Energy, Enthalpy, and Thermochemistry

Lecture 6

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The Nature of Energy

- Definition of Energy
  - The capacity to do work or to produce heat
- The law of conservation of energy:
  - Energy can be converted from one form to another but can be neither created nor destroyed.
- Energy classification:
  - Potential energy
  - Kinetic energy

Potential Energy & Kinetic Energy

- Potential Energy:
  - Energy due to position or composition
    - Water behind a dam has potential energy
    - The energy released when gasoline is burned results from differences in the attractive forces between nuclei and electrons in the reactants and products.
- Kinetic energy:
  - Due to the motion of the object and depends on the mass of the object (m) and its velocity (v):

$$\boxed{KE = \frac{1}{2}mv^2}$$

Energy Transfer through…

- Work
  - Defined as a force acting over a distance
- Heat
  - Involves the transfer of energy between two objects due to a temperature difference.
  - NOT a substance contained in an object.
  - Heat and temperature are decidedly different.
  - Temperature is a property that reflects the random motion of the particles in a particular substance. The temperature of a monatomic ideal gas is an index of the average random translational energy of the gas.

A State Function (Property)

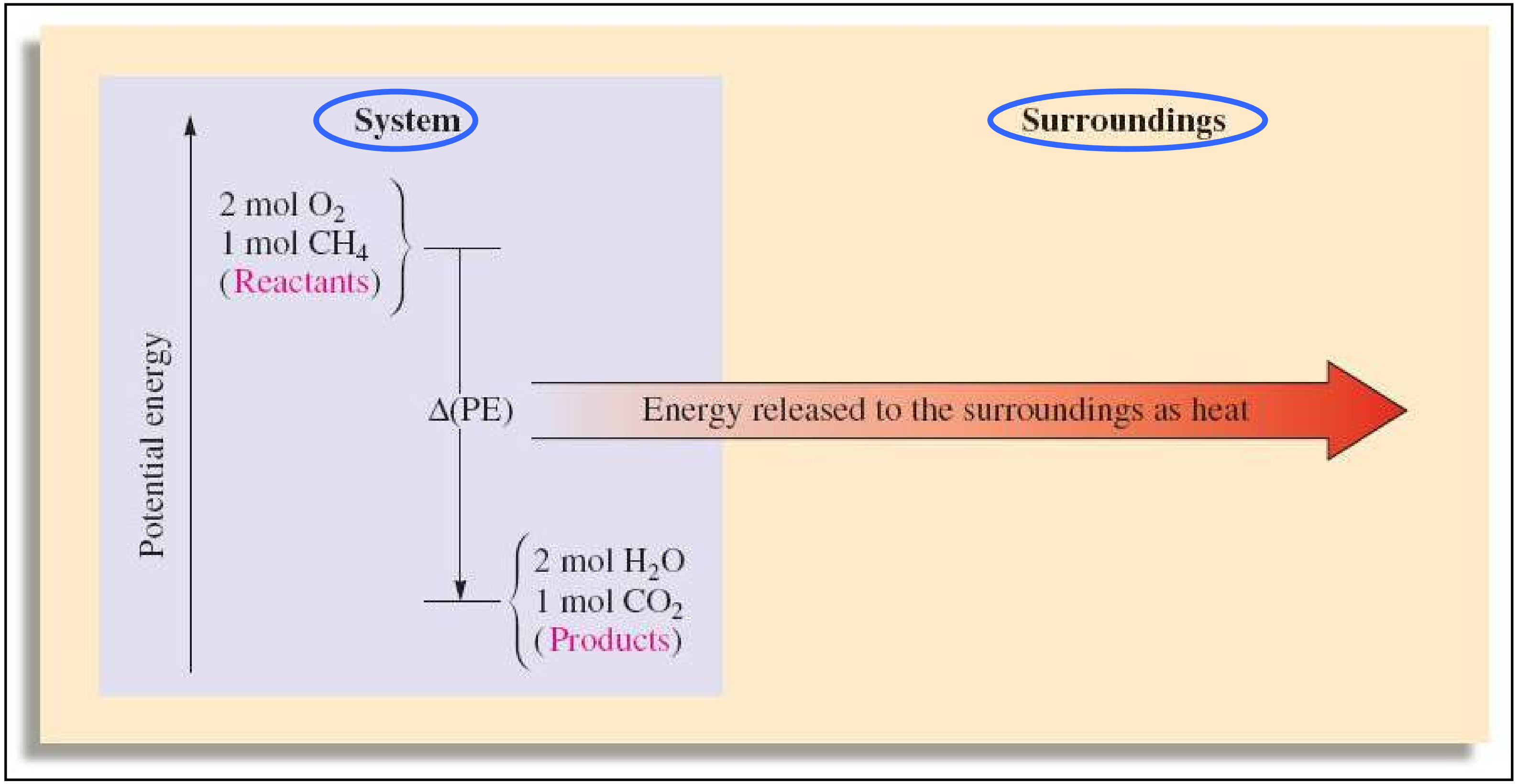
- refers to a property of the system that depends only on its present state.
- does not depend in any way on the system’s past (or future).
- the value of a state function does not depend on how the system arrived at the present state
- Of the functions considered in our present example, energy is a state function, but work and heat are not state functions.

Chemical Energy

- Exothermic reaction
  - Exo- is a prefix meaning “out of”
  - Energy flows out of the system.
- Endothermic reaction
  - Reactions that absorb energy from the surroundings.
  - When the heat flow is into a system, the process is endothermic.
- Depends on the difference in potential energy between the products and the reactants.

Exothermic reaction

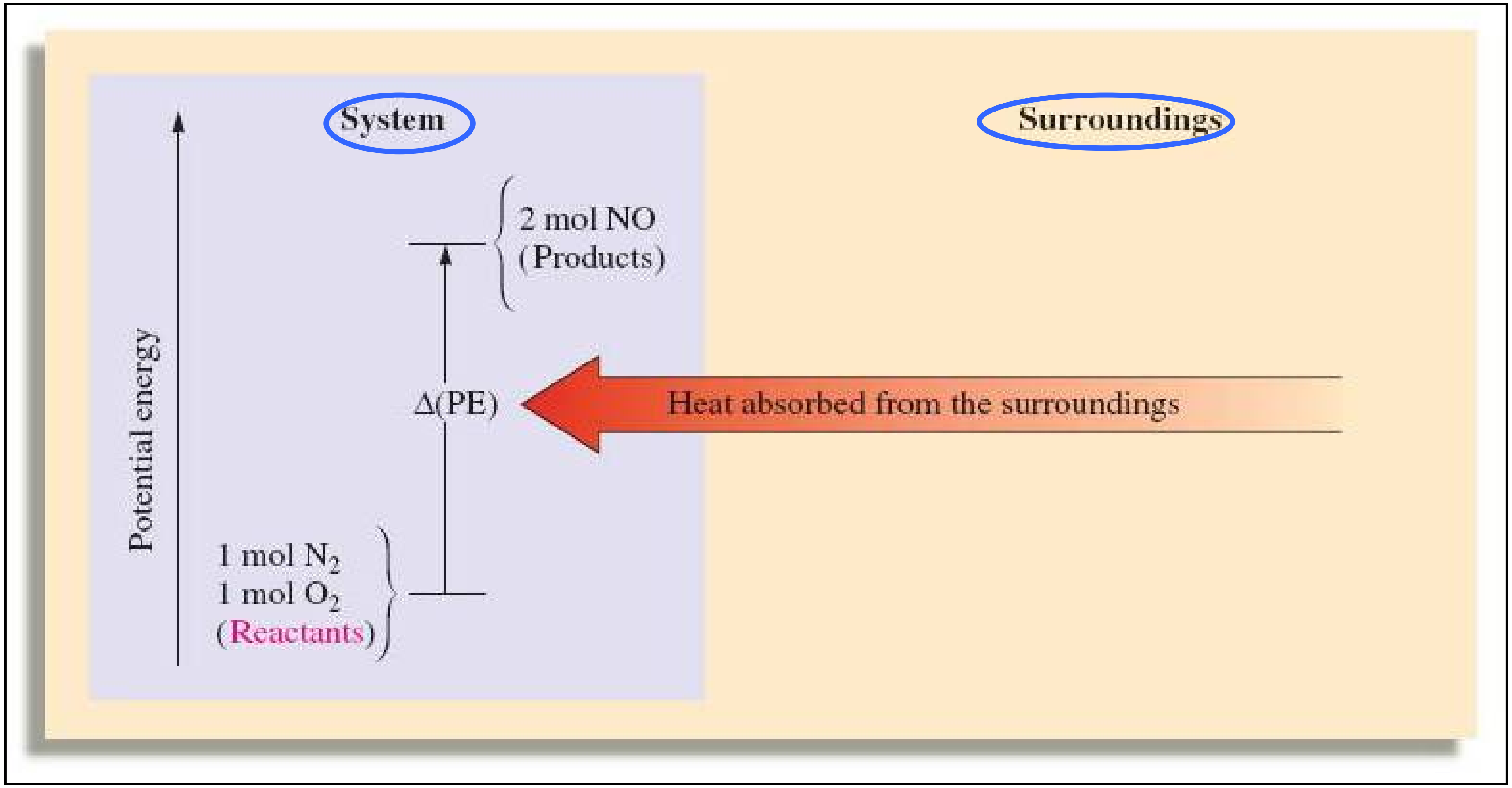
- Ex: $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + \text{energy (heat)}$



In any exothermic reaction, the potential energy stored in the chemical bonds is being converted to the thermal energy (random kinetic energy) via heat.

Endothermic reaction

- Ex: $N_2(g) + O_2(g) + \text{energy (heat)} \longrightarrow 2NO(g)$



Chemical energy △(PE)

- Represents
  - – the change in potential energy stored in the bonds of the products as compared with the bonds of the reactants
  - – the difference between the energy required to break the bonds in the reactants and the energy released when the bonds in the products are formed.

△(PE)

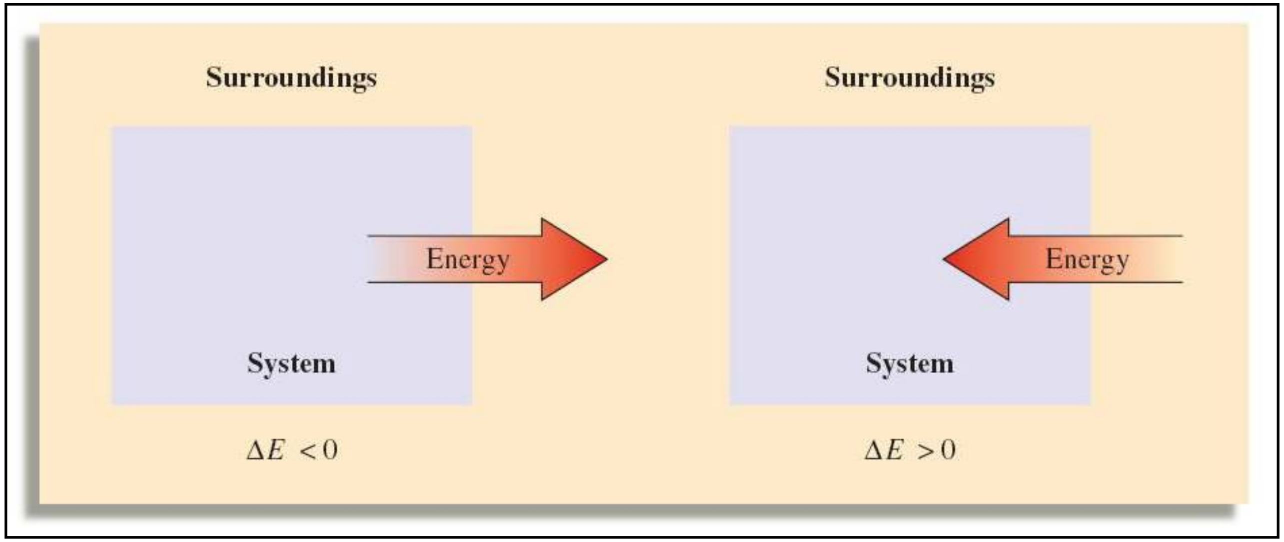
- In an exothermic process
  - the bonds in the products are stronger (on average) than those of the reactants.
  - i.e., more energy is released in forming the new bonds in the products than is consumed in breaking the bonds in the reactants.
- In an endothermic process
  - The products have higher potential energy (weaker bonds on average) than the reactants.

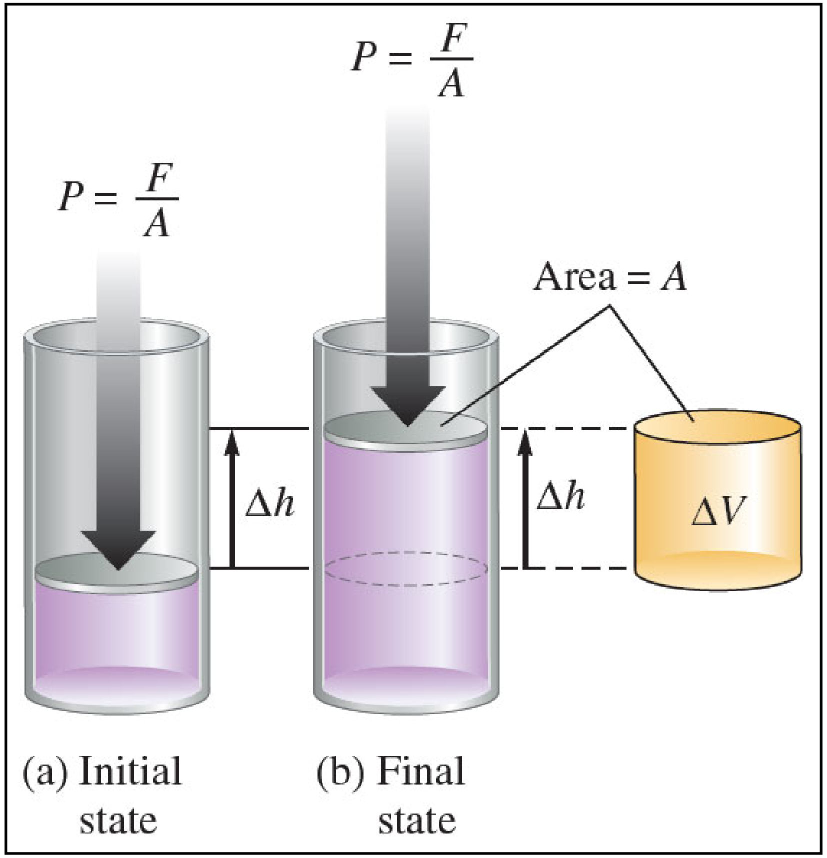
Thermodynamics

- The study of energy and its interconversions
- The first law of thermodynamics:
  - The energy of the universe is constant
  - The internal energy of a system can be changed by a flow of work, heat, or both:

$$\boxed{\Delta E = q + w}$$

    - Where the internal energy (E) of a system can be defined most precisely as the sum of the kinetic and potential energies of all of the “particles” in the system
    - The sign reflects the system’s point of view.





$$\boxed{\Delta E = q + w}$$

$$\boxed{w = -P\Delta V}$$

- The work accompanying a change in volume of a gas is often called “PV work”.
- P in PΔV always refers to the external pressure

$$|\text{Work}| = |F \times \Delta h| = |P \times A \times \Delta h|$$

Example 9.1

- A balloon is inflated to its full extent by heating the air inside it. In the final stages of this process the volume of the balloon changes from 4.00 X 10^6 L to 4.50 X 10^6 L by addition of 1.3 X 10^8 J of energy as heat. Assuming the balloon expands against a constant pressure of 1.0 atm, calculate ΔE for the process.

Solution:

$$\Delta E = q + w$$

$$q = +1.3 \times 10^8 \text{ J}$$

$$w = -P\Delta V$$

$$\begin{aligned}\Delta V &= V_{\text{final}} - V_{\text{initial}} \\ &= 4.50 \times 10^6 \text{ L} - 4.00 \times 10^6 \text{ L} = 0.50 \times 10^6 \text{ L} \\ &= 5.0 \times 10^5 \text{ L}\end{aligned}$$

P = 1.0 atm (the external pressure)

$$w = -5.0 \times 10^5 \text{ L atm} \times \frac{101.3 \text{ J}}{\text{L atm}} = -5.1 \times 10^7 \text{ J}$$

$$\Delta E = q + w = (+1.3 \times 10^8 \text{ J}) + (-5.1 \times 10^7 \text{ J}) = 8 \times 10^7 \text{ J}$$

Enthalpy

- Definition $\boxed{H = E + PV}$
  - – Since internal energy, pressure and volume are all state functions, enthalpy is also a state function.
- ΔH = *q* at constant pressure, where only “PV” work is allowed:

$$\boxed{\Delta E = q_p + w} \longrightarrow \boxed{q_p = \Delta E + P\Delta V}$$

$$\boxed{H = E + PV} \rightarrow \boxed{\Delta H = \Delta E + \Delta(PV)} \rightarrow \boxed{\Delta H = \Delta E + P\Delta V}$$

$$\Rightarrow \boxed{\Delta H = q_p}$$

Change in enthalpy, $\triangle$H

- At constant pressure (where only PV work is allowed) the change in enthalpy ($\triangle$H) of the system is equal to the energy flow as heat.
- For reactions studied at constant pressure:
  - The terms heat of reaction and change in enthalpy are used interchangeably.

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

  - At constant pressure exothermic reactions: $\triangle H < 0$
  - At constant pressure endothermic reactions: $\triangle H > 0$

Thermodynamics of Ideal Gases

- Assuming an ideal gas has no internal structure (i.e., monatomic):
  - The average, random, translational energy for 1 mole of gas at a given temperature T:

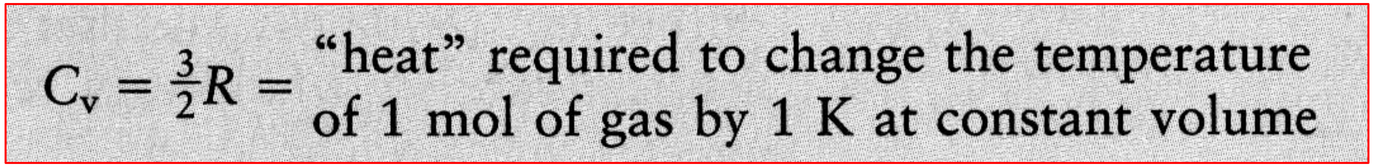
$$\boxed{(KE)_{avg} = \frac{3}{2}RT}$$

  - Hence, the energy ("heat") required to change the energy of 1 mole of an ideal gas by ΔT is,

$$\boxed{(KE)_{avg} = \frac{3}{2}R\Delta T}$$

Molar Heat Capacity of a Substance

- Defined as the energy required to raise the temperature of 1 mole of that substance by 1 K.
- Heating @ constant volume (i.e., rigid container)
  - The energy that flows into the gas is used to increase the translational energy of the gas molecules.



$C_v = \frac{3}{2}R =$ "heat" required to change the temperature of 1 mol of gas by 1 K at constant volume

Molar Heat Capacity of a Substance

- Heating @ constant pressure
  - When an ideal gas is heated at constant pressure, its volume increases and PV work occurs.
  - Energy is supplied to both the translational energy of the gas and to provide the work the gas does as it expands

Energy required = "heat" = energy needed to change the translational energy + energy needed to do the *PV* work

= 3/2 R

$$P\Delta V = nR\Delta T = R\Delta T$$

per mole

$$\Delta T = 1$$

$$P\Delta V = R$$

Heat required to increase the temperature of 1 mol of gas by 1 K (constant *P*) $= \frac{3}{2}R + R = \frac{5}{2}R$

$$C_P = C_V + R = \frac{5}{2}R$$

Heating a Polyatomic Gas

- An ideal gas with monatomic molecule structure
  - “Particles” that have no structure, $C_v = 3/2\ R$
- An ideal gas with polyatomic molecule structure
  - Polyatomic molecules absorb energy to excite rotational and vibrational motions in addition to translational motions (Note: any energy absorbed to increase the vibrational and rotational energies does not contribute directly to the translational kinetic energy/temperature.)
  - $C_v >> 3/2\ R$
  - Still, $C_P = C_V + R$

Molar Heat Capacities for Real Gases

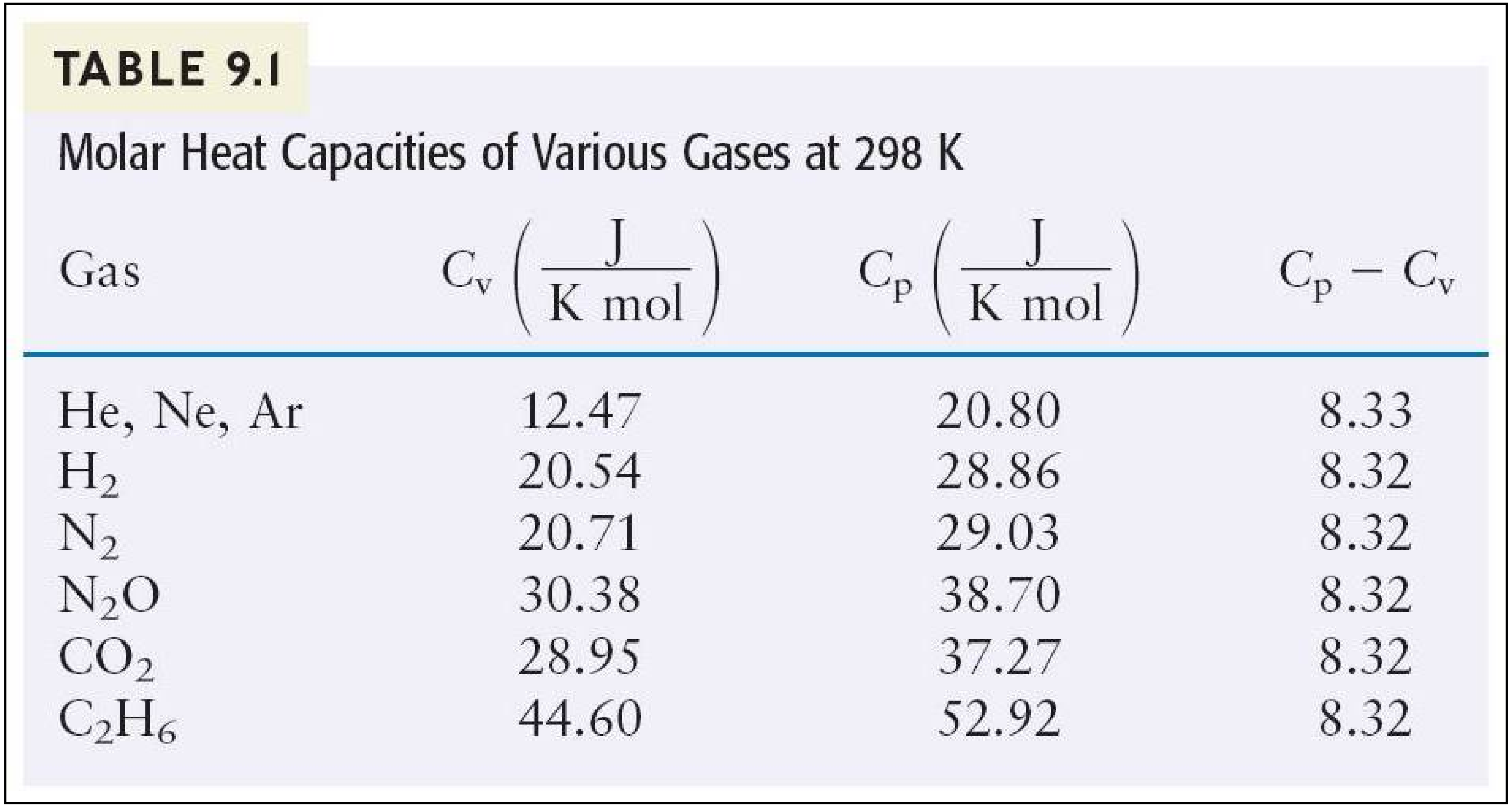


TABLE 9.1

Molar Heat Capacities of Various Gases at 298 K

Gas	$C_v \left(\frac{J}{K\ mol}\right)$	$C_p \left(\frac{J}{K\ mol}\right)$	$C_p - C_v$
He, Ne, Ar	12.47	20.80	8.33
H_2	20.54	28.86	8.32
N_2	20.71	29.03	8.32
N_2O	30.38	38.70	8.32
CO_2	28.95	37.27	8.32
C_2H_6	44.60	52.92	8.32

Heating a Gas: Energy Change

- The energy of an monatomic ideal gas can be changed only by changing the temperature:

$$\Delta E = \tfrac{3}{2}R\Delta T \qquad \text{(per mole)}$$

OR

$$\Delta E = C_v\Delta T \qquad \text{(per mole)}$$

$$\Delta E = nC_v\Delta T \qquad (n \text{ moles})$$

When a gas is heated at constant volume, all the input energy (heat) goes towards increasing E (no heat is needed to do work) .

When a gas is heated at constant pressure: the volume change and work occurs:

$$\begin{aligned} \text{“Heat” required} &= q_p = nC_p\Delta T \\ &= n(C_v + R)\Delta T \\ &= \underbrace{nC_v\Delta T}_{\nearrow \atop \Delta E} + \underbrace{nR\Delta T}_{\uparrow \atop P\Delta V = \text{work required}} \end{aligned}$$

$\triangle$E is nC$_v\triangle$T when an ideal gas is heated whether the process occurs at constant volume or constant pressure.

Heating a Gas: Enthalpy Change

- By definition:

$$H = E + PV$$

change in enthalpy

$$\Delta E = nC_v \Delta T$$

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

for ideal gas

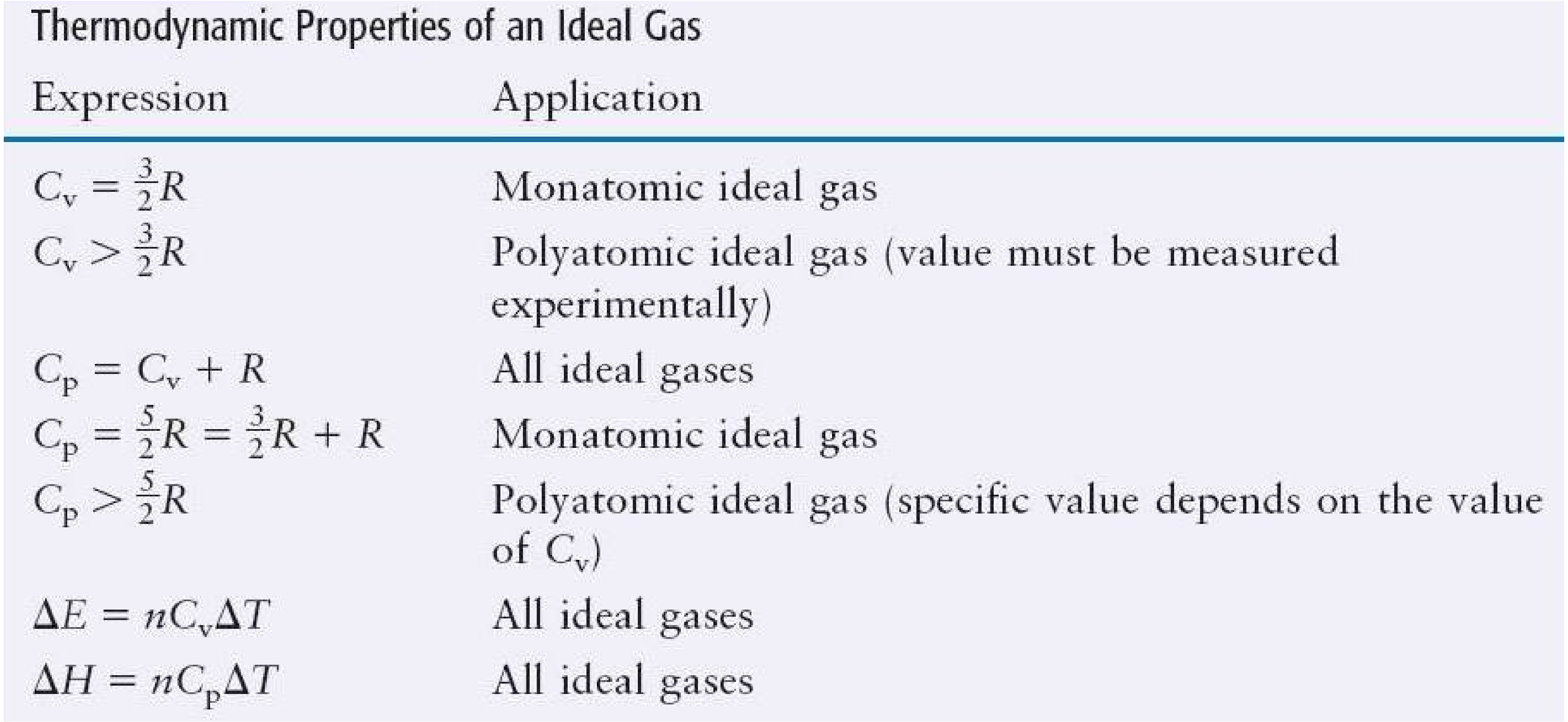
$$\Delta H = \Delta E + \Delta(nRT) = \Delta E + nR\Delta T$$

$$\Delta H = nC_v\Delta T + nR\Delta T$$

$$= n(C_v + R)\Delta T = \boxed{nC_p\Delta T}$$

$\Delta H = nC_P\Delta T$ even though we have not assumed constant pressure (or volume)

Ideal Gas Thermodynamic Properties



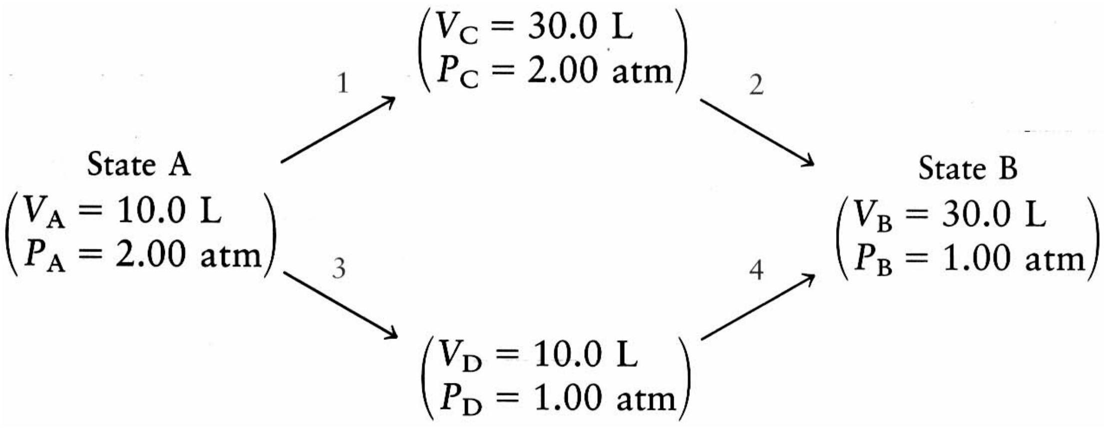
Thermodynamic Properties of an Ideal Gas

Expression	Application
$C_v = \frac{3}{2}R$	Monatomic ideal gas
$C_v > \frac{3}{2}R$	Polyatomic ideal gas (value must be measured experimentally)
$C_p = C_v + R$	All ideal gases
$C_p = \frac{5}{2}R = \frac{3}{2}R + R$	Monatomic ideal gas
$C_p > \frac{5}{2}R$	Polyatomic ideal gas (specific value depends on the value of C_v)
$\Delta E = nC_v\Delta T$	All ideal gases
$\Delta H = nC_p\Delta T$	All ideal gases

The only way to change H and E for an ideal gas is to change the temperature of the gas. Thus, for any process involving an ideal gas at constant temperature, $\Delta H = 0$ and $\Delta E = 0$.

Example 9.2

- Consider 2.00 mol of a monatomic ideal gas that is taken from state A (P_A = 2.00 atm, V_A = 10.0 L) to state B (P_B = 1.00 atm, V_B = 30.0 L) by two different pathways:



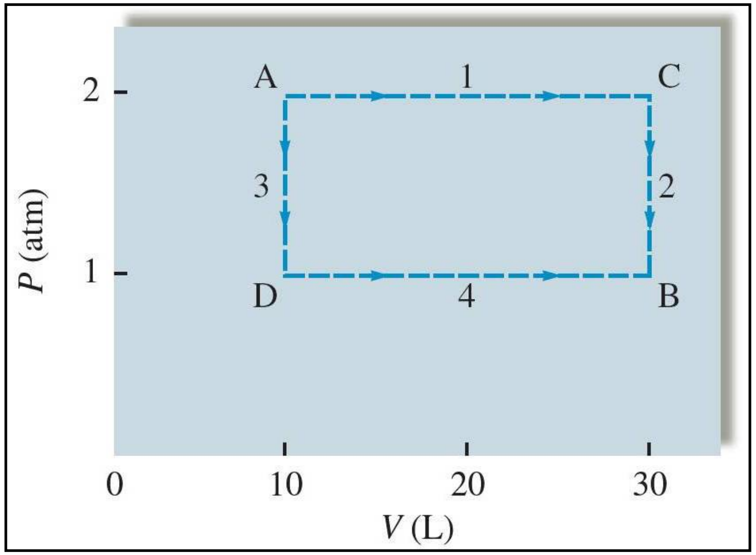
State A
$\begin{pmatrix} V_A = 10.0\ \text{L} \\ P_A = 2.00\ \text{atm} \end{pmatrix}$

1: $\begin{pmatrix} V_C = 30.0\ \text{L} \\ P_C = 2.00\ \text{atm} \end{pmatrix}$

2: State B
$\begin{pmatrix} V_B = 30.0\ \text{L} \\ P_B = 1.00\ \text{atm} \end{pmatrix}$

3: $\begin{pmatrix} V_D = 10.0\ \text{L} \\ P_D = 1.00\ \text{atm} \end{pmatrix}$

4: State B



The PV diagram

Calculate q, w △E, and △H for both pathways

- Step 1:
  - expansion from 10.0 to 30.0 L at a constant pressure of 2.00 atm
  - occur by heating the gas to produce some temperature change △T (not specified in the given data).

$$\boxed{P\Delta V = nR\Delta T} \xrightarrow[\triangle V = 30.0\text{ L} - 10.0\text{ L}]{}$$

$$\begin{aligned} P\Delta V &= (2.00\text{ atm})(20.0\text{ L}) \\ &= 4.00 \times 10^{1}\text{ L atm} \\ &= 4.05 \times 10^{3}\text{ J} \end{aligned}$$

OR

$$\Delta T = \frac{P\Delta V}{nR} = \frac{4.05 \times 10^{3}\text{ J}}{nR}$$

$$\boxed{w = -P\Delta V} \longrightarrow$$

$$\begin{aligned} w_1 &= -(2.00\text{ atm})(30.0\text{ L} - 10.0\text{ L}) \\ &= -4.00 \times 10^{1}\text{ L atm} \\ &= -4.05 \times 10^{3}\text{ J} \end{aligned}$$

$$\begin{aligned} q_1 &= q_p = nC_p\Delta T \\ &= n\left(\frac{5}{2}R\right)\left(\frac{4.05 \times 10^{3}\text{ J}}{nR}\right) = 1.01 \times 10^{4}\text{ J} \end{aligned}$$

$$\Delta E_1 = nC_v\Delta T = n\left(\frac{3}{2}R\right)\left(\frac{4.05 \times 10^{3}\text{ J}}{nR}\right) = 6.08 \times 10^{3}\text{ J}$$

$$\Delta H_1 = nC_p\Delta T = n\left(\frac{5}{2}R\right)\left(\frac{4.05 \times 10^{3}\text{ J}}{nR}\right) = 1.01 \times 10^{4}\text{ J}$$

- Step 2:
  - the gas pressure decreases from 2.00 atm to 1.00 atm at constant volume.
  - correspond to the cooling of the gas by a quantity △T

$$P\Delta V = nR\Delta T$$

$$\Delta T = \frac{\Delta P V}{nR} = \frac{(1.00\ \text{atm} - 2.00\ \text{atm})(30.0\ \text{L})}{nR}$$

$$= \frac{-30.0\ \text{L atm}}{nR} = \frac{-3.04 \times 10^{3}\ \text{J}}{nR}$$

Cooling!

Since $\Delta V = 0$; $w_2 = 0$

$$q_2 = q_v = nC_v\Delta T = n\left(\frac{3}{2}R\right)\left(\frac{-3.04 \times 10^{3}\ \text{J}}{nR}\right)$$

$$= -4.56 \times 10^{3}\ \text{J}$$

$$\Delta E_2 = nC_v\Delta T = n\left(\frac{3}{2}R\right)\left(\frac{-3.04 \times 10^{3}\ \text{J}}{nR}\right)$$

$$= -4.56 \times 10^{3}\ \text{J} = q_v$$

$$\Delta H_2 = nC_p\Delta T = n\left(\frac{5}{2}R\right)\left(\frac{-3.04 \times 10^{3}\ \text{J}}{nR}\right)$$

$$= -7.60 \times 10^{3}\ \text{J}$$

- Step 3 :

$$\Delta T = \frac{\Delta PV}{nR} = \frac{(-1.00\ \text{atm})(10.0\ \text{L})}{nR} = \frac{-10.0\ \text{L atm}}{nR}$$

$$= \frac{-1.01 \times 10^3\ \text{J}}{nR}$$

$$w_3 = 0 \qquad (\Delta V = 0)$$

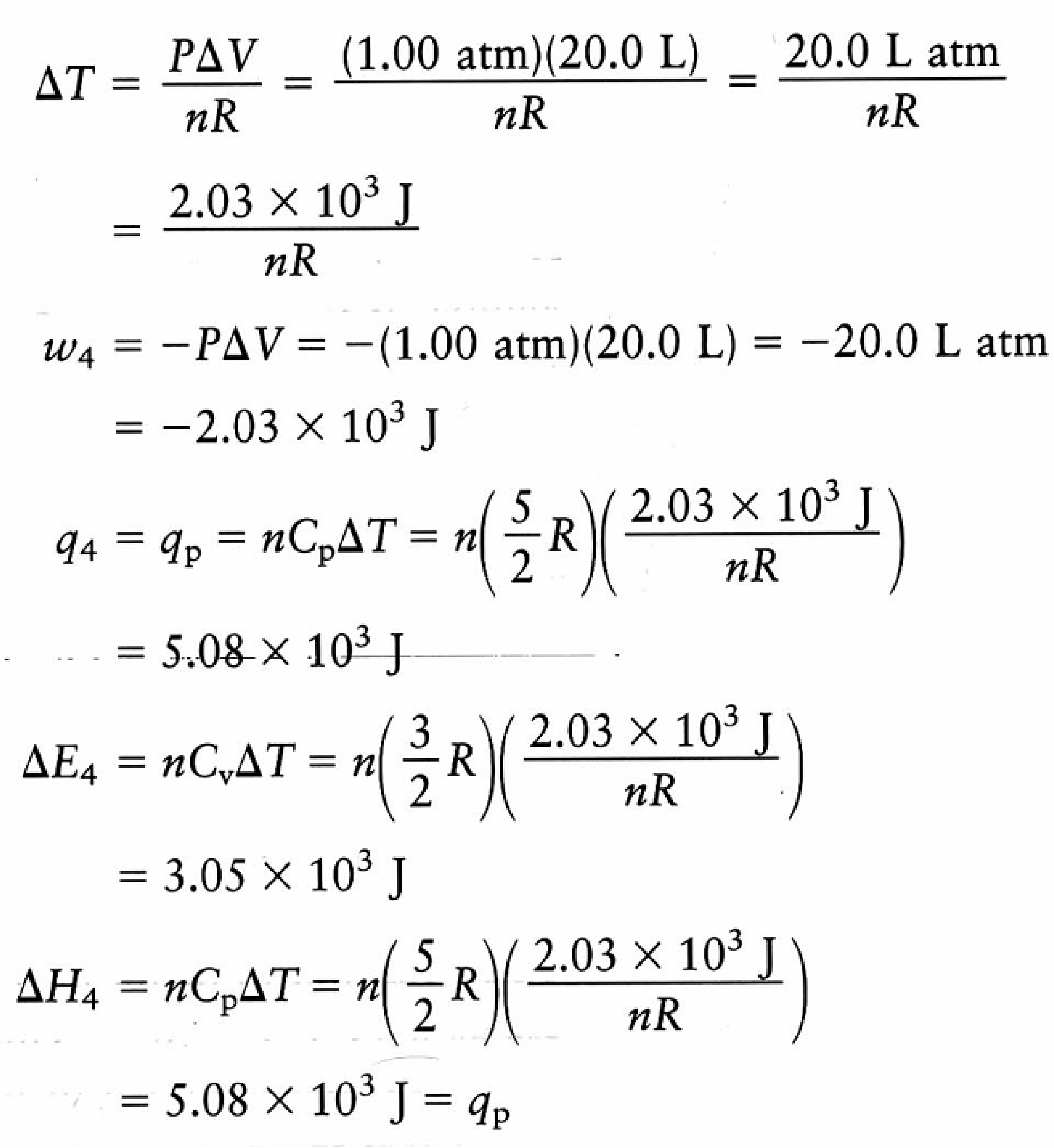
$$q_3 = q_\text{v} = n\text{C}_\text{v}\Delta T = n\left(\frac{3}{2}R\right)\left(\frac{-1.01 \times 10^3\ \text{J}}{nR}\right)$$

$$= -1.52 \times 10^3\ \text{J}$$

$$\Delta E_3 = q_\text{v} = -1.52 \times 10^3\ \text{J}$$

$$\Delta H_3 = n\text{C}_\text{p}\Delta T = n\left(\frac{5}{2}R\right)\left(\frac{-1.01 \times 10^3\ \text{J}}{nR}\right) = -2.53 \times 10^3\ \text{J}$$

- Step 4 :



$$\Delta T = \frac{P\Delta V}{nR} = \frac{(1.00\ \text{atm})(20.0\ \text{L})}{nR} = \frac{20.0\ \text{L atm}}{nR}$$

$$= \frac{2.03 \times 10^3\ \text{J}}{nR}$$

$$w_4 = -P\Delta V = -(1.00\ \text{atm})(20.0\ \text{L}) = -20.0\ \text{L atm}$$

$$= -2.03 \times 10^3\ \text{J}$$

$$q_4 = q_\text{p} = nC_\text{p}\Delta T = n\left(\frac{5}{2}R\right)\left(\frac{2.03 \times 10^3\ \text{J}}{nR}\right)$$

$$= 5.08 \times 10^3\ \text{J}$$

$$\Delta E_4 = nC_\text{v}\Delta T = n\left(\frac{3}{2}R\right)\left(\frac{2.03 \times 10^3\ \text{J}}{nR}\right)$$

$$= 3.05 \times 10^3\ \text{J}$$

$$\Delta H_4 = nC_\text{p}\Delta T = n\left(\frac{5}{2}R\right)\left(\frac{2.03 \times 10^3\ \text{J}}{nR}\right)$$

$$= 5.08 \times 10^3\ \text{J} = q_\text{p}$$

Summary

- Pathway one (steps 1 and 2):

$$\begin{aligned} q_{\text{one}} &= q_1 + q_2 = 1.01 \times 10^4\ \text{J} - 4.56 \times 10^3\ \text{J} \\ &= 5.5 \times 10^3\ \text{J} \\ w_{\text{one}} &= w_1 + w_2 = -4.05 \times 10^3\ \text{J} \\ q_{\text{one}} + w_{\text{one}} &= 1.5 \times 10^3\ \text{J} = \Delta E_{\text{one}} \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{one}} &= \Delta H_1 + \Delta H_2 \\ &= 1.01 \times 10^4\ \text{J} - 7.60 \times 10^3\ \text{J} \\ &= 2.5 \times 10^3\ \text{J} \end{aligned}$$

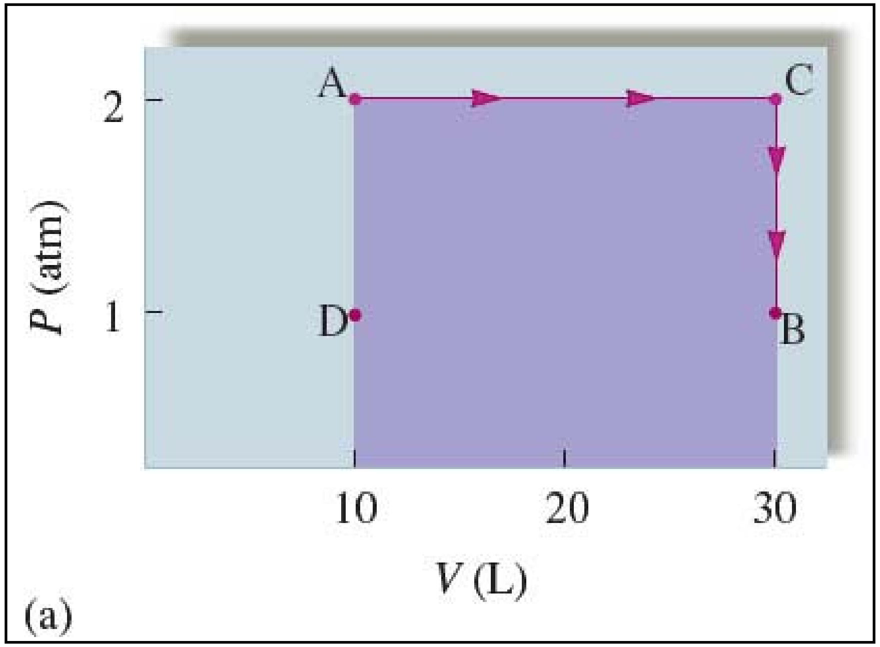
- Pathway two (steps 3 and 4):

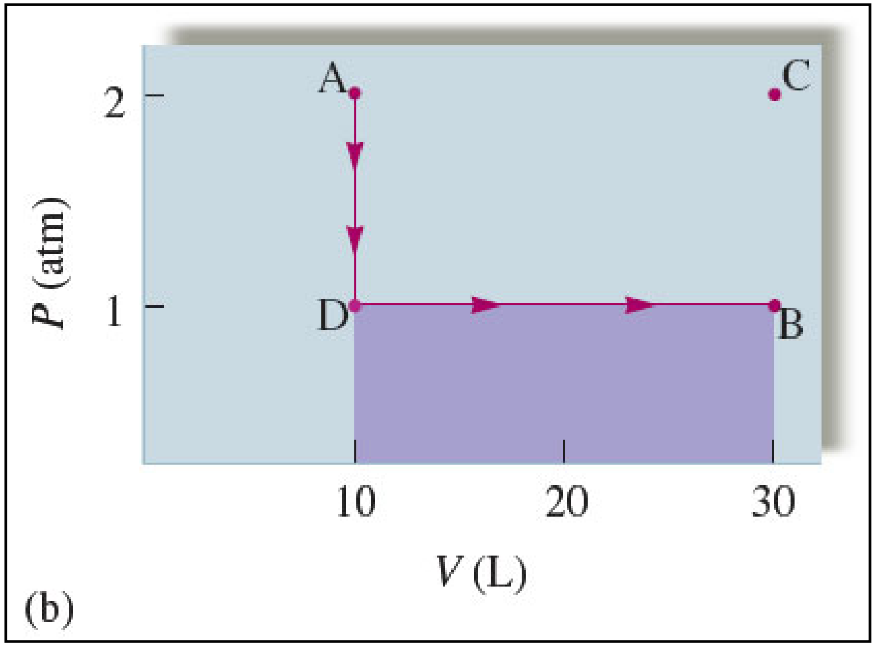
$$\begin{aligned} q_{\text{two}} &= q_3 + q_4 = -1.52 \times 10^3\ \text{J} + 5.08 \times 10^3\ \text{J} \\ &= 3.56 \times 10^3\ \text{J} \\ w_{\text{two}} &= w_3 + w_4 = -2.03 \times 10^3\ \text{J} \\ q_{\text{two}} + w_{\text{two}} &= 3.55 \times 10^3\ \text{J} - 2.03 \times 10^3\ \text{J} \\ &= 1.52 \times 10^3\ \text{J} = \Delta E_{\text{two}} \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{two}} &= \Delta H_3 + \Delta H_4 \\ &= -2.53 \times 10^3\ \text{J} + 5.08 \times 10^3\ \text{J} \\ &= 2.55 \times 10^3\ \text{J} \end{aligned}$$

Work for two different pathways

- The work and heat are different for the two pathways between states A and B
- Heat and work are both pathway-dependent.





Calorimetry

- The science of measuring heat
- Based on observing the temperature change when a body absorbs or discharges energy as heat
- Calorimeter:
  - A device used to determine the heat associated with a chemical reaction
- Heat capacity (C) of a substance:

$$\boxed{C = \frac{\text{heat absorbed}}{\text{increase in temperature}}}$$

  - the specific heat capacity:
    - per gram of substance; [J $K^{-1}g^{-1}$] or [J $^{o}C^{-1}\,g^{-1}$].
  - the molar heat capacity:
    - per gram of substance; [J $K^{-1}mol^{-1}$] or [J $^{o}C^{-1}\,mol^{-1}$].

Example 9.3

- When 1.00 L of 1.00 M $Ba(NO_3)_2$ at 25.0ºC is mixed with 1.00 L of 1.00 M Na_2SO_4 at 25ºC in a calorimeter, the white solid $BaSO_4$ forms and the temperature of the mixture increases to 28.1ºC. Assuming that the calorimeter absorbs only a negligible quantity of heat, that the specific heat capacity of the solution is 4.18 $J\,^{o}C^{-1}g^{-1}$, and that the density of the final solution is 1.0 g/mL, calculate the enthalpy change per mole of $BaSO_4$ formed.

Solution:

- The net ionic equation of the reaction

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

- Temperature increases → exothermic → ∆H is negative

Heat evolved by reaction = heat absorbed by solution

= specific heat capacity × mass of solution × increase in temperature

1.0 L of each solution is used, total solution volume is 2.0 L

$$\text{Mass of solution} = 2.00\ \text{L} \times \frac{1000\ \text{mL}}{1\ \text{L}} \times \frac{1.0\ \text{g}}{\text{mL}} = 2.0 \times 10^3\ \text{g}$$

Temperature increase = 28.1°C − 25.0°C = 3.1°C

$$q = q_p = \Delta H = -2.6 \times 10^4\ \text{J}$$

$$\text{Heat evolved} = (4.18\ \text{J °C}^{-1}\ \text{g}^{-1})(2.0 \times 10^3\ \text{g})(3.1\text{°C}) = 2.6 \times 10^4\ \text{J}$$

- 1.00 mol of solid $BaSO_4$ is formed in this experiment. Thus the enthalpy change per mole of $BaSo_4$ formed is

$$\Delta H = -2.6 \times 10^4\ J/mol = -26\ kJ/mol$$

Reactions involve volume change

- Ex: $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$
  - The volume change:

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

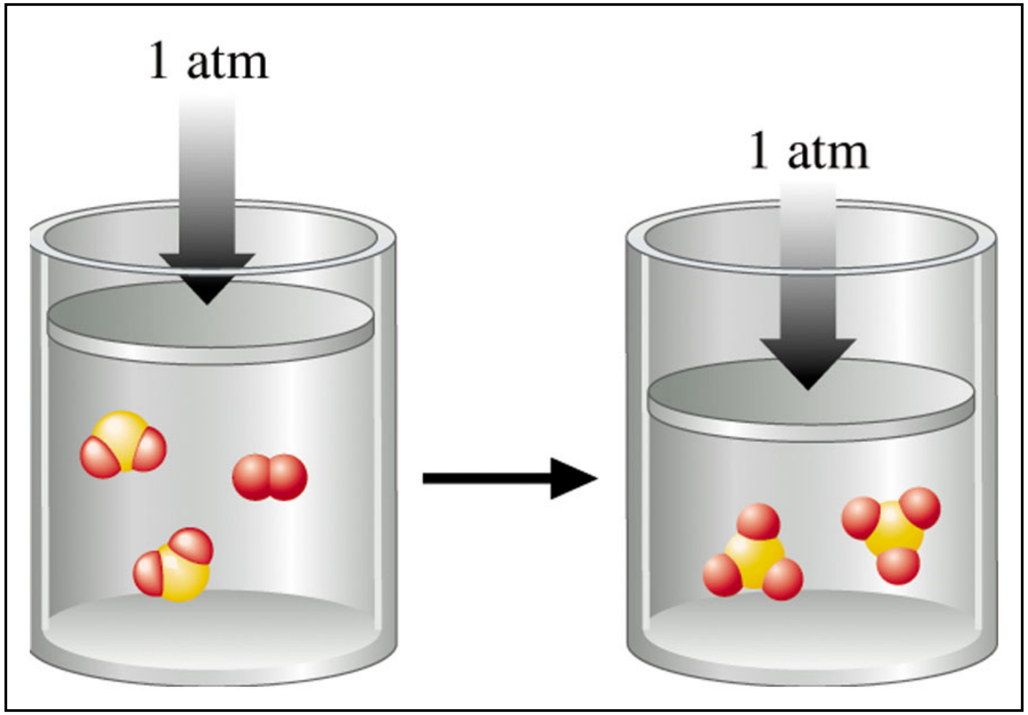
  - The work:

$$\boxed{w = -\underbrace{P\Delta V}_{\substack{\uparrow \\ \text{Negative in this case}}}}$$

  - The internal energy

$$\boxed{\Delta E = q + w}$$

$$\boxed{\Delta E = q_p + w = \Delta H + w}$$



at constant pressure

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

Example 9.4

- When 2.00 mol of SO_2 (g) reacts completely with 1.00 mol of O_2(g) to form 2.00 mol of SO_3 (g) at 25ºC and a constant pressure of 1.00 atm, 198 kJ of energy is released as heat. Calculate ΔH and ΔE for this process.

Solution:

- Constant pressure: $\boxed{\Delta H = q_P = -198 kJ}$
- The internal energy: $\boxed{\Delta E = q + w}$

$$w = -P\Delta V$$

$$\Delta V = \Delta n\left(\frac{RT}{P}\right)$$

$$\Delta n = 2\ \text{mol} - 3\ \text{mol} = -1\ \text{mol}$$

$$R = 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$T = 25°\text{C} + 273 = 298\ \text{K}$$

$$w = -(-1\ \text{mol})\left(8.3145\ \frac{\text{J}}{\text{K mol}}\right)(298\ \text{K}) = 2.48\ \text{kJ}$$

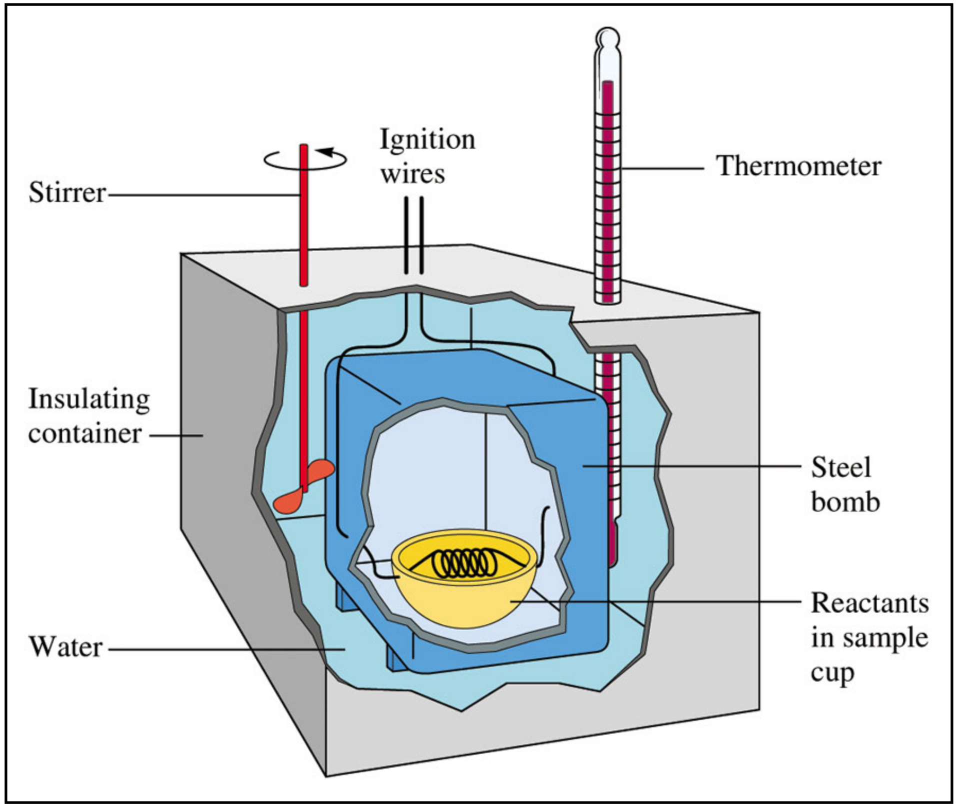
$$\boxed{\Delta E = q + w = \Delta H + w = -198\ \text{kJ} + 2.48\ \text{kJ} = -196\ \text{kJ}}$$

Calorimetry experiments @ constant volume

- constant volume → no volume change → no work

$$\Delta E = q + w = q = q_{\mathrm{v}} \qquad \text{(constant volume)}$$

- Bomb calorimeter:
  - To study the energy change in reactions under conditions of constant volume
  - Weighed reactants are placed inside the bomb and ignited.
  - The energy changed is determined by measuring the increase in the temperature of the water and other parts.



Example 9.5

- It has been suggested that hydrogen gas obtained from the decomposition of water might be a substitute for natural gas (principally methane). To compare the energies of combustion of these fuels, the following experiment was carried out, using a bomb calorimeter with a heat capacity of 11.3 kJ/ºC. When a 1.50-g sample of methane gas was burned with excess oxygen in the calorimeter, the temperature increased by 7.3ºC. When a 1.15-g sample of hydrogen gas was burned with excess oxygen, the temperature increase was 14.3ºC. Calculate the energy of combustion (per gram) for hydrogen and methane.

Solution:

$$\text{Energy } \textit{released} \text{ in the combustion of 1.50 g of } CH_4 = (11.3\ \text{kJ/°C})(7.3\text{°C}) = 83\ \text{kJ}$$

$$\text{Energy released in the combustion of 1 g of } CH_4 = \frac{83\ \text{kJ}}{1.50\ \text{g}} = 55\ \text{kJ/g}$$

$$\text{Energy } \textit{released} \text{ in the combustion of 1.15 g of } H_2 = (11.3\ \text{kJ/°C})(14.3\text{°C}) = 162\ \text{kJ}$$

$$\text{Energy released in the combustion of 1 g of } H_2 = \frac{162\ \text{kJ}}{1.15\ \text{g}} = 141\ \text{kJ/g}$$

The energy released by the combustion of 1 g of hydrogen is approximately 2.5 times that for 1 g of methane

Hess’s Law

- In going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.
- Ex: the oxidation of nitrogen to produce nitrogen dioxide

$$\boxed{N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H_1 = 68\ \text{kJ}}$$

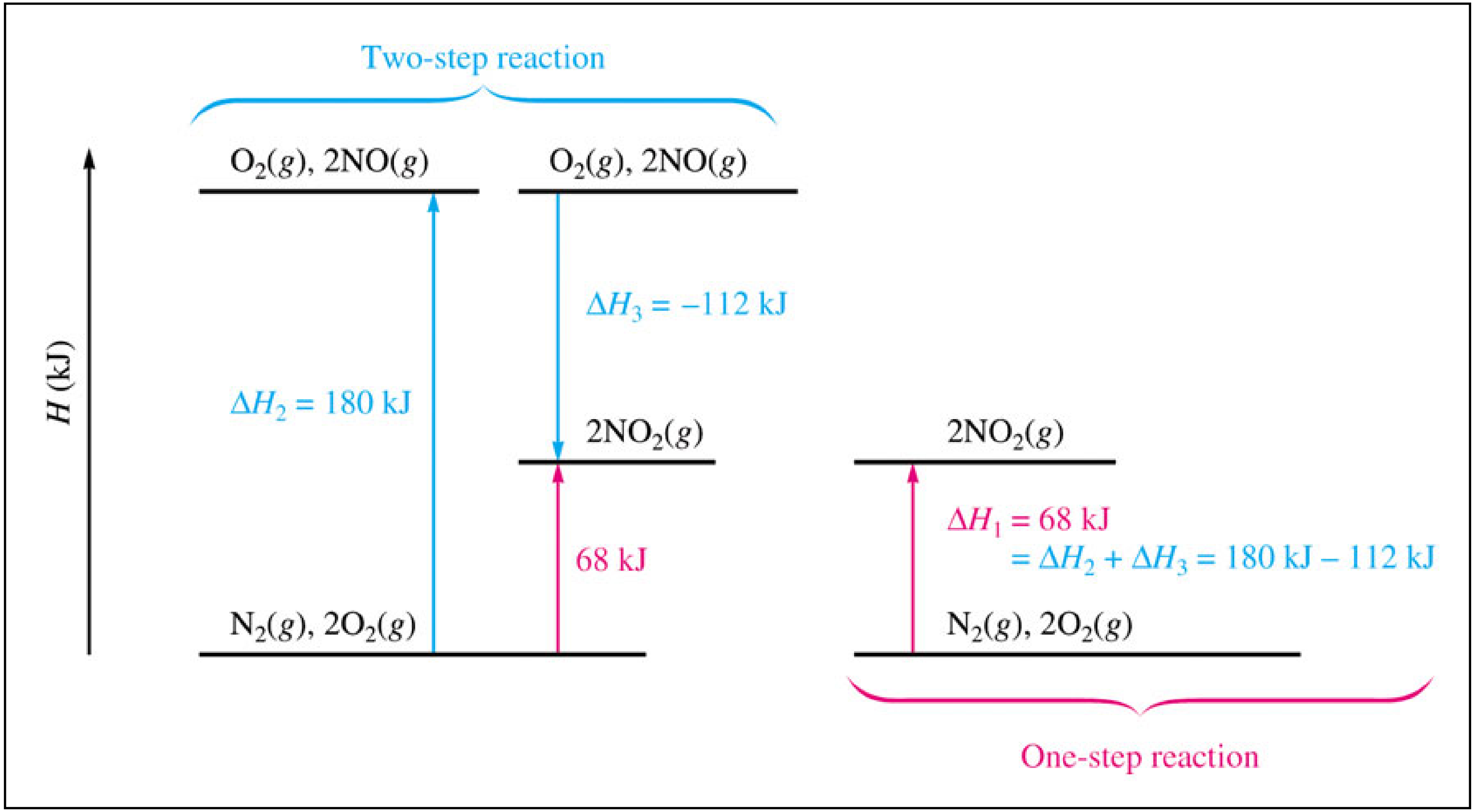
  - can be carried out in two distinct steps:

$$\begin{array}{lrcll}
 & N_2(g) + O_2(g) & \longrightarrow & 2NO(g) & \Delta H_2 = 180\ \text{kJ} \\
 & 2NO(g) + O_2(g) & \longrightarrow & 2NO_2(g) & \Delta H_3 = -112\ \text{kJ} \\
\hline
\text{Net reaction:} & N_2(g) + 2O_2(g) & \longrightarrow & 2NO_2(g) & H_2 + \Delta H_3 = 68\ \text{kJ}
\end{array}$$

  - the sum of these two steps gives the net, or overall, reaction:

$$\boxed{\Delta H_1 = \Delta H_2 + \Delta H_3 = 68\ \text{kJ}}$$

The principle of Hess's law



Characteristics of Enthalpy Changes

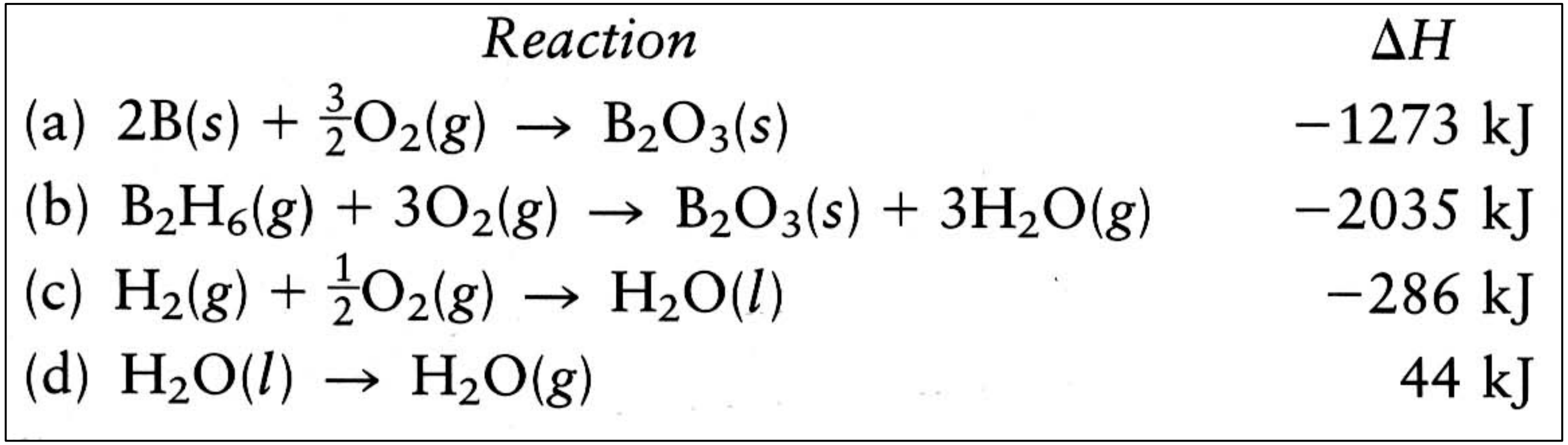
- Two characteristics of ΔH for a reaction:
  - If a reaction is reversed, the sign of ΔH is also reversed.
  - The magnitude of ΔH is directly proportional to the quantities of reactants and products in a reaction. If the coefficients in a balanced reaction are multiplied by an integer, the value of ΔH is multiplied by the same integer (i.e., an extensive property)

Example 9.6

- Diborane (B_2H_6) is a highly reactive boron hydride, which was once considered as a possible rocket fuel for the U.S. space program. Calculate ΔH for the synthesis of diborane from its elements, according to the equation

$$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g)$$

- Using the following data:



Reaction	ΔH
(a) $2B(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3(s)$	−1273 kJ
(b) $B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$	−2035 kJ
(c) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	−286 kJ
(d) $H_2O(l) \rightarrow H_2O(g)$	44 kJ

Solution:

$$\boxed{2B(s) + 3H_2(g) \longrightarrow B_2H_6(g)}$$

- This procedure can best be done by focusing on the reactants and products of the required reaction:

$$\begin{array}{llcll}
\text{(a)} & 2B(s) + \tfrac{3}{2}O_2(g) & \longrightarrow & B_2O_3(s) & \Delta H = -1273\ \text{kJ} \\
-\text{(b)} & B_2O_3(s) + 3H_2O(g) & \longrightarrow & B_2H_6(g) + 3O_2(g) & \Delta H = -(-2035\ \text{kJ}) \\
\hline
\multicolumn{2}{l}{\cancel{B_2O_3(s)} + 2B(s) + \tfrac{3}{2}O_2(g) + 3H_2O(g)} & \longrightarrow & \cancel{B_2O_3(s)} + B_2H_6(g) + 3O_2(g) & \Delta H = 762\ \text{kJ}
\end{array}$$

$$\boxed{2B(s) + 3H_2O(g) \longrightarrow B_2H_6(g) + \tfrac{3}{2}O_2(g) \qquad \Delta H = 762\ \text{kJ}}$$

Hydrogen?

$$\begin{array}{llcll}
 & 2B(s) + 3H_2O(g) & \longrightarrow & B_2H_6(g) + \tfrac{3}{2}O_2(g) & \Delta H = 762\ \text{kJ} \\
3 \times \text{(c)} & 3[H_2(g) + \tfrac{1}{2}O_2(g) & \longrightarrow & H_2O(l)] & \Delta H = 3(-286\ \text{kJ}) \\
\hline
\multicolumn{2}{l}{2B(s) + 3H_2(g) + \cancel{\tfrac{3}{2}O_2(g)} + 3H_2O(g)} & \longrightarrow & B_2H_6(g) + \cancel{\tfrac{3}{2}O_2(g)} + 3H_2O(l) & \Delta H = -96\ \text{kJ}
\end{array}$$

Water ?

$$\begin{array}{llcll}
 & 2B(s) + 3H_2(g) + 3H_2O(g) & \longrightarrow & B_2H_6(g) + 3H_2O(l) & \Delta H = -96\ \text{kJ} \\
3 \times \text{(d)} & 3[H_2O(l) & \longrightarrow & H_2O(g)] & \Delta H = 3(44\ \text{kJ}) \\
\hline
\multicolumn{2}{l}{2B(s) + 3H_2(g) + \cancel{3H_2O(g)} + \cancel{3H_2O(l)}} & \longrightarrow & B_2H_6(g) + \cancel{3H_2O(l)} + \cancel{3H_2O(g)} & \boxed{\Delta H = +36\ \text{kJ}}
\end{array}$$

Standard Enthalpies of Formation ΔH_f°

- Not all the values of Δ H for the chemical processes can be measured in a calorimeter.
  - Calculate Δ H for chemical reactions and physical changes by using standard enthalpies of formation
  - The standard enthalpy of formation (ΔH_f°) of a compound is defined as the change in enthalpy that accompanies the formation of 1 mole of a compound from its elements with all substances in their standard states.
  - The superscript zero on a thermodynamic function indicates that the corresponding process has been carried out under standard conditions.

Standard State for a substance

- A precisely defined reference state:
  - For a gas the standard state is a pressure of exactly 1 atm.
  - For a substance present in a solution, the standard state is a concentration of exactly 1 M at an applied pressure of 1 atm.
  - For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid.
  - For an element the standard state is the form in which the element exists (is most stable) under conditions of 1 atm and the temperature of interest (usually 25ºC).

**** The International Union of Pure and Applied Chemistry (IUPAC) has adopted 1 bar (100,000 Pa) as the standard pressure instead of 1 atm (101,325 Pa). Both standards are now widely used.***

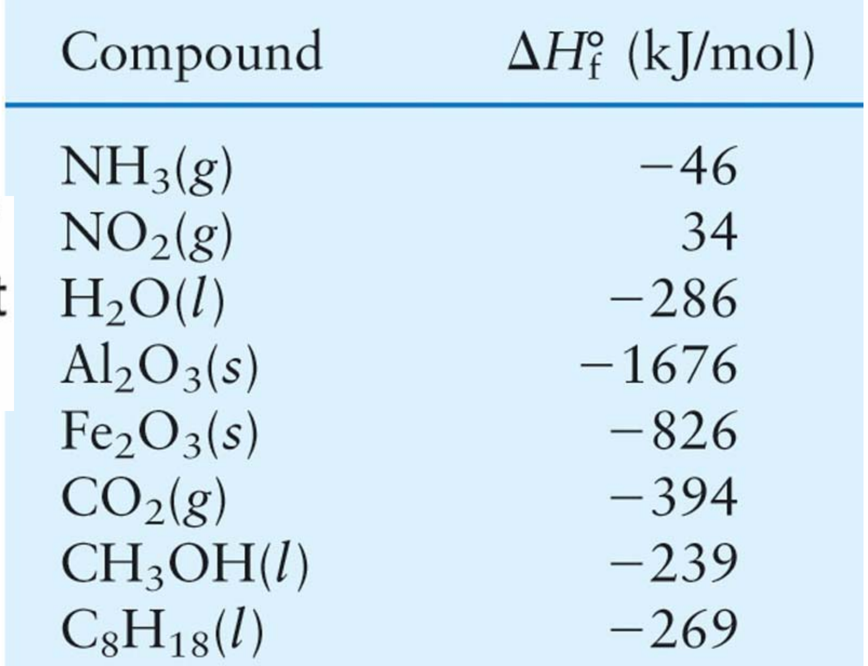
Standard Enthalpies of Formation

- Ex: $\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H_f^\circ = 34\ \text{kJ/mol}$

$$C(s) + 2H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow CH_3OH(l) \qquad \Delta H_f^\circ = -239\ \text{kJ/mol}$$

per mole of product with the product in its standard state !!

TABLE 9.4 Standard Enthalpies of Formation for Several Compounds at 25°C



Compound	ΔH_f° (kJ/mol)
$NH_3(g)$	−46
$NO_2(g)$	34
$H_2O(l)$	−286
$Al_2O_3(s)$	−1676
$Fe_2O_3(s)$	−826
$CO_2(g)$	−394
$CH_3OH(l)$	−239
$C_8H_{18}(l)$	−269

The change in enthalpy for the overall reaction

- The enthalpy change for a given reaction can be calculated by subtracting the enthalpies of formation of the reactants from the enthalpies of formation of the products:

$$\Delta H^\circ_{\text{reaction}} = \Sigma\Delta H^\circ_f\text{ (products)} - \Sigma\Delta H^\circ_f\text{ (reactants)}$$

  - Elements are not included in the calculation since elements require no change in form.
  - We have in effect defined the enthalpy of formation of an element in its standard state as zero.

Key Concepts for Doing Enthalpy Calculations

- When a reaction is reversed, the magnitude of ΔH remains the same, but the sign changes.
- When the balanced equation for a reaction is multiplied by an integer, the value of Δ H for that reaction must be multiplied by the same integer.
- The change in enthalpy for a given reaction can be calculated from the enthalpies of formation of the reactants and products:

$$\Delta H^\circ_{\text{reaction}} = \Sigma\Delta H^\circ_{\text{f}}\ (\text{products}) - \Sigma\Delta H^\circ_{\text{f}}\ (\text{reactants})$$

- Elements in their standard states are not included in the $\Delta H_{\text{reaction}}$ calculations. That is, $\Delta H_{\text{f}}^{\circ}$ for an element in its standard state is zero.

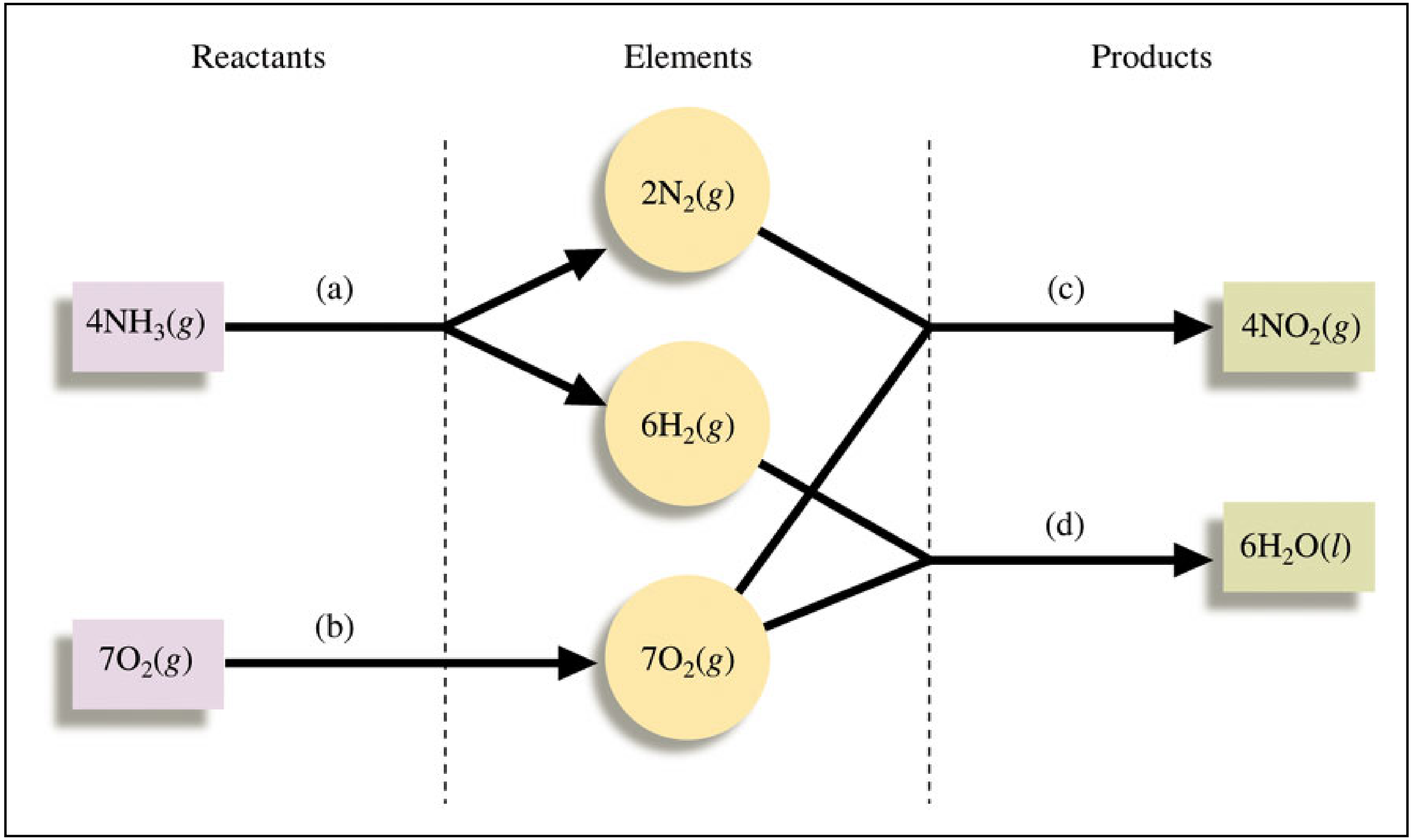
Example 9.7

- Using the standard enthalpies of formation listed in Table 9.4, calculate the standard enthalpy change for the overall reaction that occurs when ammonia is burned in air to form nitrogen dioxide and water. This is the first step in the manufacture of nitric acid.

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

Solution:

- The pathways:



$$\Delta H^\circ_{\text{reaction}} = \Delta H^\circ_{(a)} + \Delta H^\circ_{(b)} + \Delta H^\circ_{(c)} + \Delta H^\circ_{(d)}$$

$$\Delta H^\circ_{\text{reaction}} = \Sigma \Delta H^\circ_f \text{ (products)} - \Sigma \Delta H^\circ_f \text{ (reactants)}$$

Solution:

- Step (a): Decomposition of $NH_3(g)$ into elements

  $$\boxed{4NH_3(g) \longrightarrow 2N_2(g) + 6H_2(g)}$$

  - Since $\boxed{\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \longrightarrow NH_3(g) \qquad \Delta H_f^\circ = -46\ \text{kJ/mol}}$

  $$\boxed{\Delta H^\circ_{(a)} = 4\ \text{mol}[-(-46\ \text{kJ/mol})] = 184\ \text{kJ}}$$

- Step (b): $O_2(g)$ is an element in its standard state:

  $$\boxed{\Delta H^\circ_{(b)} = 0}$$

- Step (c): Synthesis of 4 mol of NO_2 (g) from the elements:

  $$\boxed{4 \times [\tfrac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g)]}$$

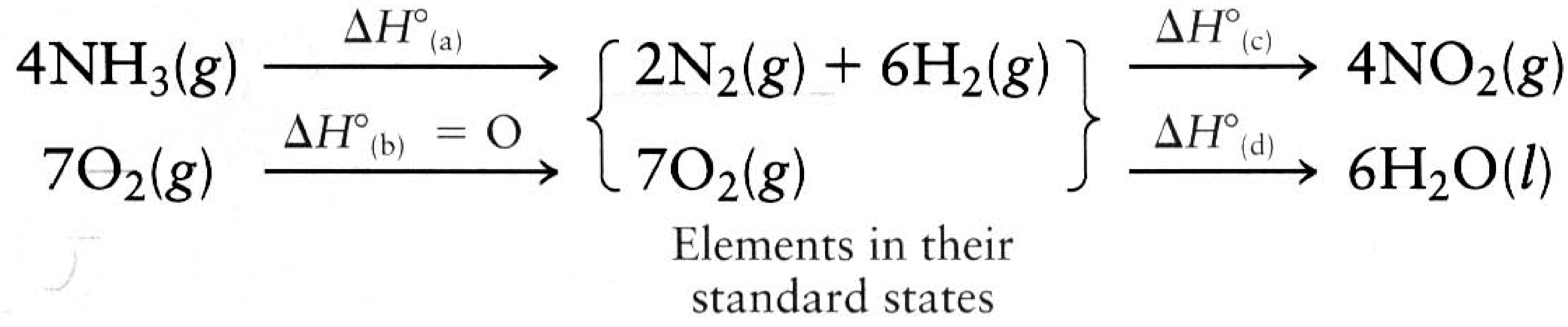
  - Thus, $\boxed{\Delta H^\circ_{(c)} = 4\ \text{mol} \times 34\ \text{kJ/mol} = 136\ \text{kJ}}$

- Step (d): Synthesis of 6 mol of $H_2O(l)$ from the elements:

  $$\boxed{6 \times [H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)]}$$

  - Thus, $\boxed{\Delta H^\circ_{(d)} = 6\ \text{mol}(-286\ \text{kJ/mol}) = -1716\ \text{kJ}}$

- To summarize:



$$\begin{array}{l} 4NH_3(g) \xrightarrow{\Delta H^\circ_{(a)}} \\ 7O_2(g) \xrightarrow{\Delta H^\circ_{(b)} = 0} \end{array} \left\{\begin{array}{l} 2N_2(g) + 6H_2(g) \\ 7O_2(g) \end{array}\right\} \begin{array}{l} \xrightarrow{\Delta H^\circ_{(c)}} 4NO_2(g) \\ \xrightarrow{\Delta H^\circ_{(d)}} 6H_2O(l) \end{array}$$

Elements in their
standard states

$$\begin{aligned} \Delta H^\circ_{\text{reaction}} &= \Delta H^\circ_{(a)} + \Delta H^\circ_{(b)} + \Delta H^\circ_{(c)} + \Delta H^\circ_{(d)} \\ &= 4 \times -\Delta H^\circ_f\ [\text{for } NH_3(g)] + 0 + 4 \times \Delta H^\circ_f\ [\text{for } NO_2(g)] \\ &\quad + 6 \times \Delta H^\circ_f\ [\text{for } H_2O(l)] \\ &= 4 \times \Delta H^\circ_f\ [\text{for } NO_2(g)] + 6 \times \Delta H^\circ_f\ [\text{for } H_2O(l)] \\ &\quad - 4 \times \Delta H^\circ_f\ [\text{for } NH_3(g)] \\ &= \Delta H^\circ_f\ (\text{products}) - \Delta H^\circ_f\ (\text{reactants}) \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{\text{reaction}} &= 6 \times (-286\ \text{kJ}) + 4 \times (34\ \text{kJ}) - 4 \times (-46\ \text{kJ}) \\ &= -1396\ \text{kJ} \end{aligned}$$

Example 9.8

- Methanol (CH_3OH) is sometimes used as a fuel in high-performance engines. Using the data in Table 9.4, compare the standard enthalpy of combustion per gram of methanol with that of gasoline. Gasoline is actually a mixture of compounds, but assume for this problem that gasoline is pure liquid octane (C_8H_{18}).

- The combustion of methanol

$$2CH_3OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l)$$

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= 2 \times \Delta H^\circ_f\,[\text{for } CO_2(g)] + 4 \times \Delta H^\circ_f\,[\text{for } H_2O(l)] \\ &\quad - 2 \times \Delta H^\circ_f\,[\text{for } CH_3OH(l)] \\ &= 2 \times (-394\text{ kJ}) + 4 \times (-286\text{ kJ}) - 2 \times (-239\text{ kJ}) \\ &= -1454\text{ kJ}\end{aligned}$$

For 2 mol (or 64 g) of methanol

$$\frac{-1454\text{ kJ}}{64.0\text{ g}} = -22.7\text{ kJ/g}$$

- The combustion of octane

$$2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(l)$$

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= 16 \times \Delta H^\circ_f\,[\text{for } CO_2(g)] + 18 \times \Delta H^\circ_f\,[\text{for } H_2O(l)] \\ &\quad - 2 \times \Delta H^\circ_f\,[\text{for } C_8H_{18}(l)] \\ &= 16 \times (-394\text{ kJ}) + 18 \times (-286\text{ kJ}) - 2 \times (-269\text{ kJ}) \\ &= -1.09 \times 10^4\text{ kJ}\end{aligned}$$

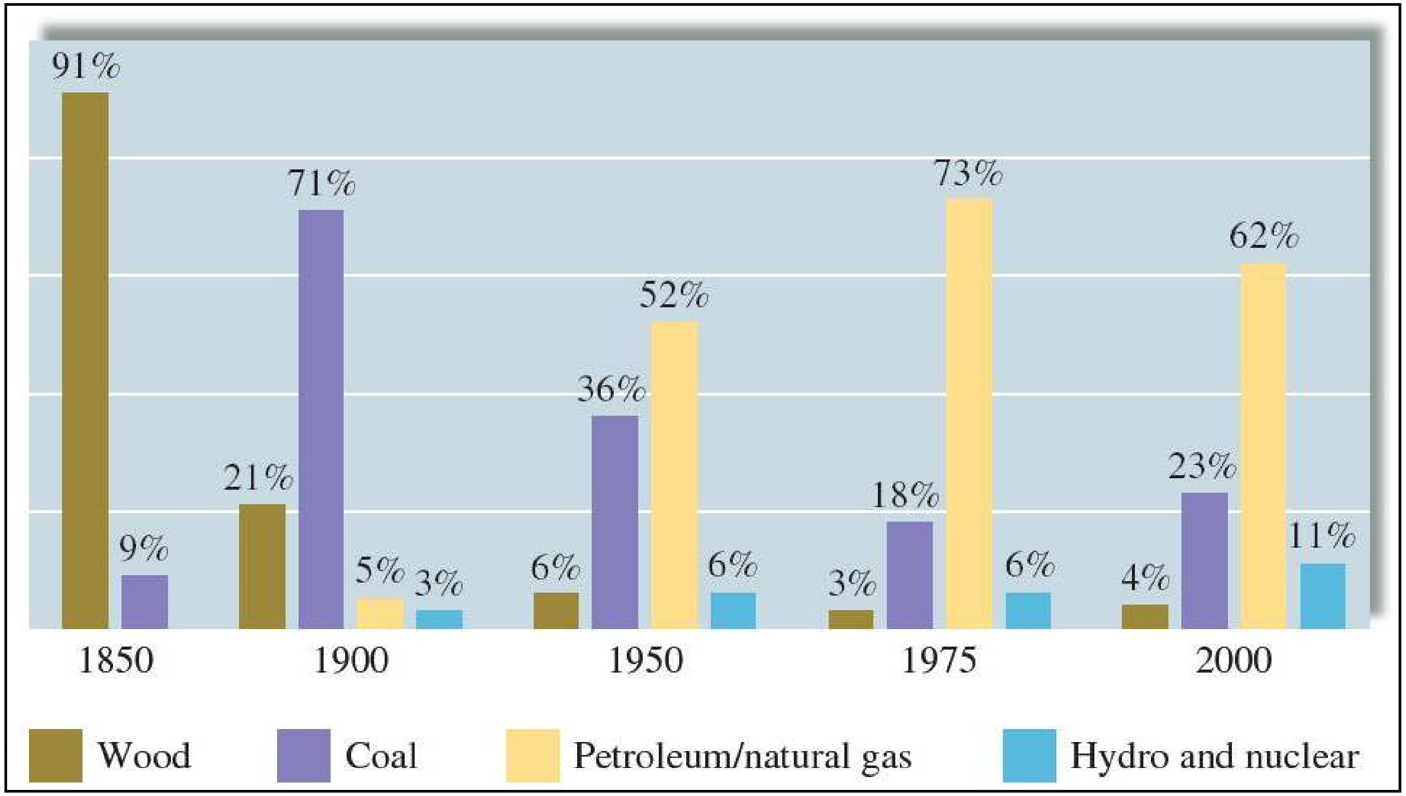
For 2 mol (or 228.4 g) of octane

$$\frac{-1.09 \times 10^4\text{ kJ}}{2(114.2\text{ g})} = -47.7\text{ kJ/g}$$

The enthalpy of combustion per gram of octane is about twice that per gram of methanol !!

Present Sources of Energy

- By the process of photosynthesis, plants store energy that can be claimed by burning the plants themselves or the decay products that have been converted to fossil fuels



Energy sources used in the United States

Petroleum and Natural Gas

- Petroleum:
  - a thick, dark liquid composed mostly of compounds called hydrocarbons that contain carbon and hydrogen. Most likely formed from the remains of marine organisms that lived c.a. 500 million years ago.
  - It consists mostly of hydrocarbons having chains that contain from 5 to more than 25 carbons.
- Natural gas:
  - usually associated with petroleum deposits, consists mostly of methane but also contains significant amounts of ethane, propane, and butane.

Hydrocarbons

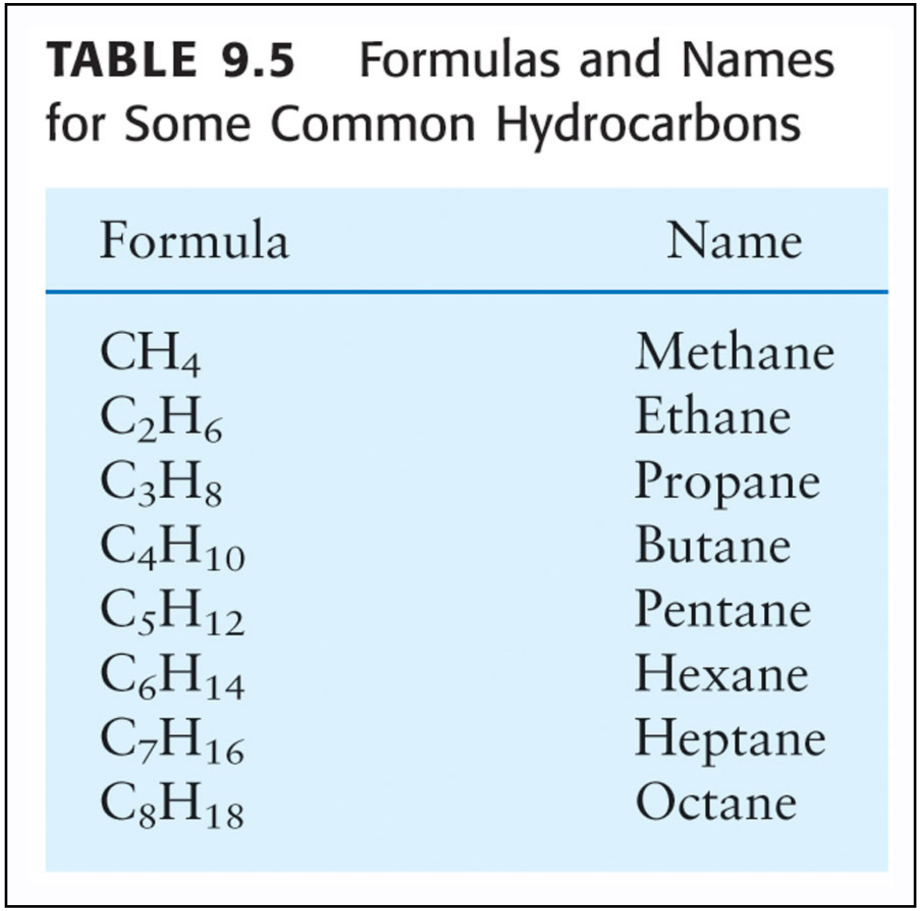


TABLE 9.5 Formulas and Names for Some Common Hydrocarbons

Formula	Name
CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane
C_5H_{12}	Pentane
C_6H_{14}	Hexane
C_7H_{16}	Heptane
C_8H_{18}	Octane

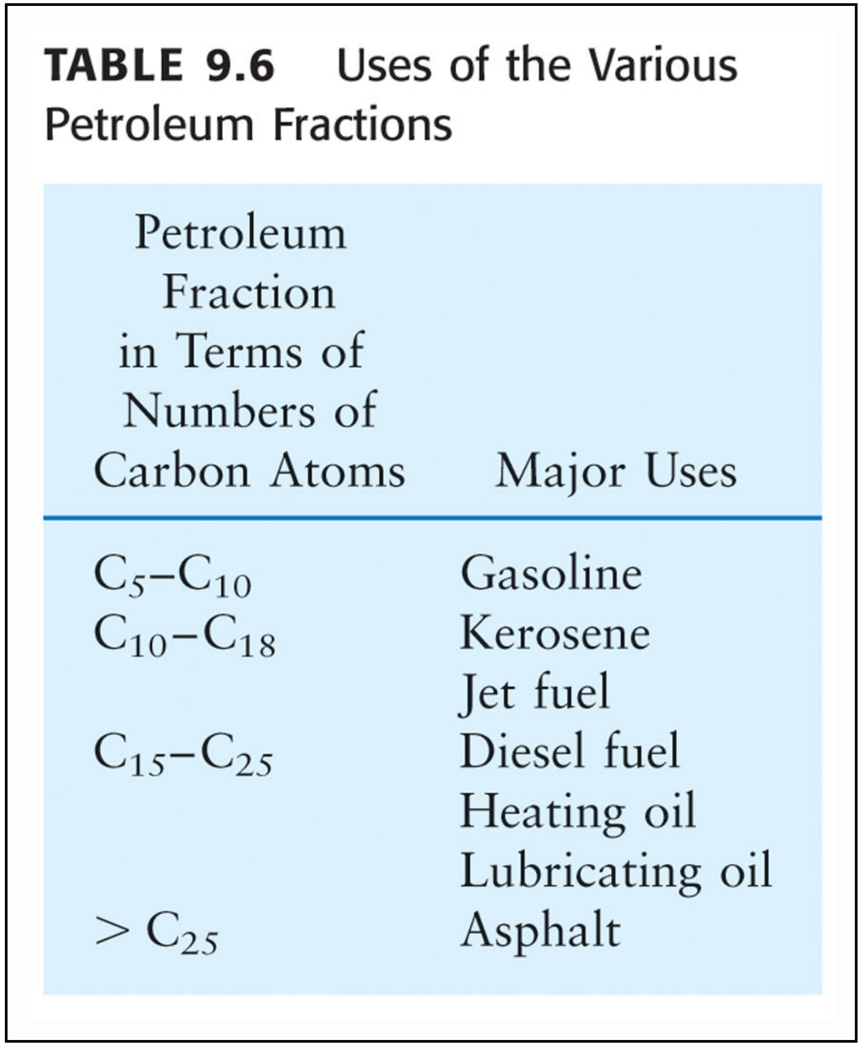


TABLE 9.6 Uses of the Various Petroleum Fractions

Petroleum Fraction in Terms of Numbers of Carbon Atoms	Major Uses
C_5–C_{10}	Gasoline
C_{10}–C_{18}	Kerosene Jet fuel
C_{15}–C_{25}	Diesel fuel Heating oil Lubricating oil
$> C_{25}$	Asphalt

Coal

- From the remains of plants that were buried and subjected to pressure and heat over long periods of time
- Coal “matures” through four stages: lignite, subbituminous, bituminous, and anthracite. Each stage has a higher carbon-to-oxygen and carbon-to-hydrogen ratio.

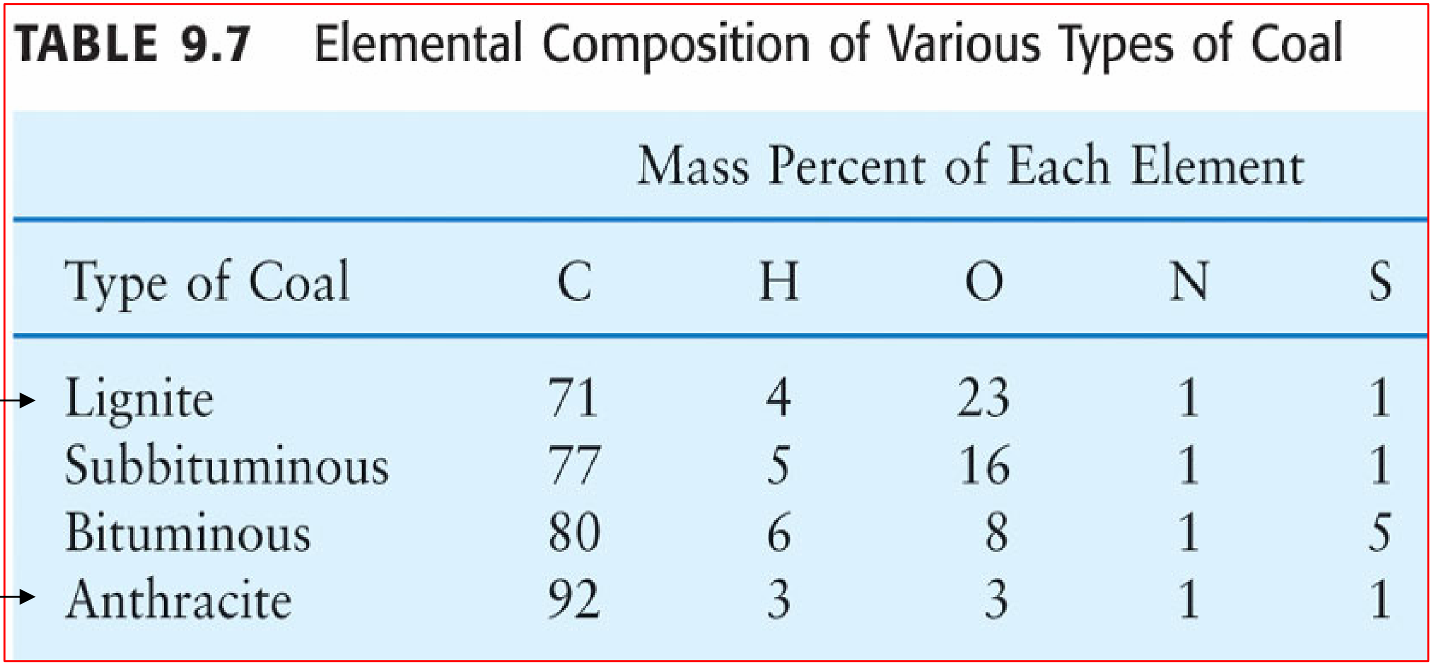


TABLE 9.7 Elemental Composition of Various Types of Coal

	Mass Percent of Each Element				
Type of Coal	C	H	O	N	S
Lignite	71	4	23	1	1
Subbituminous	77	5	16	1	1
Bituminous	80	6	8	1	5
Anthracite	92	3	3	1	1

least valuable → Lignite

most valuable → Anthracite

Effects of Carbon Dioxide on Climate

- Radiant energy from the sun:
  - ~ 30% is reflected into space by the atmosphere
  - Some is absorbed by plants to drive photosynthesis and by the ocean to evaporate water
  - MOST is absorbed by soil, rock and water, resulting an increase in the temperature of the earth's surface. (In turn radiated from the heated surface mainly as infrared radiation (often called heat radiation))
- Molecules in the atmosphere, principally H_2O and CO_2, strongly absorb infrared radiation, trapping it in the earth's atmosphere

Greenhouse Effect

- H_2O
  - The atmosphere’s water content is controlled by the water cycle (evaporation and precipitation) and the average content remains constant over the years.
- CO_2
  - The increase of the CO_2 concentration was 16% from 1880 to 1980.
  - Some projections indicate that the CO_2 concentration may be double in the 21 century what it was in 1880. The earth’s average temperature could increase by 3ºC.

FIGURE 9.14
The earth's atmosphere is transparent to visible light from the sun. This visible light strikes the earth, and part of it is changed to infrared radiation. The infrared radiation from the earth's surface is strongly absorbed by CO_2, H_2O, and other molecules present in smaller amounts (for example, CH_4 and N_2O) in the atmosphere. In effect, the atmosphere traps some of the energy, acting like the glass in a greenhouse and keeping the earth warmer than it would otherwise be.

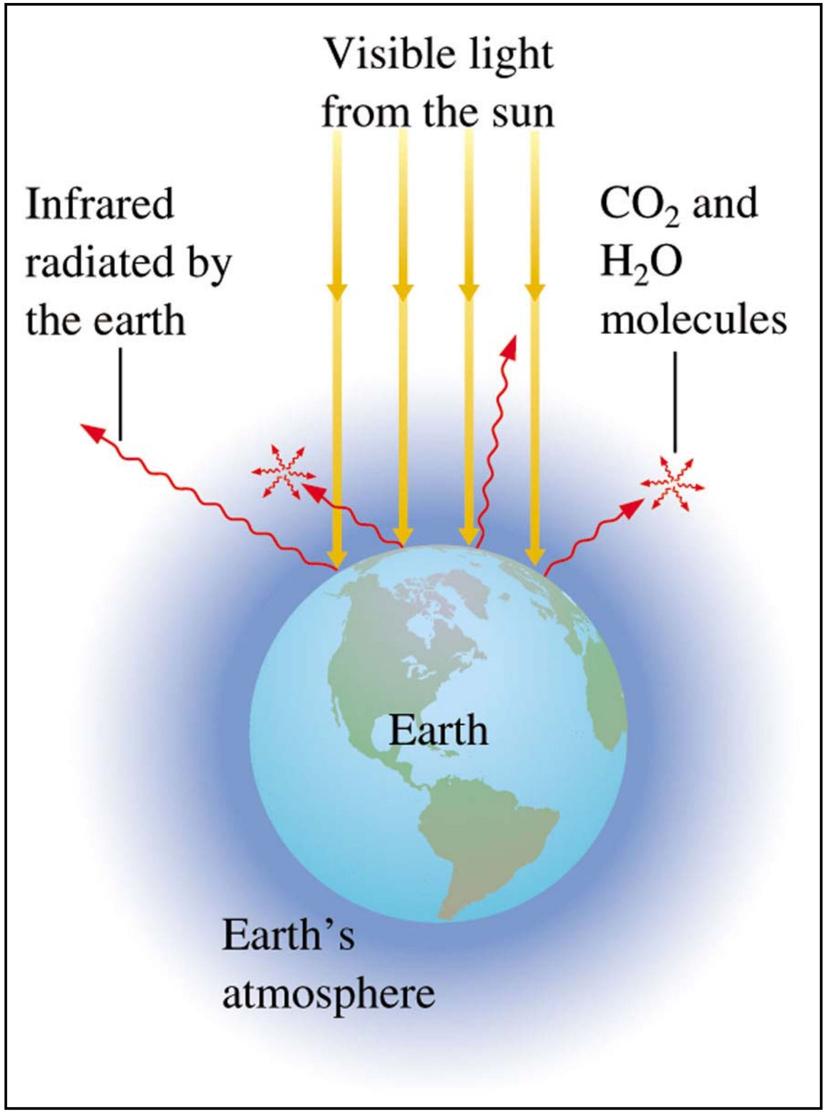
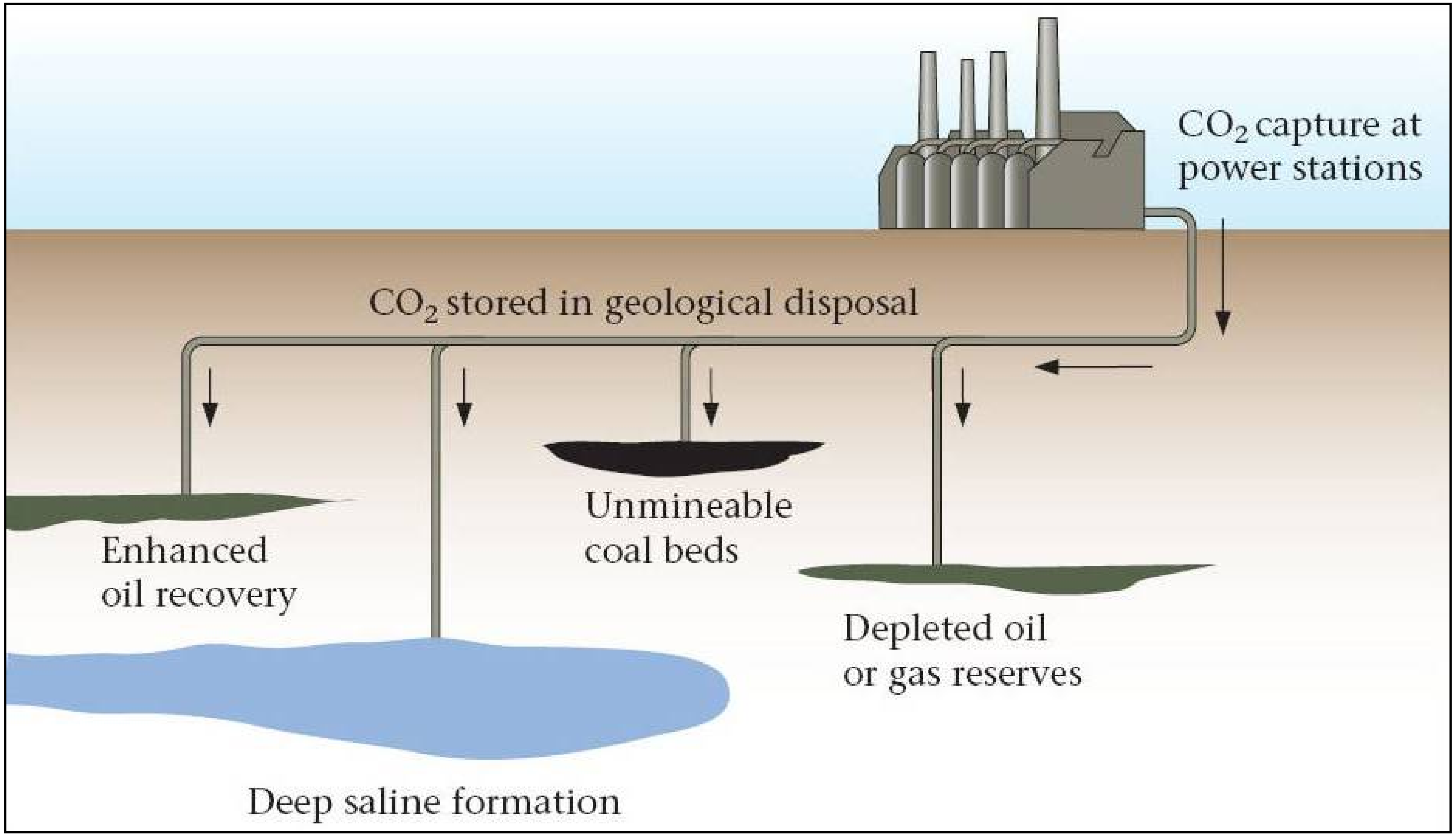


Diagram of Storage of CO_2



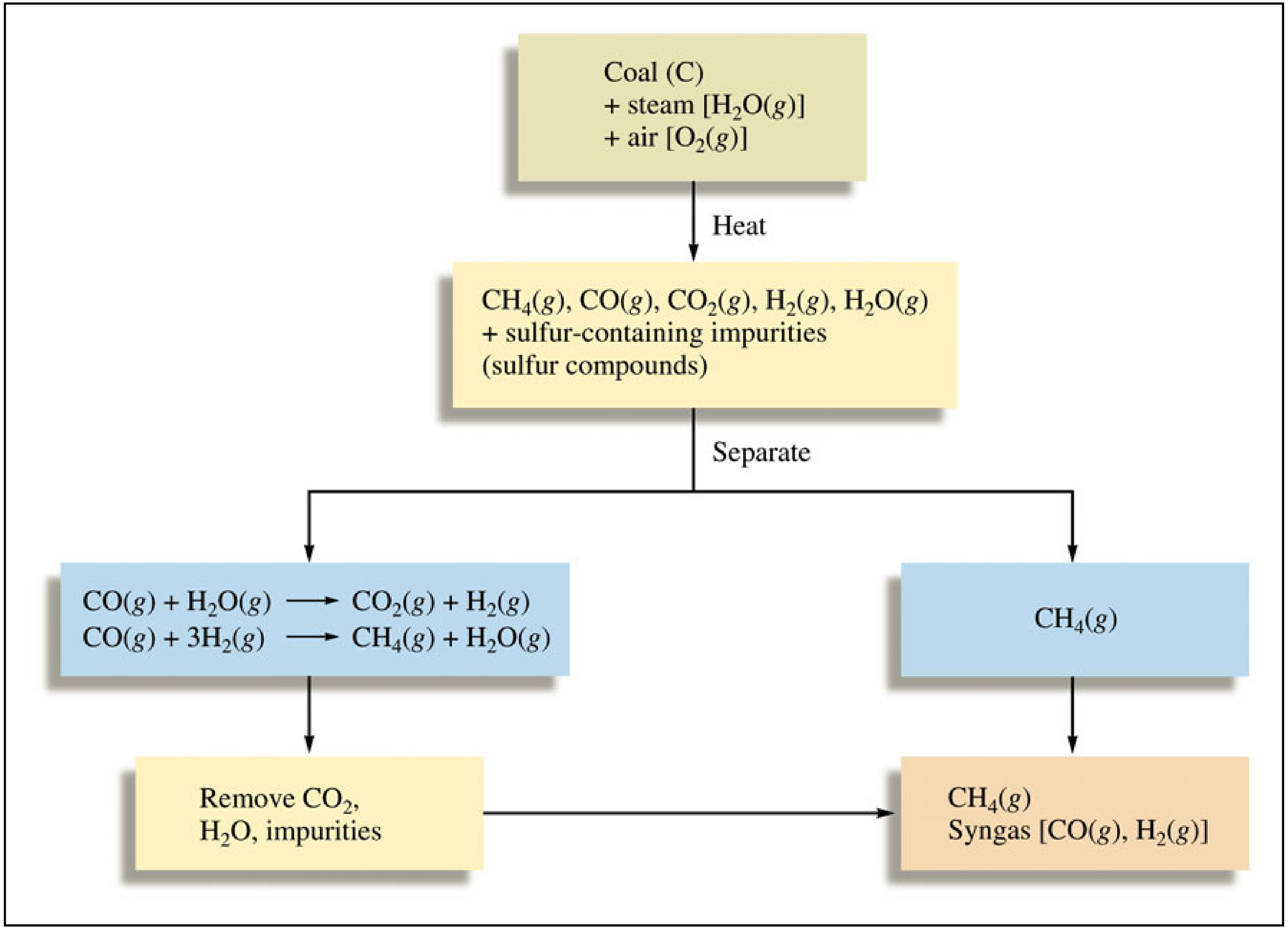
New Energy Sources

- Should consider economic, climatic and supply factors.
- Several potential energy sources:
  - The sun (solar)
  - Nuclear processes (fission and fusion)
  - Biomass (plants)
  - Synthetic fuels
  - Others

Coal conversion

- Transportation costs for solid coal are high, more energy-efficient fuels are being developed → gaseous fuel → convert coal from a solid to a gas requires reducing the size of the molecules
- Coal gasification:
  - A process which breaks down the coal structure.
  - Many of the carbon-carbon bonds are replaced by carbon-hydrogen and carbon-oxygen bonds as the coal fragments react with the water and oxygen.
  - The product consists of synthetic gas, or syngas (a mixture of carbon monoixde and hydrogen) and methane gas.

Coal Gasification



Coal (C)
+ steam [$H_2O(g)$]
+ air [$O_2(g)$]

Heat

$CH_4(g)$, $CO(g)$, $CO_2(g)$, $H_2(g)$, $H_2O(g)$
+ sulfur-containing impurities
(sulfur compounds)

Separate

$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$
$CO(g) + 3H_2(g) \longrightarrow CH_4(g) + H_2O(g)$

$CH_4(g)$

Remove CO_2,
H_2O, impurities

$CH_4(g)$
Syngas [$CO(g)$, $H_2(g)$]

Coal…

- In the gasification process:

$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta H^\circ = -75\ \text{kJ}$$

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H^\circ = -111\ \text{kJ}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ = -394\ \text{kJ}$$

exothermic

$$C(s) + H_2O(g) \longrightarrow H_2(g) + CO(g) \qquad \Delta H^\circ = 131\ \text{kJ}$$

endothermic

- Methanol formation

$$CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)$$

  - can be used in the production of synthetic fibers, plastics and gasoline
- Coal slurry
  - Pulverized coal mixed with water
  - Might replace solid coal and residual oil (a heavy oil from petroleum accounting for 13% of U.S. petroleum imports.)

Hydrogen as a Fuel

- The heat of combustion of $H_2(g)$ per gram is about 2.5 times that of natural gas:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -286\ \text{kJ}$$

- Only water as the product
- Three main problems:
  - The costs of production
  - Storage and transport
    - On metal surface, H_2 decomposes to atoms, migrates into the metal, causing structural changes that make its brittle
    - Relative small amount of energy that is available per unit volume of hydrogen (1/3 of methane)

Hydrogen

- Current production:

$$CH_4(g) + H_2O(g) \longrightarrow 3H_2(g) + CO(g)$$

$$\begin{aligned}\Delta H^\circ &= \Sigma\Delta H^\circ_f\ (\text{products}) - \Sigma\Delta H^\circ_f\ (\text{reactants})\\ &= \Delta H^\circ_f\ [\text{for } CO(g)] - \Delta H^\circ_f\ [\text{for } CH_4(g)] - \Delta H^\circ_f\ [\text{for } H_2O(g)]\\ &= -111\ \text{kJ} - (-75\ \text{kJ}) - (-242\ \text{kJ}) = 206\ \text{kJ}\end{aligned}$$

  - Highly endothermic; treating methane with steam is not an efficient way

- Water splitting:

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

  - requires 286 kJ per mole of liquid water; not economically feasible. Other methods?

Hydrogen from water

- Electrolysis of water
  - Still too expensive
- Thermal decomposition of water

$$
\begin{array}{rll}
2HI \longrightarrow I_2 + H_2 & & (425°C) \\
2H_2O + SO_2 + I_2 \longrightarrow H_2SO_4 + 2HI & & (90°C) \\
H_2SO_4 \longrightarrow SO_2 + H_2O + \tfrac{1}{2}O_2 & & (825°C) \\
\hline
\text{Net reaction:} \quad H_2O \longrightarrow H_2 + \tfrac{1}{2}O_2 & &
\end{array}
$$

Lower temp?

- Biological decomposition of water
  - Only small-scale currently

Other Energy Alternatives

- Oil shale
  - Not fluid and cannot be pumped out
  - Heating to 250ºC (expensive) and large quantities of waste rock (environmental impact)
- Ethanol
  - Mostly from corn fermentation process
  - E85 gasohol (85% ethanol + 15% gasoline)
- Biodiesel
  - Energy efficient: a 93% net energy gain (Note, the net energy gain for ethanol is only about 25%)