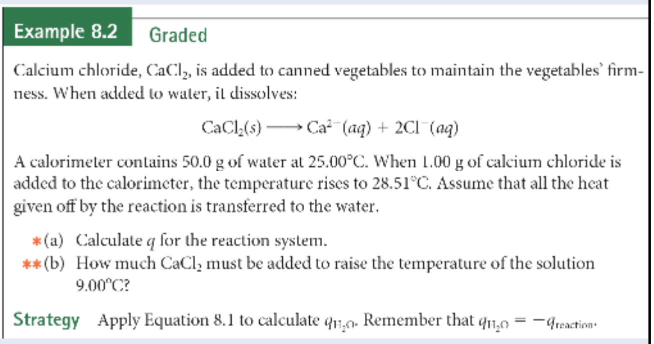


Coffee-cup Calorimeter

- For a reaction performed in a coffee-cup calorimeter

$$q_{reaction} = -m_{water} \times 4.18 \frac{J}{g \cdot {}^{\circ}C} \times \Delta t$$

Example 8.2



Example 8.2 **Graded**

Calcium chloride, $CaCl_2$, is added to canned vegetables to maintain the vegetables' firmness. When added to water, it dissolves:

$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2Cl^-(aq)$$

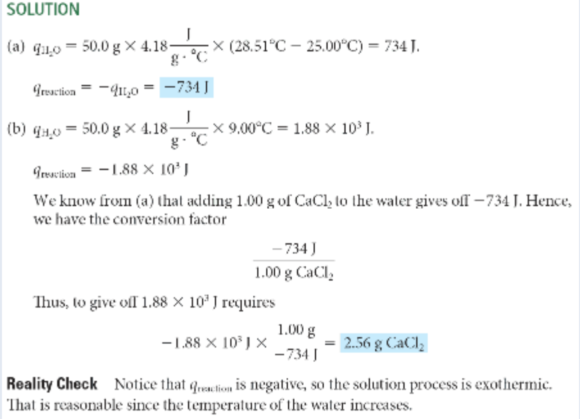
A calorimeter contains 50.0 g of water at 25.00°C. When 1.00 g of calcium chloride is added to the calorimeter, the temperature rises to 28.51°C. Assume that all the heat given off by the reaction is transferred to the water.

*(a) Calculate q for the reaction system.

**(b) How much $CaCl_2$ must be added to raise the temperature of the solution 9.00°C?

Strategy Apply Equation 8.1 to calculate q_{H_2O}. Remember that $q_{H_2O} = -q_{reaction}$.

Example 8.2, (Cont'd)



SOLUTION

(a) $q_{H_2O} = 50.0\text{ g} \times 4.18\frac{\text{J}}{\text{g}\cdot{}^\circ\text{C}} \times (28.51^\circ\text{C} - 25.00^\circ\text{C}) = 734\text{ J}.$

$q_{reaction} = -q_{H_2O} = -734\text{ J}$

(b) $q_{H_2O} = 50.0\text{ g} \times 4.18\frac{\text{J}}{\text{g}\cdot{}^\circ\text{C}} \times 9.00^\circ\text{C} = 1.88 \times 10^3\text{ J}.$

$q_{reaction} = -1.88 \times 10^3\text{ J}$

We know from (a) that adding 1.00 g of $CaCl_2$ to the water gives off −734 J. Hence, we have the conversion factor

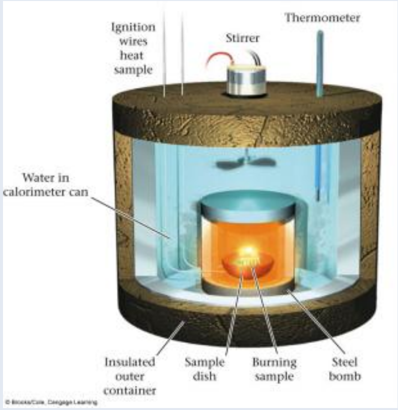
$$\frac{-734\text{ J}}{1.00\text{ g }CaCl_2}$$

Thus, to give off 1.88×10^3 J requires

$$-1.88 \times 10^3\text{ J} \times \frac{1.00\text{ g}}{-734\text{ J}} = 2.56\text{ g }CaCl_2$$

Reality Check Notice that $q_{reaction}$ is negative, so the solution process is exothermic. That is reasonable since the temperature of the water increases.

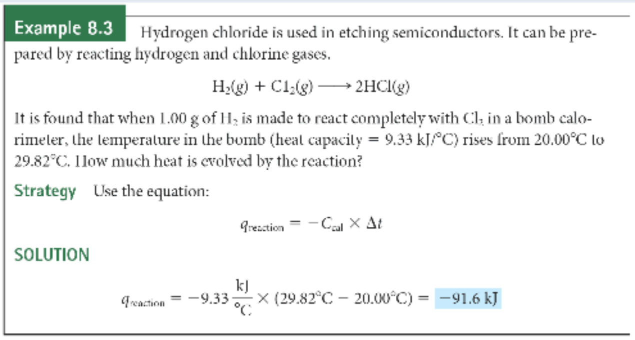
Figure 8.3



Bomb Calorimeter

- The bomb calorimeter is more versatile than the coffee-cup calorimeter
  - Reactions involving high temperature
  - Reactions involving gases
- The bomb is a heavy metal vessel that is usually surrounded by water
- $q_{reaction} = -q_{calorimeter}$
- $q_{reaction} = -C_{cal}\Delta t$
- C_{cal} is a function of the calorimeter and can be measured experimentally

Example 8.3



Example 8.3 Hydrogen chloride is used in etching semiconductors. It can be prepared by reacting hydrogen and chlorine gases.

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

It is found that when 1.00 g of H_2 is made to react completely with Cl_2 in a bomb calorimeter, the temperature in the bomb (heat capacity = 9.33 kJ/°C) rises from 20.00°C to 29.82°C. How much heat is evolved by the reaction?

Strategy Use the equation:

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

SOLUTION

$$q_{reaction} = -9.33\frac{\text{kJ}}{^\circ\text{C}} \times (29.82^\circ\text{C} - 20.00^\circ\text{C}) = -91.6\text{ kJ}$$

Enthalpy

- The heat flow at constant pressure is equal to the difference in enthalpy (heat content) between products and reactants
- The symbol for enthalpy is H
- We measure changes in enthalpy using a calorimeter and a reaction run at constant pressure:
  - $\Delta H = H_{products} - H_{reactants}$
- The sign of the enthalpy change is the same as for heat flow:
  - $\Delta H > 0$ for endothermic reactions
  - $\Delta H < 0$ for exothermic reactions
  - ***Enthalpy is a state variable***

Exothermic Reactions


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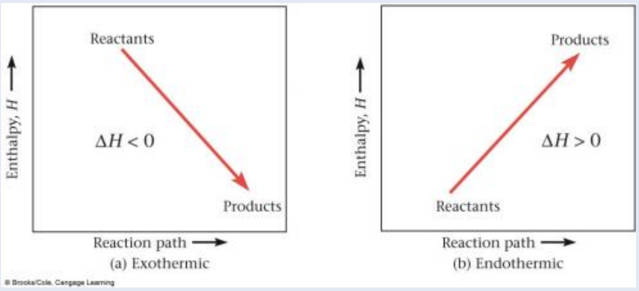
Figure 8.4 – Enthalpy of Reaction



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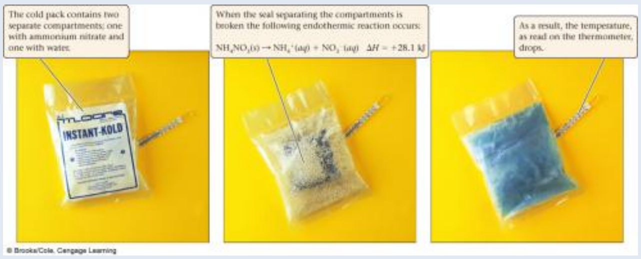
Thermochemical Equations

- A thermochemical equation is a chemical equation with the ΔH for the reaction included
- Example
  - NH_4NO_3 (s) → NH_4^+ (aq) + NO_3^- (aq)
    - Experiment gives qreaction = 351 J for one gram of ammonium nitrate
    - For one mole, this is

$$\frac{351J}{1.00g} \times \frac{80.05g}{1mol} = 2.81X10^4 J = 28.1kJ$$

  - The thermochemical equation is
    - NH_4NO_3 (s) → NH_4^+ (aq) + NO_3^- (aq)   ΔH = +28.1 kJ

Figure 8.5 – An Endothermic Reaction



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Conventions for Thermochemical Equations

1. The sign of ΔH indicates whether the reaction is endothermic or exothermic
2. The coefficients of the thermochemical equation represent the number of moles of reactant and product
3. The phases of all reactant and product species must be stated
4. The value of ΔH applies when products and reactants are at the same temperature, usually 25 °C

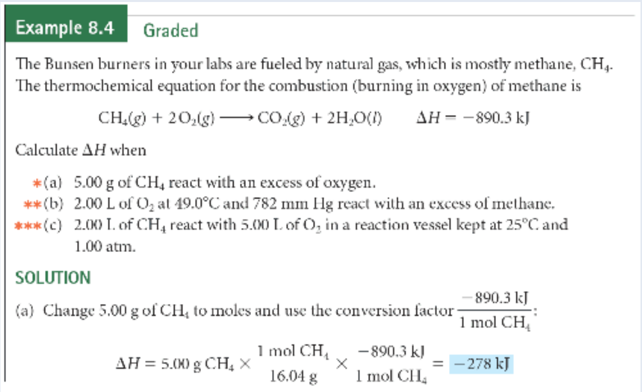
Rules of Thermochemistry

1. The magnitude of ΔH is directly proportional to the amount of reactant or product
2. ΔH for the reaction is equal in magnitude but opposite in sign for ΔH for the reverse of the reaction
3. The value of ΔH is the same whether the reaction occurs in one step or as a series of steps

   This rule is a direct consequence of the fact that ΔH is a state variable

   This rule is a statement of Hess's Law

Example 8.4



Example 8.4 Graded

The Bunsen burners in your labs are fueled by natural gas, which is mostly methane, CH_4. The thermochemical equation for the combustion (burning in oxygen) of methane is

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890.3\ \text{kJ}$$

Calculate ΔH when

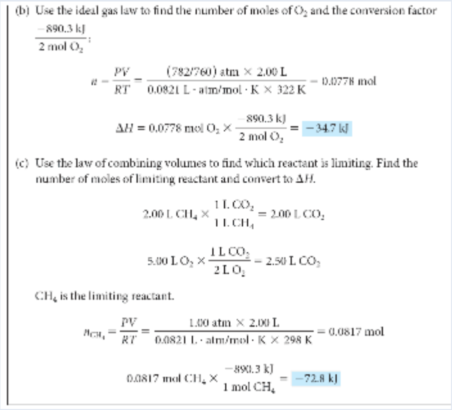
- *(a) 5.00 g of CH_4 react with an excess of oxygen.
- **(b) 2.00 L of O_2 at 49.0°C and 782 mm Hg react with an excess of methane.
- ***(c) 2.00 L of CH_4 react with 5.00 L of O_2 in a reaction vessel kept at 25°C and 1.00 atm.

SOLUTION

(a) Change 5.00 g of CH_4 to moles and use the conversion factor $\frac{-890.3\ \text{kJ}}{1\ \text{mol CH}_4}$:

$$\Delta H = 5.00\ \text{g CH}_4 \times \frac{1\ \text{mol CH}_4}{16.04\ \text{g}} \times \frac{-890.3\ \text{kJ}}{1\ \text{mol CH}_4} = -278\ \text{kJ}$$

Example 8.4, (Cont'd)



(b) Use the ideal gas law to find the number of moles of O_2 and the conversion factor $\frac{-890.3\ \text{kJ}}{2\ \text{mol O}_2}$:

$$n = \frac{PV}{RT} = \frac{(782/760)\ \text{atm} \times 2.00\ \text{L}}{0.0821\ \text{L}\cdot\text{atm/mol}\cdot\text{K} \times 322\ \text{K}} = 0.0778\ \text{mol}$$

$$\Delta H = 0.0778\ \text{mol O}_2 \times \frac{-890.3\ \text{kJ}}{2\ \text{mol O}_2} = -34.7\ \text{kJ}$$

(c) Use the law of combining volumes to find which reactant is limiting. Find the number of moles of limiting reactant and convert to ΔH.

$$2.00\ \text{L CH}_4 \times \frac{1\ \text{L CO}_2}{1\ \text{L CH}_4} = 2.00\ \text{L CO}_2$$

$$5.00\ \text{L O}_2 \times \frac{1\ \text{L CO}_2}{2\ \text{L O}_2} = 2.50\ \text{L CO}_2$$

CH_4 is the limiting reactant.

$$n_{CH_4} = \frac{PV}{RT} = \frac{1.00\ \text{atm} \times 2.00\ \text{L}}{0.0821\ \text{L}\cdot\text{atm/mol}\cdot\text{K} \times 298\ \text{K}} = 0.0817\ \text{mol}$$

$$0.0817\ \text{mol CH}_4 \times \frac{-890.3\ \text{kJ}}{1\ \text{mol CH}_4} = -72.8\ \text{kJ}$$

Enthalpy of Phase Changes

- Phase changes involve enthalpy
  - There is no change in temperature during a phase change
  - Endothermic: melting or vaporization
  - Exothermic: freezing or condensation
- Pure substances have a value of ΔH that corresponds to melting (reverse, fusion) or vaporization (reverse, condensation)

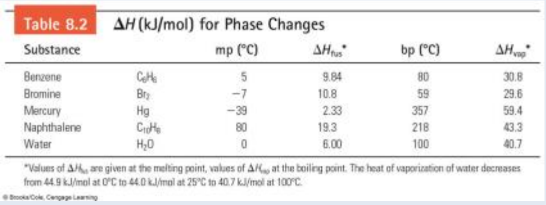
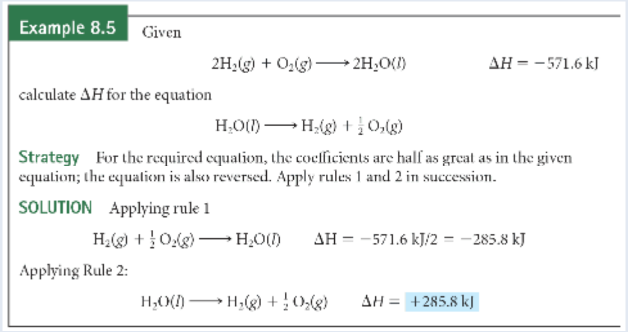


Table 8.2 ΔH (kJ/mol) for Phase Changes

Substance		mp (°C)	ΔH_{fus}*	bp (°C)	ΔH_{vap}*
Benzene	C_6H_6	5	9.84	80	30.8
Bromine	Br_2	−7	10.8	59	29.6
Mercury	Hg	−39	2.33	357	59.4
Naphthalene	$C_{10}H_8$	80	19.3	218	43.3
Water	H_2O	0	6.00	100	40.7

*Values of ΔH_{fus} are given at the melting point, values of ΔH_{vap} at the boiling point. The heat of vaporization of water decreases from 44.9 kJ/mol at 0°C to 44.0 kJ/mol at 25°C to 40.7 kJ/mol at 100°C.

Example 8.5



Example 8.5 Given

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H = -571.6\ \text{kJ}$$

calculate ΔH for the equation

$$H_2O(l) \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$

Strategy For the required equation, the coefficients are half as great as in the given equation; the equation is also reversed. Apply rules 1 and 2 in succession.

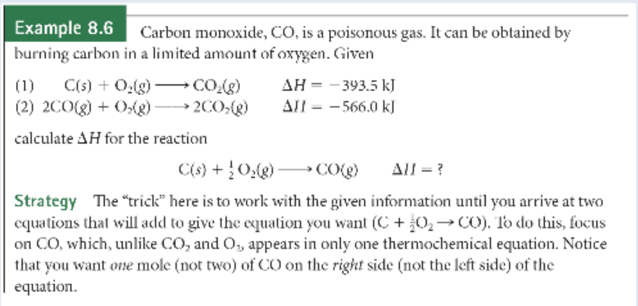
SOLUTION Applying rule 1

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -571.6\ \text{kJ}/2 = -285.8\ \text{kJ}$$

Applying Rule 2:

$$H_2O(l) \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H = +285.8\ \text{kJ}$$

Example 8.6



Example 8.6 Carbon monoxide, CO, is a poisonous gas. It can be obtained by burning carbon in a limited amount of oxygen. Given

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

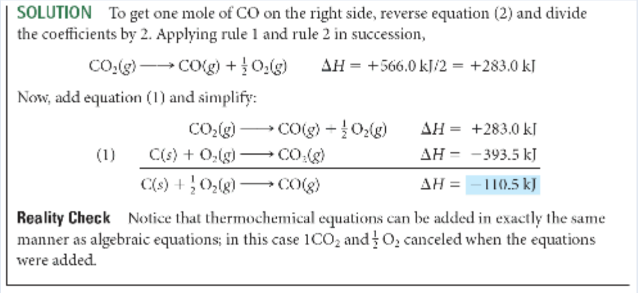
(2) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H = -566.0\ \text{kJ}$

calculate ΔH for the reaction

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H = ?$$

Strategy The "trick" here is to work with the given information until you arrive at two equations that will add to give the equation you want ($C + \frac{1}{2}O_2 \rightarrow CO$). To do this, focus on CO, which, unlike CO_2 and O_2, appears in only one thermochemical equation. Notice that you want *one* mole (not two) of CO on the *right* side (not the left side) of the equation.

Example 8.6, (Cont'd)



SOLUTION To get one mole of CO on the right side, reverse equation (2) and divide the coefficients by 2. Applying rule 1 and rule 2 in succession,

$$CO_2(g) \longrightarrow CO(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H = +566.0\ \text{kJ}/2 = +283.0\ \text{kJ}$$

Now, add equation (1) and simplify:

$$\begin{array}{lll} & CO_2(g) \longrightarrow CO(g) + \tfrac{1}{2}O_2(g) & \Delta H = +283.0\ \text{kJ} \\ (1) & C(s) + O_2(g) \longrightarrow CO_2(g) & \Delta H = -393.5\ \text{kJ} \\ \hline & C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) & \Delta H = -110.5\ \text{kJ} \end{array}$$

Reality Check Notice that thermochemical equations can be added in exactly the same manner as algebraic equations; in this case 1CO_2 and $\frac{1}{2}O_2$ canceled when the equations were added.

Recap of the Rules of Thermochemistry

- ΔH is directly proportional to the amount of reactant or product
  - If a reaction is divided by 2, so is ΔH
  - If a reaction is multiplied by 6, so is ΔH
- ΔH changes sign when the reaction is reversed
- ΔH has the same value regardless of the number of steps

Enthalpies of Formation

- The standard molar enthalpy of formation, ΔH_f°, is equal to the enthalpy change
  - For one mole of a compound
  - At constant pressure of 1 atm
  - At a fixed temperature of 25 ˚C
  - From elements in their stable states at that temperature and pressure
- Enthalpies of formation are tabulated in Table 8.3 and in Appendix 1 in the back of the textbook

Table 8.3

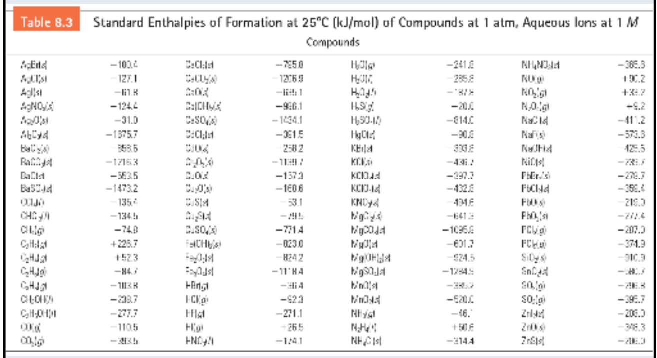
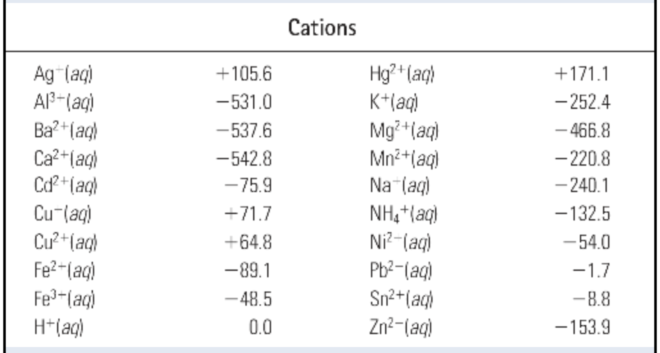


Table 8.3 Standard Enthalpies of Formation at 25°C (kJ/mol) of Compounds at 1 atm, Aqueous Ions at 1 *M*

Compounds

$AgBr(s)$	−100.4	$CaCl_2(s)$	−795.8	$H_2O(g)$	−241.8	$NH_4NO_3(s)$	−365.6
$AgCl(s)$	−127.1	$CaCO_3(s)$	−1206.9	$H_2O(l)$	−285.8	$NO(g)$	+90.2
$AgI(s)$	−61.8	$CaO(s)$	−635.1	$H_2O_2(l)$	−187.8	$NO_2(g)$	+33.2
$AgNO_3(s)$	−124.4	$Ca(OH)_2(s)$	−986.1	$H_2S(g)$	−20.6	$N_2O_4(g)$	+9.2
$Ag_2O(s)$	−31.0	$CaSO_4(s)$	−1434.1	$H_2SO_4(l)$	−814.0	$NaCl(s)$	−411.2
$Al_2O_3(s)$	−1675.7	$CdCl_2(s)$	−391.5	$HgO(s)$	−90.8	$NaF(s)$	−573.6
$BaCl_2(s)$	−858.6	$CdO(s)$	−258.2	$KBr(s)$	−393.8	$NaOH(s)$	−425.6
$BaCO_3(s)$	−1216.3	$Cr_2O_3(s)$	−1139.7	$KCl(s)$	−436.7	$NiO(s)$	−239.7
$BaO(s)$	−553.5	$CuO(s)$	−157.3	$KClO_3(s)$	−397.7	$PbBr_2(s)$	−278.7
$BaSO_4(s)$	−1473.2	$Cu_2O(s)$	−168.6	$KClO_4(s)$	−432.8	$PbCl_2(s)$	−359.4
$CCl_4(l)$	−135.4	$CuS(s)$	−53.1	$KNO_3(s)$	−494.6	$PbO(s)$	−219.0
$CHCl_3(l)$	−134.5	$Cu_2S(s)$	−79.5	$MgCl_2(s)$	−641.3	$PbO_2(s)$	−277.4
$CH_4(g)$	−74.8	$CuSO_4(s)$	−771.4	$MgCO_3(s)$	−1095.8	$PCl_3(g)$	−287.0
$C_2H_2(g)$	+226.7	$Fe(OH)_3(s)$	−823.0	$MgO(s)$	−601.7	$PCl_5(g)$	−374.9
$C_2H_4(g)$	+52.3	$Fe_2O_3(s)$	−824.2	$Mg(OH)_2(s)$	−924.5	$SiO_2(s)$	−910.9
$C_2H_6(g)$	−84.7	$Fe_3O_4(s)$	−1118.4	$MgSO_4(s)$	−1284.9	$SnO_2(s)$	−580.7
$C_3H_8(g)$	−103.8	$HBr(g)$	−36.4	$MnO(s)$	−385.2	$SO_2(g)$	−296.8
$CH_3OH(l)$	−238.7	$HCl(g)$	−92.3	$MnO_2(s)$	−520.0	$SO_3(g)$	−395.7
$C_2H_5OH(l)$	−277.7	$HF(g)$	−271.1	$NH_3(g)$	−46.1	$ZnI_2(s)$	−208.0
$CO(g)$	−110.5	$HI(g)$	+26.5	$N_2H_4(l)$	+50.6	$ZnO(s)$	−348.3
$CO_2(g)$	−393.5	$HNO_3(l)$	−174.1	$NH_4Cl(s)$	−314.4	$ZnS(s)$	−206.0

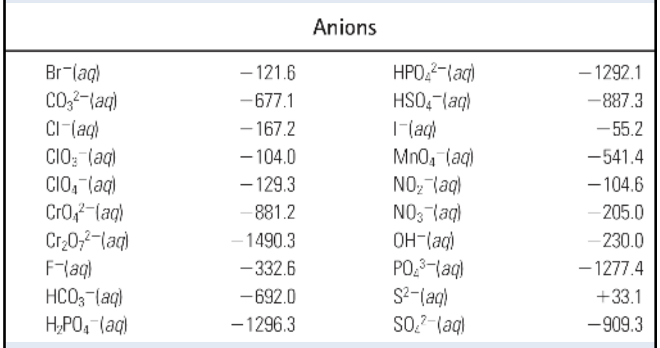
Table 8.3, (Cont'd)



Cations

$Ag^+(aq)$	+105.6	$Hg^{2+}(aq)$	+171.1
$Al^{3+}(aq)$	−531.0	$K^+(aq)$	−252.4
$Ba^{2+}(aq)$	−537.6	$Mg^{2+}(aq)$	−466.8
$Ca^{2+}(aq)$	−542.8	$Mn^{2+}(aq)$	−220.8
$Cd^{2+}(aq)$	−75.9	$Na^+(aq)$	−240.1
$Cu^+(aq)$	+71.7	$NH_4^+(aq)$	−132.5
$Cu^{2+}(aq)$	+64.8	$Ni^{2+}(aq)$	−54.0
$Fe^{2+}(aq)$	−89.1	$Pb^{2+}(aq)$	−1.7
$Fe^{3+}(aq)$	−48.5	$Sn^{2+}(aq)$	−8.8
$H^+(aq)$	0.0	$Zn^{2+}(aq)$	−153.9

Table 8.3, (Cont'd)



Anions

$Br^-(aq)$	−121.6	$HPO_4^{2-}(aq)$	−1292.1
$CO_3^{2-}(aq)$	−677.1	$HSO_4^-(aq)$	−887.3
$Cl^-(aq)$	−167.2	$I^-(aq)$	−55.2
$ClO_3^-(aq)$	−104.0	$MnO_4^-(aq)$	−541.4
$ClO_4^-(aq)$	−129.3	$NO_2^-(aq)$	−104.6
$CrO_4^{2-}(aq)$	−881.2	$NO_3^-(aq)$	−205.0
$Cr_2O_7^{2-}(aq)$	−1490.3	$OH^-(aq)$	−230.0
$F^-(aq)$	−332.6	$PO_4^{3-}(aq)$	−1277.4
$HCO_3^-(aq)$	−692.0	$S^{2-}(aq)$	+33.1
$H_2PO_4^-(aq)$	−1296.3	$SO_4^{2-}(aq)$	−909.3

Enthalpies of Formation of Elements and of H^+ (aq)

- The enthalpy of formation of an element in its standard state at 25 ˚C is zero

$$\Delta H_f^\circ Br_2(l) = \Delta H_f^\circ H_2O(l) = 0$$

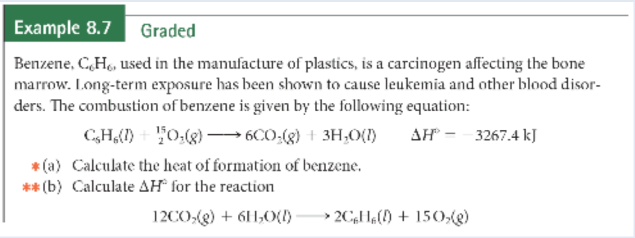
- The enthalpy of formation of H^+ (aq) is also zero

Calculation of ΔH°

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

- The symbol Σ refers to "the sum of"
- Elements in their standard states may be omitted, as their enthalpies of formation are zero
- The coefficients of reactants and products in the balanced equation must be accounted for

Example 8.7



Example 8.7 Graded

Benzene, C_6H_6, used in the manufacture of plastics, is a carcinogen affecting the bone marrow. Long-term exposure has been shown to cause leukemia and other blood disorders. The combustion of benzene is given by the following equation:

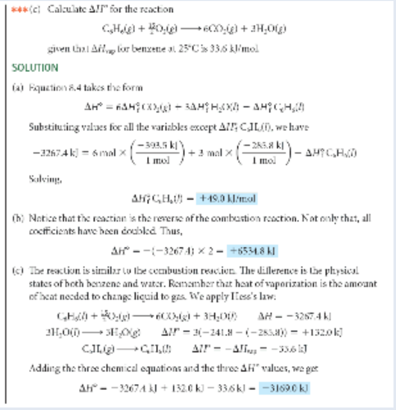
$$C_6H_6(l) + \tfrac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l) \qquad \Delta H^\circ = -3267.4\ \text{kJ}$$

*(a) Calculate the heat of formation of benzene.

**(b) Calculate ΔH° for the reaction

$$12CO_2(g) + 6H_2O(l) \longrightarrow 2C_6H_6(l) + 15O_2(g)$$

Example 8.7, (Cont'd)



***(c) Calculate ΔH° for the reaction

$$C_6H_6(g) + \tfrac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(g)$$

given that ΔH_{vap} for benzene at 25°C is 33.6 kJ/mol

SOLUTION

(a) Equation 8.4 takes the form

$$\Delta H^\circ = 6\Delta H_f^\circ CO_2(g) + 3\Delta H_f^\circ H_2O(l) - \Delta H_f^\circ C_6H_6(l)$$

Substituting values for all the variables except $\Delta H_f^\circ C_6H_6(l)$, we have

$$-3267.4\ \text{kJ} = 6\ \text{mol} \times \left(\frac{-393.5\ \text{kJ}}{1\ \text{mol}}\right) + 3\ \text{mol} \times \left(\frac{-285.8\ \text{kJ}}{1\ \text{mol}}\right) - \Delta H_f^\circ C_6H_6(l)$$

Solving,

$$\Delta H_f^\circ C_6H_6(l) = +49.0\ \text{kJ/mol}$$

(b) Notice that the reaction is the reverse of the combustion reaction. Not only that, all coefficients have been doubled. Thus,

$$\Delta H^\circ = -(-3267.4) \times 2 = +6534.8\ \text{kJ}$$

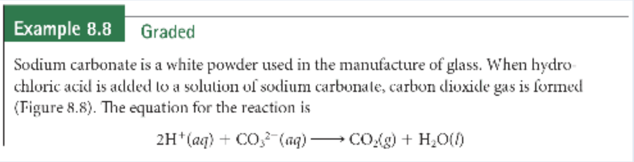
(c) The reaction is similar to the combustion reaction. The difference is the physical states of both benzene and water. Remember that heat of vaporization is the amount of heat needed to change liquid to gas. We apply Hess's law:

$$C_6H_6(l) + \tfrac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l) \qquad \Delta H = -3267.4\ \text{kJ}$$
$$3H_2O(l) \longrightarrow 3H_2O(g) \qquad \Delta H^\circ = 3(-241.8 - (-285.8)) = +132.0\ \text{kJ}$$
$$C_6H_6(g) \longrightarrow C_6H_6(l) \qquad \Delta H^\circ = -\Delta H_{vap} = -33.6\ \text{kJ}$$

Adding the three chemical equations and the three ΔH° values, we get

$$\Delta H^\circ = -3267.4\ \text{kJ} + 132.0\ \text{kJ} - 33.6\ \text{kJ} = -3169.0\ \text{kJ}$$

Example 8.8

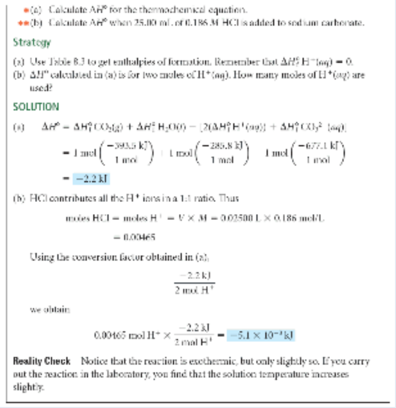


Example 8.8 Graded

Sodium carbonate is a white powder used in the manufacture of glass. When hydrochloric acid is added to a solution of sodium carbonate, carbon dioxide gas is formed (Figure 8.8). The equation for the reaction is

$$2H^+(aq) + CO_3^{2-}(aq) \longrightarrow CO_2(g) + H_2O(l)$$

Example 8.8, (Cont'd)



*(a) Calculate ΔH° for the thermochemical equation.

**(b) Calculate ΔH° when 25.00 mL of 0.186 M HCl is added to sodium carbonate.

Strategy

(a) Use Table 8.3 to get enthalpies of formation. Remember that $\Delta H_f^\circ H^+(aq) = 0$.

(b) ΔH° calculated in (a) is for two moles of $H^+(aq)$. How many moles of $H^+(aq)$ are used?

SOLUTION

(a)
$$\Delta H^\circ = \Delta H_f^\circ CO_2(g) + \Delta H_f^\circ H_2O(l) - [2(\Delta H_f^\circ H^+(aq)) + \Delta H_f^\circ CO_3^{2-}(aq)]$$
$$= 1\ \text{mol}\left(\frac{-393.5\ \text{kJ}}{1\ \text{mol}}\right) + 1\ \text{mol}\left(\frac{-285.8\ \text{kJ}}{1\ \text{mol}}\right) - 1\ \text{mol}\left(\frac{-677.1\ \text{kJ}}{1\ \text{mol}}\right)$$
$$= -2.2\ \text{kJ}$$

(b) HCl contributes all the H^+ ions in a 1:1 ratio. Thus

$$\text{moles HCl} = \text{moles } H^+ = V \times M = 0.02500\ \text{L} \times 0.186\ \text{mol/L}$$
$$= 0.00465$$

Using the conversion factor obtained in (a),

$$\frac{-2.2\ \text{kJ}}{2\ \text{mol } H^+}$$

we obtain

$$0.00465\ \text{mol } H^+ \times \frac{-2.2\ \text{kJ}}{2\ \text{mol } H^+} = -5.1 \times 10^{-3}\ \text{kJ}$$

Reality Check Notice that the reaction is exothermic, but only slightly so. If you carry out the reaction in the laboratory, you find that the solution temperature increases slightly.

Bond Enthalpy

- Chemical bonds store ***energy***
- The ***bond enthalpy is defined as ΔH when one mole of chemical bonds is broken in the gaseous state***

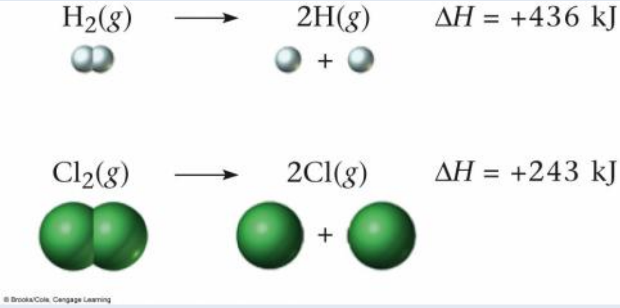


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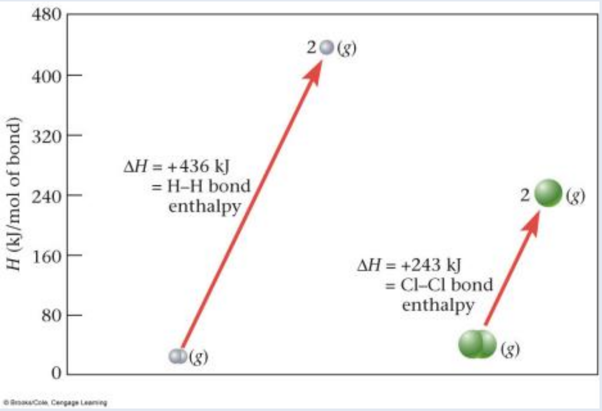
Figure 8.9



Notes on Bond Enthalpy

- ***The bond enthalpy is always a positive quantity***
  - Energy is required to break a chemical bond
- When a chemical bond forms, the sign of the enthalpy change is negative
- For ***endothermic*** reactions
  - The ***bonds are stronger in the reactants than in the products,*** and/or
  - There are ***more bonds in the reactants than in the products***

Figure 8.9

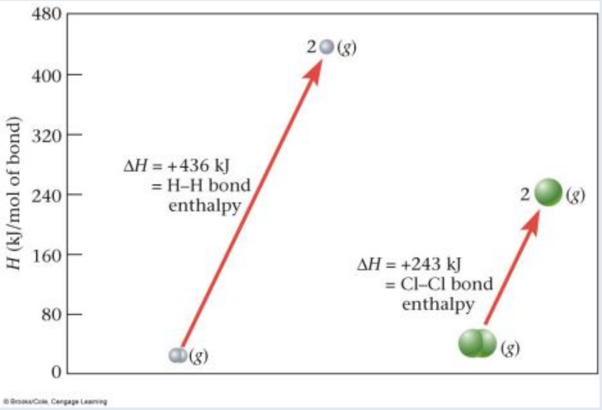


Table 8.4

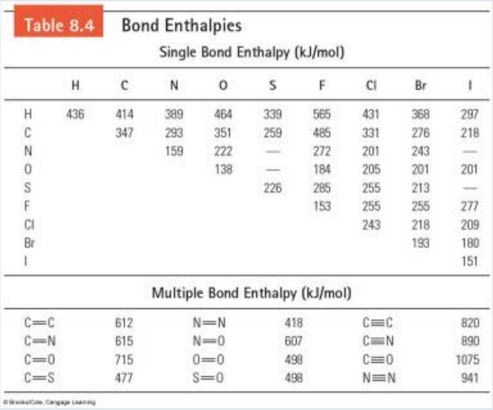


Table 8.4 Bond Enthalpies

Single Bond Enthalpy (kJ/mol)

	H	C	N	O	S	F	Cl	Br	I
H	436	414	389	464	339	565	431	368	297
C		347	293	351	259	485	331	276	218
N			159	222	—	272	201	243	—
O				138	—	184	205	201	201
S					226	285	255	213	—
F						153	255	255	277
Cl							243	218	209
Br								193	180
I									151

Multiple Bond Enthalpy (kJ/mol)

C=C	612	N=N	418	C≡C	820
C=N	615	N=O	607	C≡N	890
C=O	715	O=O	498	C≡O	1075
C=S	477	S=O	498	N≡N	941

Bond Enthalpies and Multiple Bonds

- As the order of a bond increases from single to double to triple, the bond enthalpy also increases
  - C-C single, 347 kJ/mol
  - C-C double, 612 kJ/mol
  - C-C triple, 820 kJ/mol
- Whenever a bond involves two different atoms, the enthalpy is an approximation, because it must be averaged over two different species
  - H-O-H (g) → H (g) + OH (g) ΔH = +499 J
  - H-O (g) → H (g) + O (g) ΔH = +428 kJ

Bond Enthalpy vs. Enthalpy of Formation

- When ΔH is calculated, we can use enthalpies of formation or bond enthalpies
  - Using enthalpy of formation, results are accurate to 0.1 kJ
  - Using bond enthalpies, results can produce an error of 10 kJ or more
- Use enthalpies of formation to calculate ΔH wherever possible

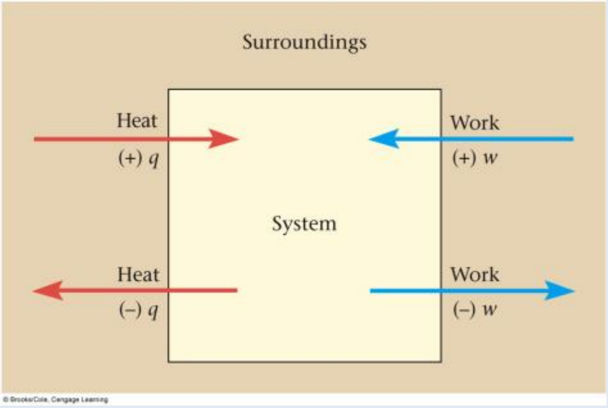
The First Law of Thermodynamics

- Thermodynamics
  - Deals with all kinds of energy effects in all kinds of processes
  - Two types of energy
    - Heat (q)
    - Work (w)
  - The Law of Conservation of Energy
    - $\Delta E_{system} = -\Delta E_{surroundings}$
  - The First Law
    - $\Delta E = q + w$
    - The ***total change in energy*** is equal to the ***sum of the heat and work transferred*** between the system and the surroundings

Conventions

- q and w are positive
  - When the heat or work enters the system from the surroundings
- q and w are negative
  - When the heat or work leaves the system for the surroundings

Figure 8.10



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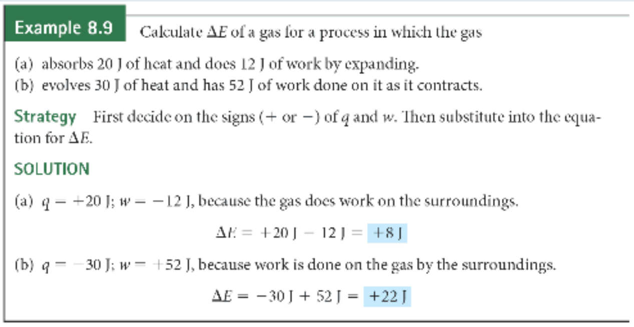
Example 8.9



Example 8.9 Calculate ΔE of a gas for a process in which the gas

(a) absorbs 20 J of heat and does 12 J of work by expanding.
(b) evolves 30 J of heat and has 52 J of work done on it as it contracts.

Strategy First decide on the signs (+ or −) of q and w. Then substitute into the equation for ΔE.

SOLUTION

(a) $q = +20$ J; $w = -12$ J, because the gas does work on the surroundings.

$$\Delta E = +20 \text{ J} - 12 \text{ J} = +8 \text{ J}$$

(b) $q = -30$ J; $w = +52$ J, because work is done on the gas by the surroundings.

$$\Delta E = -30 \text{ J} + 52 \text{ J} = +22 \text{ J}$$

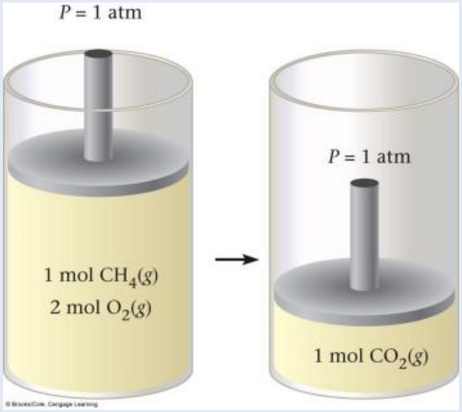
Heat

- Ordinarily, when a chemical reaction is carried out in the laboratory, energy is evolved as heat
  - CH_4 (g) + $2O_2$ (g) → CO_2 (g) + H_2O (ℓ) $\Delta E = -885$ kJ
  - The combustion of methane in a Bunsen burner produces nearly 885 kJ of heat per mol
  - The decrease in volume that takes place is a 1% work effect

Work

- In an internal combustion engine, a significant fraction of the energy of combustion is converted to useful work
  - The expansion of the combustion gases produces a volume and a pressure change
  - The system does work on its surroundings
    - Propels the car forward
    - Overcomes friction
    - Charges battery
  - Like ΔH, ***ΔE is a state variable***
    - ***q and w are not state variables***

Figure 8.11 – Pressure-Volume Work



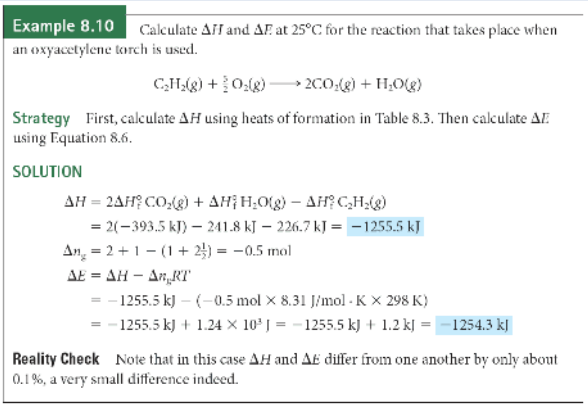
ΔH and ΔE

- Constant pressure
  - Coffee-cup calorimeter
  - $\Delta H = q_p$
- Constant volume
  - In a bomb calorimeter, there is no pressure-volume work done
  - $\Delta E = q_v$

ΔH and ΔE, (Cont'd)

- H = E + PV
- ΔH = ΔE + PΔV
  - The PV product is important only where gases are involved; it is negligible when only liquids or solids are involved
- $\Delta H = \Delta E + \Delta n_g RT$
  - Δn_g is the change in the number of moles of gas as the reaction proceeds

Example 8.10



Example 8.10 Calculate ΔH and ΔE at 25°C for the reaction that takes place when an oxyacetylene torch is used.

$$C_2H_2(g) + \tfrac{5}{2}\,O_2(g) \longrightarrow 2CO_2(g) + H_2O(g)$$

Strategy First, calculate ΔH using heats of formation in Table 8.3. Then calculate ΔE using Equation 8.6.

SOLUTION

$$\begin{aligned}\Delta H &= 2\Delta H_f^\circ\,CO_2(g) + \Delta H_f^\circ\,H_2O(g) - \Delta H_f^\circ\,C_2H_2(g)\\ &= 2(-393.5\text{ kJ}) - 241.8\text{ kJ} - 226.7\text{ kJ} = \boxed{-1255.5\text{ kJ}}\\ \Delta n_g &= 2 + 1 - (1 + 2\tfrac{1}{2}) = -0.5\text{ mol}\\ \Delta E &= \Delta H - \Delta n_g RT\\ &= -1255.5\text{ kJ} - (-0.5\text{ mol} \times 8.31\text{ J/mol}\cdot\text{K} \times 298\text{ K})\\ &= -1255.5\text{ kJ} + 1.24 \times 10^3\text{ J} = -1255.5\text{ kJ} + 1.2\text{ kJ} = \boxed{-1254.3\text{ kJ}}\end{aligned}$$

Reality Check Note that in this case ΔH and ΔE differ from one another by only about 0.1%, a very small difference indeed.

Key Concepts

1. Relate heat flow to specific heat, m and Δt
2. Calculate q for a reaction from calorimetric data.
3. Apply the rules of thermochemistry
4. Apply Hess's law to calculate ΔH
5. Relate ΔH° to the enthalpies of formation
6. Relate ΔE, q and w
7. Relate ΔH and ΔE