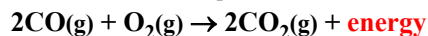## Thermochemistry

– studies the energy aspects of chemical reactions

– chemical reactions either produce or consume energy

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g) + \text{energy}$$
$$2H_2O(g) + \text{energy} \rightarrow 2H_2(g) + O_2(g)$$

6.1 Forms of Energy

- **Kinetic energy** (E_k) – due to motion (for an object with mass m and velocity u: $E_k = (1/2)mu^2$)
- **Potential energy** (E_p) – due to position or interactions (formulas for E_p depend on the type of interactions)


- The **total energy** (E_{tot}) is the sum of kinetic and potential energies

$$E_{tot} = E_k + E_p$$

- **Internal energy** (E) – the total energy of all atoms, molecules and other particles in a sample of matter
- **Law of conservation of energy** - the total energy of an isolated object (or a system of objects) is constant

  – E_k and E_p can change, but $E_k + E_p$ = constant

Systems and Surroundings

- **System** – part of the universe under investigation
- **Surroundings** – the rest of the universe outside the system
 – In practice, only the nearest surroundings relevant to the system are considered

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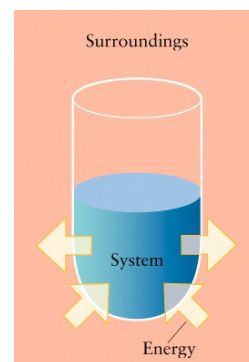
- Energy transfer between the system and its surroundings results in a change of the system's internal energy
- **Internal energy change (ΔE)**

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

  – If the system gains energy, $E_{final} > E_{initial}$ and $\Delta E > 0$
  – If the system loses energy, $E_{final} < E_{initial}$ and $\Delta E < 0$

- The energy gained by the system must be lost by the surroundings and vice versa (conservation of energy)

- **Open systems** – can exchange both matter and energy with the surroundings
  – open flask, fire, rocket engine, ...
- **Closed systems** – can exchange energy, but not matter with the surroundings
  – sealed flask, weather balloon, battery, ...
- **Isolated systems** – can exchange neither energy nor matter with the surroundings
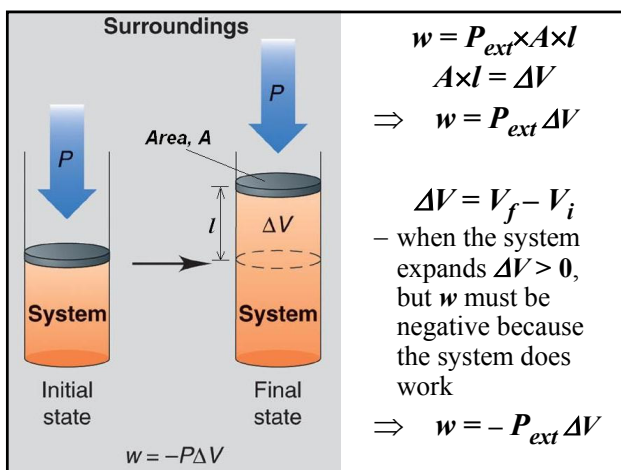 – sealed and thermally isolated container

Heat and Work

- **Thermal energy** – the energy of the random (thermal) motion of particles in a sample of matter (a part of the internal energy)
- **Heat (q)** – transfer of thermal energy as a result of a temperature difference
  - thermal energy flows from places with high to places with low temperatures
  - heating changes the internal energy of a system
  - heating can change the temperature or the physical state of a system

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- **Work (w)** – transfer of energy in the form of a motion against an opposing force (mechanical)
  - causes an uniform molecular motion
  - changes the internal energy of the system
- Energy can be transferred by heat and/or work
  $$\Rightarrow \Delta E = q + w$$
- Heat and work are considered positive ($q > 0$ and $w > 0$), if they increase the internal energy of the system
  - Heat flowing into the system is positive
  - Work done on the system is positive

- Energy diagrams

$$2Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$
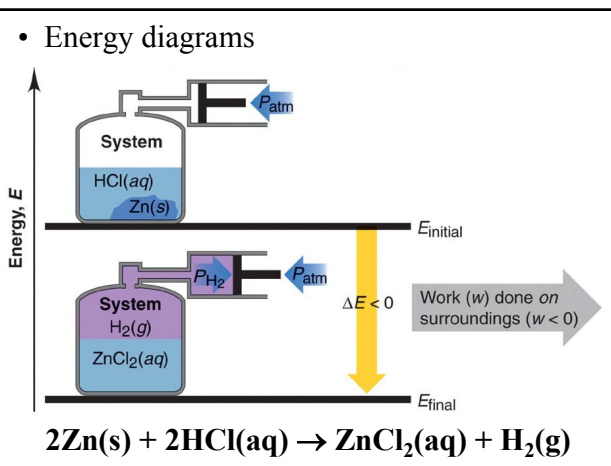
- **Expansion (PV) work** – due to changes in the volume of the system (important for reactions involving gases)
- If an object is moved over a distance (l) against an opposing force (F), the work is:
  $$w = F \times l$$
- If a system expands against an external pressure (P_{ext}) applied over an area (A), the opposing force (F) is:
  $$F = P_{ext} \times A \qquad \Rightarrow \qquad w = P_{ext} \times A \times l$$

$w = P_{ext} \times A \times l$
$A \times l = \Delta V$
$\Rightarrow \quad w = P_{ext} \Delta V$

$\Delta V = V_f - V_i$
– when the system expands $\Delta V > 0$, but w must be negative because the system does work

$\Rightarrow \quad w = -P_{ext} \Delta V$

The First Law of Thermodynamics

- **1st Law** – **The total energy of the universe is constant** (energy can't be created or destroyed, it can only be converted from one form to another)
  $$\Delta E_{univ} = \Delta E_{sys} + \Delta E_{surr} = 0$$
- An **isolated system** can be viewed as a "small universe" ($q = 0$ and $w = 0$)
  $$\Delta E = q + w = 0 \quad \Rightarrow \quad E = \text{constant}$$
- **1st Law** – The internal energy of an isolated system is constant (energy can not be created or destroyed within an isolated system)

- Energy units (same units are used for E, q and w)
  - SI unit → **joule**, **J** $(1\ J = 1\ kg \cdot m^2/s^2)$
  - Other units → **calorie, cal** $(1\ cal = 4.184\ J)$
    → **1 cal** – the energy needed to increase the temperature of 1g of water by 1ºC

Example: Calculate the change of the internal energy of a system that gains 200 kJ as heat while doing 300 kJ of work.

$q = +200\ kJ$ $w = -300\ kJ$

$\Delta E = q + w = 200\ kJ + (-300\ kJ) = -100\ kJ$

- Units of PV work
  - If P_{ext} is in **Pa** and ΔV is in m^3, than w is in **J**

  $1\ Pa \cdot m^3 = 1\ (kg/m \cdot s^2) \times 1\ m^3 = 1\ kg \cdot m^2/s^2 = 1\ J$

  - If P_{ext} is in **atm** and ΔV is in **L**, than w is in **L·atm**

  $1\ L \cdot atm = 10^{-3}\ m^3 \times 101325\ Pa = 101.325\ J$

Example: Calculate the work done when a gas is compressed from **12.0 L** to **5.0 L** by an external pressure of **2.6 atm.**

$w = -P_{ext}\Delta V = -2.6\ atm \times (5.0\ L - 12.0\ L)$

   $= -2.6 \times (-7.0)\ L \cdot atm = 18\ L \cdot atm$

18 L·atm $\times (101.325\ J/1\ L \cdot atm) = 1.8 \times 10^3\ J = 1.8\ kJ$

- **State function** – a property that depends on the present state of the system (P, V, T, n), but not on the way it arrived in that state
  - E is a state function $\Rightarrow \Delta E$ depends only on the initial and final states of the system, but not on the path between these states → $\Delta E = E_{final} - E_{initial}$
  - q and w are not state functions because they depend on the path the system takes between two states

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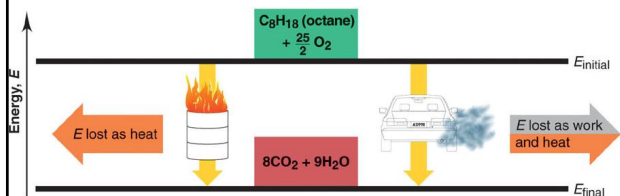
6.2 Reaction Enthalpy

- If only expansion work is done:

$$\Delta E = q + w = q - P_{ext}\Delta V$$

- At constant volume (rigid, sealed container):

$$\Delta V = 0 \quad \Rightarrow \quad \Delta E = q \quad \rightarrow \quad \boxed{\Delta E = q_v}$$

  - **The heat transferred at constant volume, q_v, is equal to the change in the internal energy**

- At constant pressure (open container), if the system pressure equals the external pressure:

$$P = P_{ext} \qquad \Delta E = q - P\Delta V$$

- **Enthalpy** (H) – a state function defined as:

$$H = E + PV$$

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

- At constant pressure → $\Delta(PV) = P\Delta V$

$\Delta H = \Delta E + P\Delta V$ and $\Delta E = q - P\Delta V$

$\Delta H = q - P\Delta V + P\Delta V = q \quad \rightarrow \quad \boxed{\Delta H = q_p}$

  - **The heat transferred at constant pressure, q_p, is equal to the change in the enthalpy**

- For processes at constant pressure

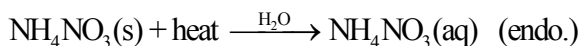$$\Delta E = q_p - P\Delta V = \Delta H - P\Delta V$$
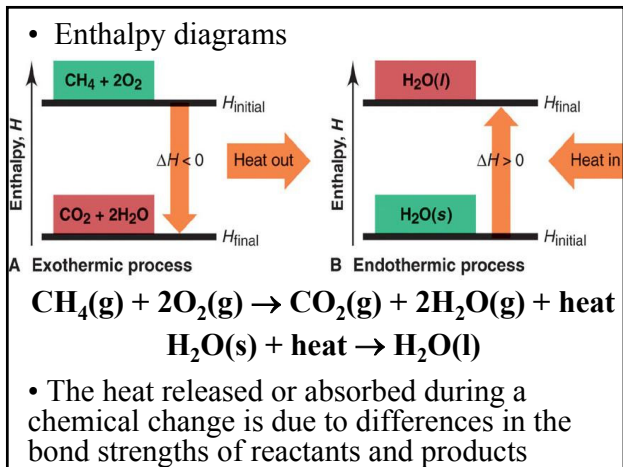

Exothermic and endothermic processes

- **Exothermic process** – the system releases heat in the surroundings ($q < 0$)
  - at constant pressure ($\Delta H = q_p$) $\Rightarrow \Delta H < 0$
- **Endothermic process** – the system absorbs heat from the surroundings ($q > 0$)
  - at constant pressure ($\Delta H = q_p$) $\Rightarrow \Delta H > 0$

$NaOH(s) \xrightarrow{\ H_2O\ } NaOH(aq) + heat$ (exo.)

$NH_4NO_3(s) + heat \xrightarrow{\ H_2O\ } NH_4NO_3(aq)$ (endo.)

- Enthalpy diagrams

A **Exothermic process**   B **Endothermic process**

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + heat$$

$$H_2O(s) + heat \rightarrow H_2O(l)$$

- The heat released or absorbed during a chemical change is due to differences in the bond strengths of reactants and products
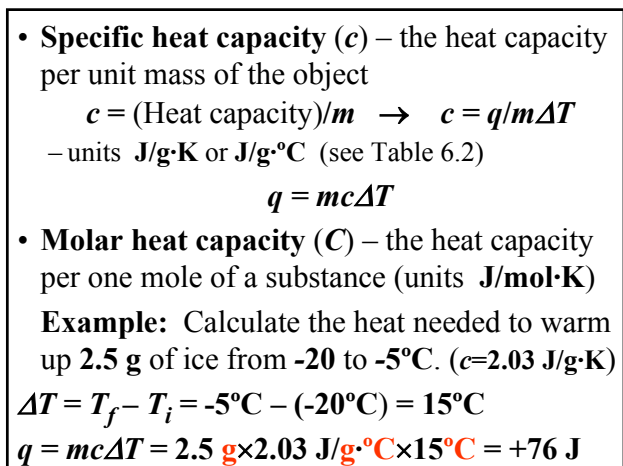

6.3 Heat Measurements

- Heat transfer in or out of an object can be estimated by measuring the temperature change in the object
- **Heat capacity** – the heat required to increase the temperature of an object by **1 K** (or **ºC**)

  Heat capacity = $q/\Delta T$

  – units **J/K** or **J/ºC**
- The heat capacity is an extensive property that increases with the size of the object

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- **Specific heat capacity** (c) – the heat capacity per unit mass of the object

  c = (Heat capacity)/m $\rightarrow$ $c = q/m\Delta T$

  – units **J/g·K** or **J/g·ºC** (see Table 6.2)

  $$q = mc\Delta T$$

- **Molar heat capacity** (C) – the heat capacity per one mole of a substance (units **J/mol·K**)

  Example: Calculate the heat needed to warm up **2.5 g** of ice from **-20** to **-5ºC**. (c=2.03 J/g·K)

  $\Delta T = T_f - T_i = -5ºC - (-20ºC) = 15ºC$

  $q = mc\Delta T = 2.5$ g×2.03 J/g·ºC×15ºC = +76 J

- **Calorimeter** – a device used to measure heat transfers
  – thermally insulated container with a known heat capacity supplied with a thermometer
  – the system is placed in the calorimeter which serves as its surroundings
  – the heat transfer is estimated from the temperature change of the calorimeter contents
  – the system can be a chemical reaction
- Types of calorimeters
  – constant pressure calorimeters ($q_p = \Delta H$)
  – constant volume calorimeters ($q_v = \Delta E$)

- The heat released by the system is absorbed by the surroundings

$$q_{sys} = -q_{surr}$$
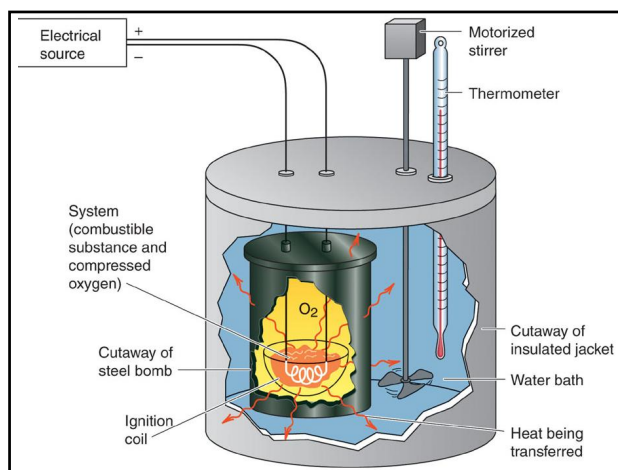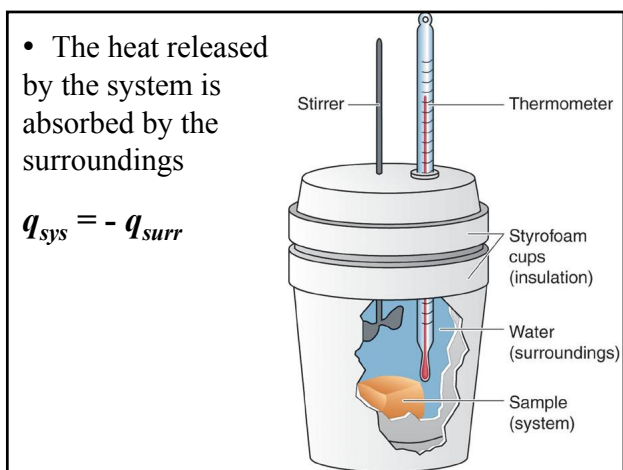
Example: **27 g** of brass at **105ºC** are placed in a coffee-cup calorimeter filled with **100 g** of water at **20ºC**. The water temperature increases to **22ºC**. Calculate the specific heat capacity of brass. (c_{water} = **4.18 J/g·ºC**)

$$q_{water} = -q_{brass} \quad \Rightarrow \quad (mc\Delta T)_w = -(mc\Delta T)_b$$

$$(c)_b = -\frac{(mc\Delta T)_w}{(m\Delta T)_b} = -\frac{100\ g \times 4.18\dfrac{J}{g\cdot ºC}\times(22-20)ºC}{27\ g\times(22-105)ºC}$$

$$= -\frac{100\times 4.18\times 2}{27\times(-83)}\ \frac{J}{g\cdot ºC} = 0.37\ \frac{J}{g\cdot ºC}$$

• Specific heats of dilute aqueous solutions are taken to be the same as that of water.

Example: A reaction between **50 g** of dilute HCl and **50 g** of dilute NaOH takes place in a coffee-cup calorimeter. The temperature rises by **2.1ºC**. What is the heat of the reaction.

$c \approx c_{water}$ = **4.18 J/g·ºC**

m = **50 g + 50 g = 100 g** ΔT = **+2.1ºC**

q_{sys} = - q_{surr} = - $mc\Delta T$

= **-100 g×4.18 J/g·ºC×2.1ºC = -8.8×10² J**

= **-0.88 kJ**   → $q_p = \Delta H$ = **-0.88 kJ**

Example:

A sample of **1.82 g** sugar is burned in a bomb calorimeter with heat capacity **9.20 kJ/K**. The temperature rises by **3.2ºC**. What is the heat of the reaction per gram of sugar.
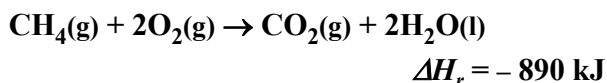
q_{sys} = - q_{surr} = - *(Heat capacity)*×ΔT

= **-9.20 kJ/ºC×3.2ºC = -29 kJ**

$q_v = \Delta E$ = **-29 kJ**

Heat per gram = -29 kJ/1.82 g = -16 kJ/g

6.4 Reaction Enthalpy and Stoichiometry

• **Thermochemical equation** – the chemical equation with physical states and the reaction enthalpy (heat of reaction) → ΔH_r
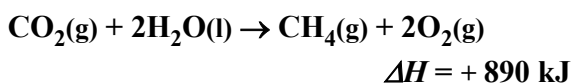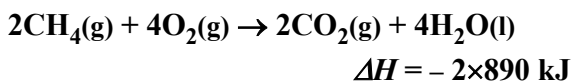
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$
$$\Delta H_r = -\ 890\ kJ$$

    ΔH_r **is for 1 mol CH_4 and 2 mol of O_2**

• The value of ΔH_r depends on the way the chemical equation is written (stoichiometric coefficients)


• Properties of thermochemical equations
  – multiplying an equation by a number multiplies the ΔH_r value by the same number
  – reversing the direction of a reaction changes the sign of the ΔH_r value

$$2CH_4(g) + 4O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$$
$$\Delta H = -\ 2\times 890\ kJ$$
$$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$$
$$\Delta H = +\ 890\ kJ$$

Example: When **2.31 g** of solid **P** reacts with gaseous **Cl_2** to form liquid **PCl_3** in a constant pressure calorimeter **23.9 kJ** of heat are released to the surroundings. Write the thermochemical equation.
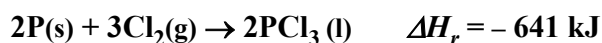
P = **constant**

$\Rightarrow \Delta H = q_p$ = **– 23.9 kJ**   **(for 2.31 g P)**

Chem. Eq: $2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(l)$
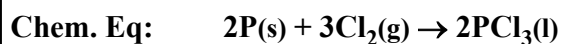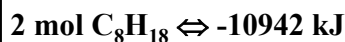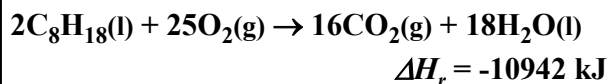
$\Rightarrow$ **need ΔH_r for 2 mol P**

$$2.31 \text{ g P} \times \left(\frac{1 \text{ mol P}}{30.97 \text{ g P}} \right) = 7.46 \times 10^{-2} \text{ mol P}$$

$$\Delta H_r = \frac{-23.9 \text{ kJ}}{7.46 \times 10^{-2} \text{mol P}} \times 2 \text{ mol P} = -641 \text{ kJ}$$

$$2P(s) + 3Cl_2(g) \rightarrow 2PCl_3 \text{ (l)} \qquad \Delta H_r = -641 \text{ kJ}$$

- The reaction enthalpy (ΔH_r) is treated stoichiometrically as a product of the reaction

  Example: Calculate the enthalpy change for the combustion of **15 g** of octane by the reaction:

$$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$$
$$\Delta H_r = -10942 \text{ kJ}$$

$$2 \text{ mol } C_8H_{18} \Leftrightarrow -10942 \text{ kJ}$$

$$15.0 \text{ g } C_8H_{18} \left(\frac{1 \text{ mol } C_8H_{18}}{114 \text{ g } C_8H_{18}} \right) \left(\frac{-10942 \text{ kJ}}{2 \text{ mol } C_8H_{18}} \right) = -718 \text{ kJ}$$

6.5 Hess's Law

- The enthalpy is a state function – ΔH is independent of the path of the process
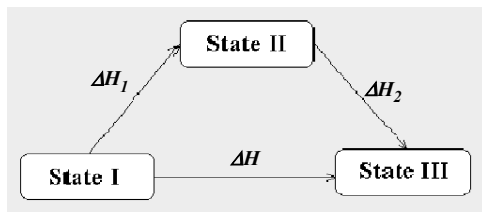
$$\Delta H = \Delta H_1 + \Delta H_2$$

- **Hess's law** – the reaction enthalpy of an overall process is the sum of the reaction enthalpies of the individual steps into which the process can be divided
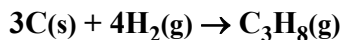
  ⇒The addition of two or more thermochemical equations results in an equation with a ΔH value equal to the sum of the ΔH values of the added equations

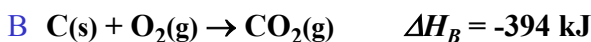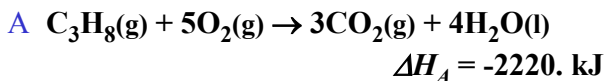 ⇒Multiplying an equation by a factor multiplies the ΔH value by the same factor

  ⇒Reversing the direction of a reaction changes the sign of the ΔH value
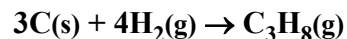

Example:

Calculate ΔH for the reaction

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

given the following:

A $\quad C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$
$$\Delta H_A = -2220. \text{ kJ}$$

B $\quad C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_B = -394 \text{ kJ}$

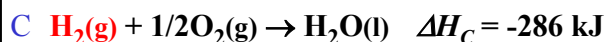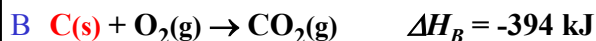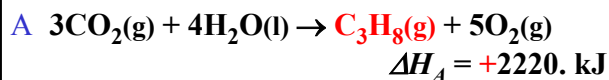C $\quad H_2(g) + 1/2O_2(g) \rightarrow H_2O(l) \quad \Delta H_C = -286 \text{ kJ}$

Procedure: 1) Rewrite the given equations by placing the reactants and products from the overall equation on the left and right side of the given equations, respectively (if necessary, reverse the direction of the reactions)
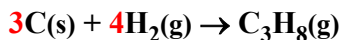
$$3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$$

⇒**reverse direction of eq. A (change sign of ΔH_1)**

A $\quad 3CO_2(g) + 4H_2O(l) \rightarrow C_3H_8(g) + 5O_2(g)$
$$\Delta H_A = +2220. \text{ kJ}$$

B $\quad C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_B = -394 \text{ kJ}$

C $\quad H_2(g) + 1/2O_2(g) \rightarrow H_2O(l) \quad \Delta H_C = -286 \text{ kJ}$

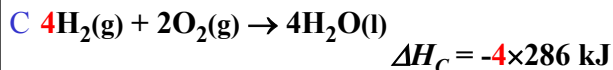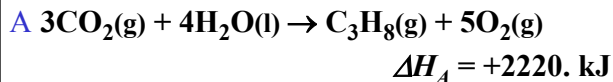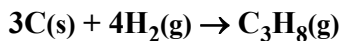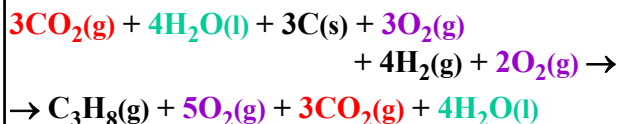**2)** Multiply the given equations by factors in order to match the stoichiometric coefficients of the reactants and products in the overall equation

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

⇒multiply eq. **B** by 3 and eq. **C** by 4 (multiply ΔH by 3 and 4, respectively)

A $3CO_2(g) + 4H_2O(l) \rightarrow C_3H_8(g) + 5O_2(g)$
$$\Delta H_A = +2220. \text{ kJ}$$

B $3C(s) + 3O_2(g) \rightarrow 3CO_2(g)$ $\Delta H_B = -3 \times 394$ kJ

C $4H_2(g) + 2O_2(g) \rightarrow 4H_2O(l)$
$$\Delta H_C = -4 \times 286 \text{ kJ}$$

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3) Add the sequence of equations and cancel the the species appearing on both sides of the resulting equation

$3CO_2(g) + 4H_2O(l) + 3C(s) + 3O_2(g)$
$\qquad\qquad\qquad\qquad + 4H_2(g) + 2O_2(g) \rightarrow$
$\rightarrow C_3H_8(g) + 5O_2(g) + 3CO_2(g) + 4H_2O(l)$

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

4) Add the resulting reaction enthalpies to obtain the overall reaction enthalpy

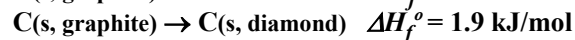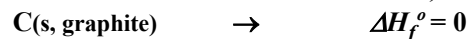$\Delta H_r = +2220. + (-3 \times 394) + (-4 \times 286) = -106$ kJ

$3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$ $\qquad \Delta H_r = -106$ kJ
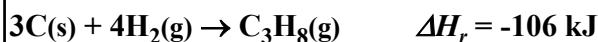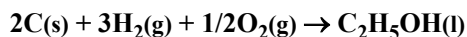

6.6 Standard Reaction Enthalpies

- ΔH_r depends on the physical states of reactants an products, **P** and **T**
- **Standard state** – the state of a pure substance in its most stable form at **1 atm** and a given temperature (usually **298 K**). For substances in solutions, the standard state is at concentrations **1 mol/L**
- **Standard reaction enthalpy** (ΔH_r^o) – ΔH_r for a reaction in which all reactants and products are in their standard states

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- **Standard enthalpy of formation** (ΔH_f^o) – the standard enthalpy change for the formation of **1 mol** of a substance from its elements in their most stable form (Appendix B)
  - For elements in their standard states, $\Delta H_f^o = 0$
  C(s, graphite) $\rightarrow$ $\Delta H_f^o = 0$
  C(s, graphite) $\rightarrow$ **C(s, diamond)** $\Delta H_f^o = 1.9$ kJ/mol
  - For compounds, ΔH_f^o can be positive or negative

  $2C(s) + 3H_2(g) + 1/2 O_2(g) \rightarrow C_2H_5OH(l)$
  $\qquad \Delta H_f^o(C_2H_5OH, l) = -277.7$ kJ/mol C_2H_5OH
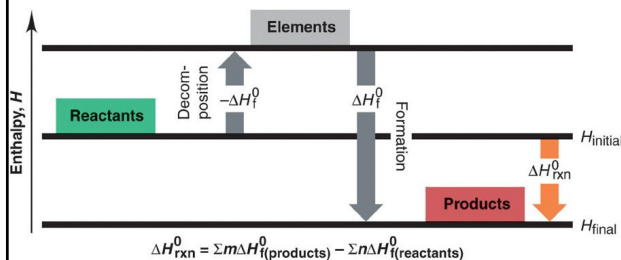 - Most compounds have $\Delta H_f^o < 0$ – such compounds are more stable than their elements

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$$\Delta H_r^o = H_{final}^o - H_{initial}^o$$
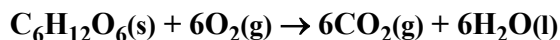$$\Delta H_r^o = \Sigma m \Delta H_f^o(\text{products}) - \Sigma n \Delta H_f^o(\text{reactants})$$
(**n, m** - stoichiometric coefficients of reactants or products)
$\rightarrow$ Follows from Hess's law

Example: Calculate the standard enthalpy of combustion of glucose, $C_6H_{12}O_6$, using ΔH_f^o data from Appendix B.

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

$\Delta H_r^o = \Sigma n \Delta H_f^o(\text{products}) - \Sigma n \Delta H_f^o(\text{reactants})$

$\Delta H_r^o = [6 \times \Delta H_f^o(CO_2(g)) + 6 \times \Delta H_f^o(H_2O(l))] -$
$\qquad\qquad - [1 \times \Delta H_f^o(C_6H_{12}O_6(s)) + 6 \times \Delta H_f^o(O_2(g))]$

$= [6 \times (-393.5) + 6 \times (-285.8)] - [1 \times (-1273) + 6 \times 0]$

$= -2803$ kJ

$\Delta H_c^o = -2803$ kJ/1 mol $C_6H_{12}O_6 = -2803$ kJ/mol