Chapter 6
Thermochemistry: Energy Flow and Chemical Change

6.1 **Forms of Energy and Their Interconversion**

6.2 **Enthalpy: Heats of Reaction and Chemical Change**

6.3 **Calorimetry: Laboratory Measurement of Heats of Reaction**

6.4 **Stoichiometry of Thermochemical Equations**

6.5 **Hess's Law of Heat Summation**

6.6 **Standard Heats of Reaction (ΔH^0_{rxn})**

Thermochemistry:
Energy Flow and Chemical Change

- **This unit looks at energy relationships in chemical reactions.......**

- **But what is Energy?????**

Energy:
Capacity to do work or supply heat

- Water over a dam:

  May perform work by turning turbine

- Burning of propane, food, etc.

Two Major Forms of Energy:
Kinetic Energy and *Potential Energy*

- **Kinetic Energy : Energy of Motion**

$$E_K = 1/2 \ mv^2$$

- **SI unit of energy = Joule**

  $1 \ J = 1 \ kg*m^2/s^2$ $1 \ kJ = 1000 \ J$

- Calculate the E_K possessed by a 50. kg person on a bike traveling at 10. m/s (~ 36 km/hr or 22 m.p.h..)

  - Answer: 2500 Joules or 2.5 kJ

Units of Energy

- ## 1 calorie

  - » **Amount of energy needed to raise the temperature of 1gram of water by 1ºC** (more precisely, from 14.5 ºC to 15.5 ºC)

  - » 1 cal = 4.184 J

  - » 1 kcal = 1000 cal = 4.184 kJ

  - » 1 kcal = 1 Food Calorie = 1000 cal

- *British Thermal Unit:* **1 Btu = 1055**

Potential Energy, E_p: Stored Energy

- **E_p <u>is either in the object or due to the object's position</u>**

- **E_p is due to attractions and repulsions between objects or their parts**
  - » **E_p increases when.....**
    - –**repelling objects are forced together**
    - –**separating attracting objects**

Internal Energy, E

- ## Internal Energy, E

  - ❖ the total energy of a system

$$E_{(system)} = E_{K\,(system)} + E_{P\,(system)}$$

- ### *Examples of PE and KE changes...*

What happens to KE and PE when .....

- A spring is stretched and then released? Compressed and then released?
- Water flowing over a dam?
- A ball is tossed in the air?
- Gasoline burns?
- A sodium atom loses an electron?
- A sodium ion approaches a chloride ion?
- Water is heated from 20 ºC to 70 ºC?
- Water boils (liquid → gas) at constant temperature?

Temperature vs. Heat

- **Heat**
  - » **A sum of the kinetic energy of all particles in the sample**
  - » **Number of particles α Amount of Heat**
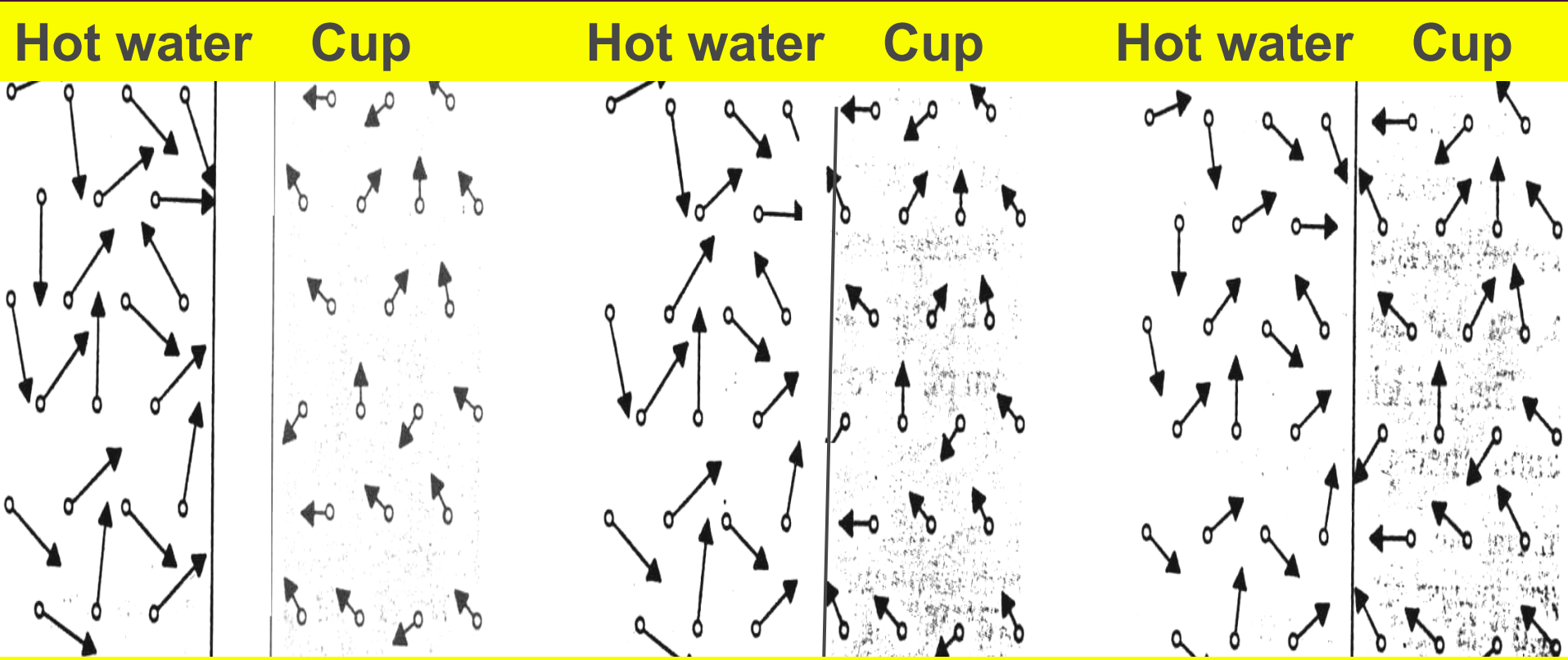- **Direction of Heat transfer**
  - » **Warmer object $\rightarrow$ Cooler object**
    - – **Sitting by a window on a cold night**
    - – **Sleeping on the ground**
    - – **How a Thermos works**

Energy transfer from a warmer to a cooler object

Hot water **Cup** **Hot water** **Cup** **Hot water** **Cup**

Time

Temperature

- **A measure of the average kinetic energy of the particles in a sample**

- **Measures the intensity or degree of heat, *not* the amount of heat**

  » **e.g.   Cup of water at 20 °C Vs Gallon of water at 20 °C**

Kinetic Molecular Theory : The particles (e.g. molecules) that make-up matter are in constant motion

- **Kinds of Kinetic Energy:**

  Translational, rotational and vibrational K.E.
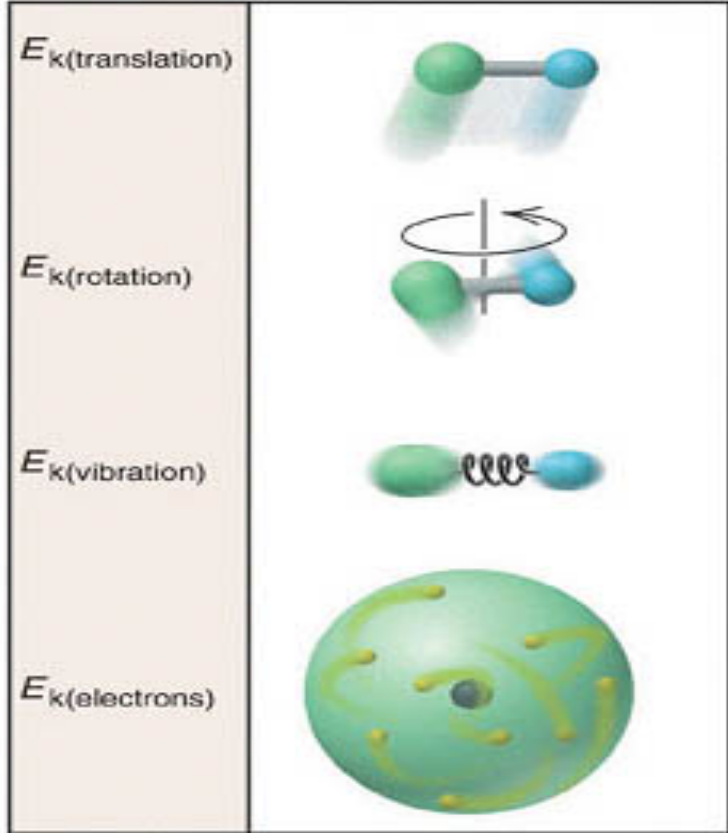
- **Gases and Liquids**: Have all three

- **Solids:** Only Vibrational Kinetic Energy

- Some particles in a sample move faster that others

  » **Average Molecular Speed** α **T** (Kelvin)
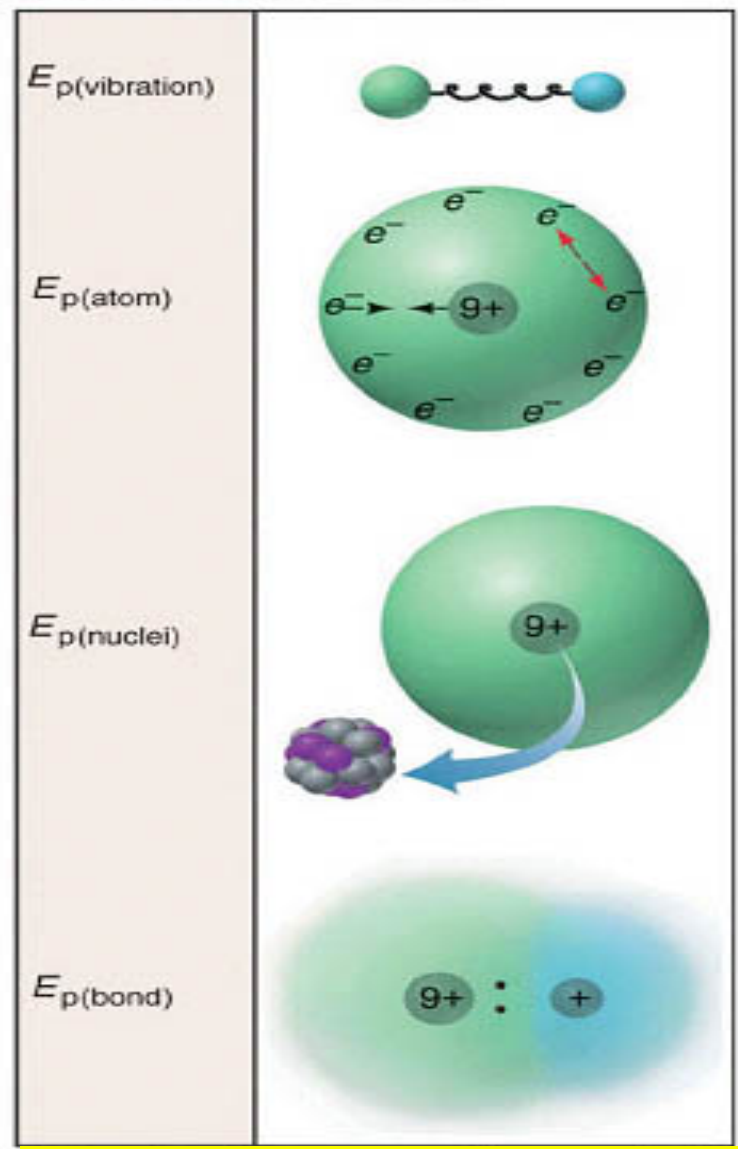
Figure 6.9

Components of internal energy (E)

Contributions to Kinetic Energy

Contributions to Potential Energy

Distribution of Molecular Speeds at Three Temperatures

Number of molecules with speed, u, Molecular Velocity

Molecular Speed α T (Kelvin)

273 K

Most probable speed at 1273 K

1273 K

2273 K

1000   2000   3
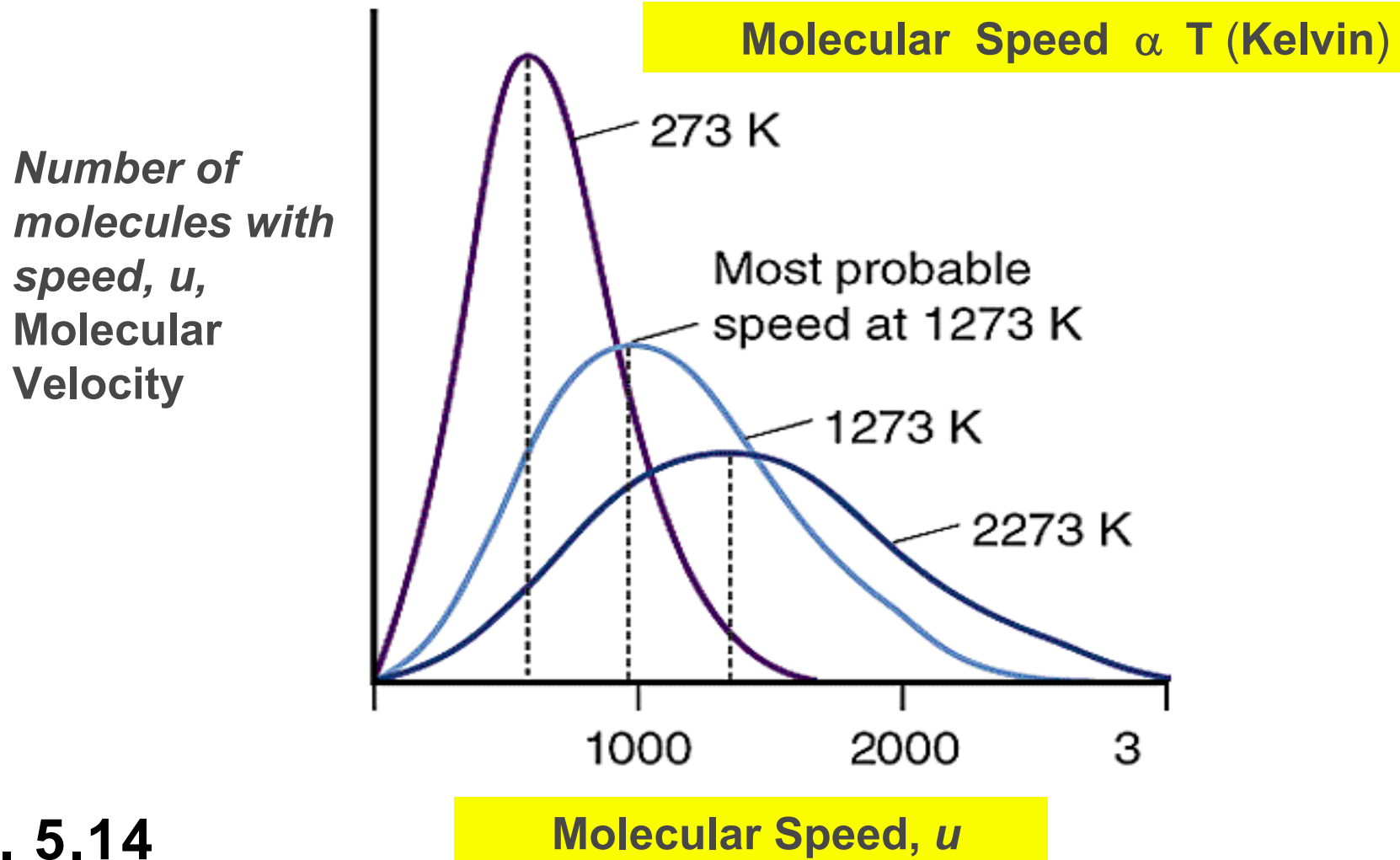
Fig. 5.14

Molecular Speed, *u*

Contributions to Kinetic and Potential Energy

1. *Contributions to the Kinetic Energy*

- Molecule moving through space, $E_{k \text{ (translation)}}$
- Molecule rotating, $E_{k \text{ (rotation)}}$
- Bound atoms vibrating, $E_{k \text{ (vibration)}}$
- Electrons moving within each atom, $E_{k \text{ (electron)}}$

Contributions to Kinetic and Potential Energy

2. *Contributions to the potential energy*

- Forces between the bound atoms vibrating, $E_{P\,\text{(vibration)}}$
- Forces between nucleus and electrons and between electrons in each atom, $E_{P\,\text{(atom)}}$
- Forces between the protons and neutrons in each nucleus, $E_{P\,\text{(nucleus)}}$
- Forces between nuclei and shared electron pair in each bond, $E_{P\,\text{(bond)}}$

Thermochemical Definitions

System : That part of the Universe whose change we are going to measure.

Surroundings : Every thing else that is relevant to the change is defined as the "surroundings".

Internal Energy : The sum of the kinetic and potential energy of all the particles in a system.

Boundary: Separates system from surroundings. e.g. walls of reaction vessel

A Chemical System and its Surroundings

System = orange liquid, therefore……..

Surroundings = flask and the laboratory

Fig. 6.1

133 © McGraw-Hill Higher Education/Stephen Frisch, photographer

Fig. 6.1

1ˢᵗ Law of Thermodynamics: Law of Conservation of Energy

- Energy can neither created not destroyed, only transformed from one form to another

- Energy of a system is constant

$$\Delta E_{(Universe)} = \Delta E_{(system)} + \Delta E_{(surroundings)} = 0$$

Energy Interconversions and the 1st Law

- **Energy can be transformed from one formed to another, but not destroyed in the process**

  e.g.   Solar energy → Photosynthesis → Plant makes Chemical Energy (e.g. sugars) → Sugars ingested by animal → Cellular respiration → Energy released to power life functions
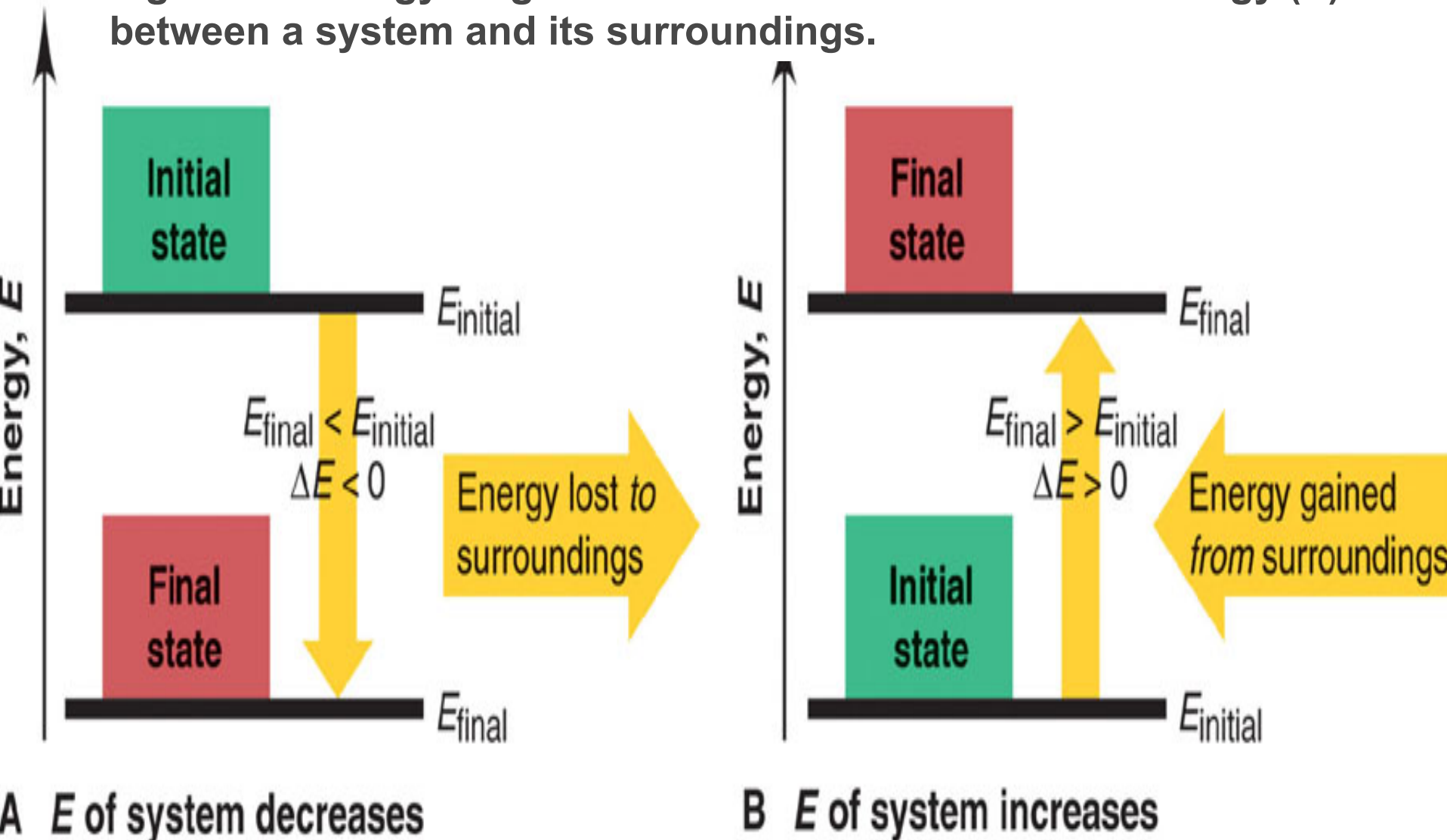
  Note: Each energy transfer is only 5-40% efficient

Energy Change of a system, ΔE

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

- A change in energy of a system is always accompanied by an <u>equal but opposite</u> change in energy of the surroundings.
  - E.g. Carbide cannon demo
    - **Is ΔE positive or negative?**
  - Illustrate the energy flow/transfer with an energy diagram.

Fig. 6.2   Energy diagrams for the transfer of internal energy (E) between a system and its surroundings.

Energy, E

Initial state

$E_{initial}$

$E_{final} < E_{initial}$
$\Delta E < 0$

Energy lost *to* surroundings

Final state

E_{final}

A *E of system decreases*

Energy, E

Final state

E_{final}

$E_{final} > E_{initial}$
$\Delta E > 0$

Energy gained *from* surroundings

Initial state

$E_{initial}$

B *E of system increases*

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

Energy Diagrams: Exothermic Reactions

- **Exothermic Reactions (E decreases)**
  - » **Result in products with Lower E than the reactants**
    - –e.g.   cellular respiration of glucose
  - » **What happens to the temperature of the surroundings?**
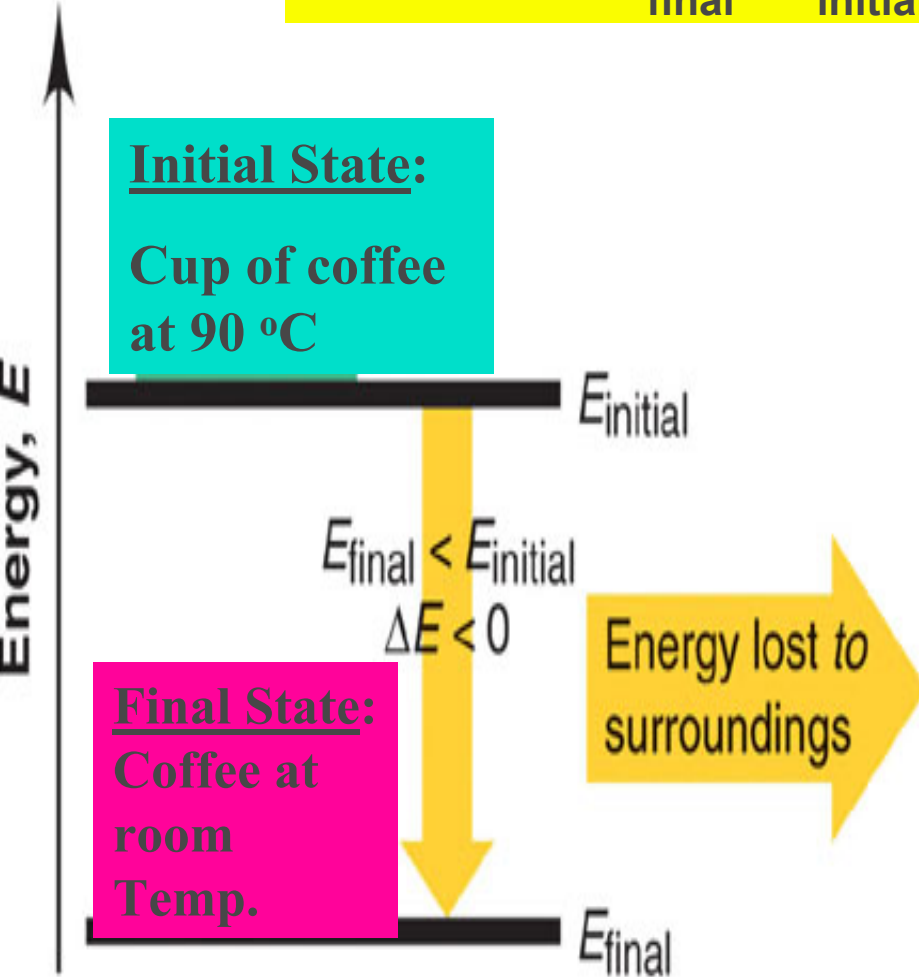
Energy Diagrams: Endothermic Reactions

- **Endothermic Reactions (E increases)**
  - » **Result in products with higher E than the reactants**
  - » **What happens to the temperature of the surroundings?**
  - » **e.g.   Photosynthesis as an endothermic process**
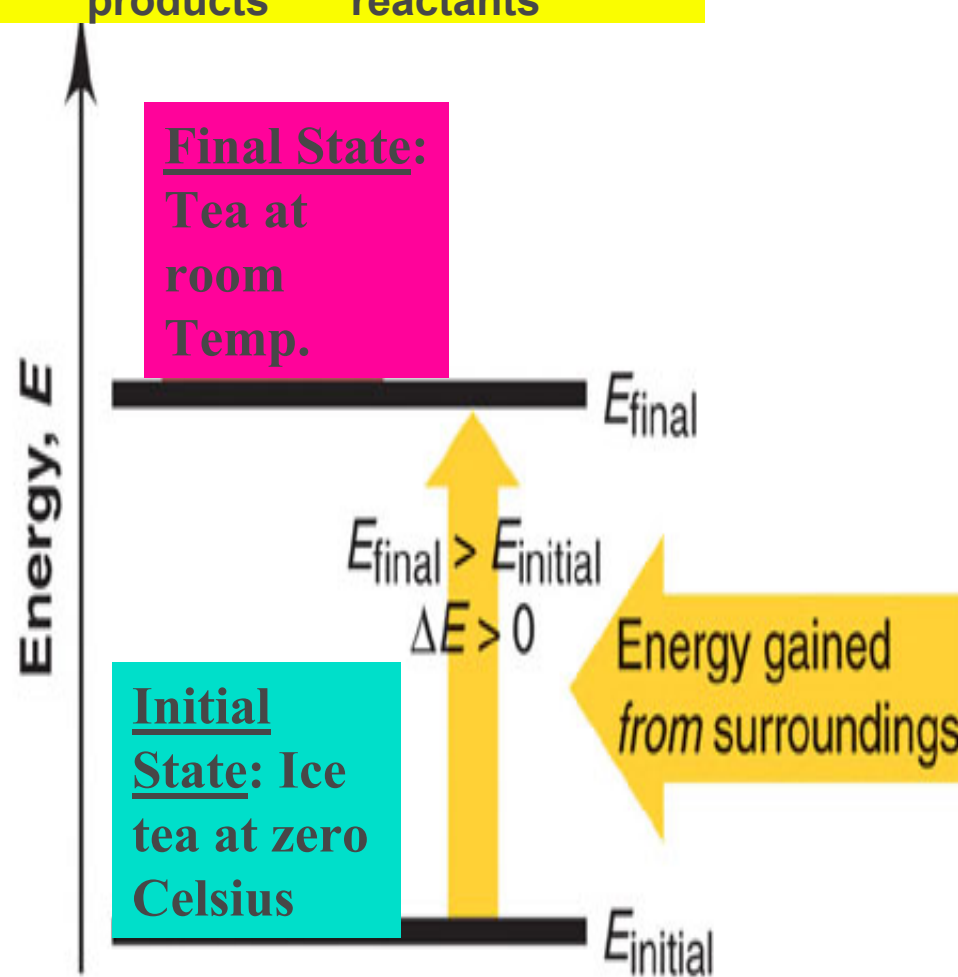
Practice: Energy Diagrams

Make energy diagrams for….

1. A cup of coffee at 90 ^{o}C that has cooled to room temperature.

2. A cup of ice tea that has warmed to room temperature.

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

Initial State:

Cup of coffee at 90 °C

$E_{initial}$

$E_{final} < E_{initial}$
$\Delta E < 0$

Energy lost *to* surroundings

Final State: Coffee at room Temp.

E_{final}

A *E* of system decreases

Final State: Tea at room Temp.

E_{final}

$E_{final} > E_{initial}$
$\Delta E > 0$

Energy gained *from* surroundings

Initial State: Ice tea at zero Celsius

$E_{initial}$

B *E* of system increases

Energy Changes in Chemical Reactions

- **What determines if a *reaction* is endo- or exothermic?**

- **Demo's**
  - » **Gummi bear**
  - » **Methanol cannon**

    $$CH_3OH + 2.5\ O_2 \rightarrow CO_2 + 2\ H_2O + 726.4\ kJ$$
  - » **Heats of solution**

Energy Changes in Chemical Reactions

- **Chemical reactions involve the breaking of bonds and then the making of new bonds.**
- **What determines if a *reaction* is endo- or exothermic?**
  - » **Bond breaking is endothermic**
    - – **Energy must be added**
  - » **Bond making is exothermic**
    - – **Energy is released**
  - • **The one greater in magnitude determines if a reaction is exo- or endothermic**

ΔH and the Strengths of Bonds

Enthalpy, H

$H_2(g) + F_2(g)$

Weaker bonds

$\Delta H_{rxn} = -546$ kJ

$2HF(g)$

Stronger bonds

Note:

ΔH = Enthalpy change

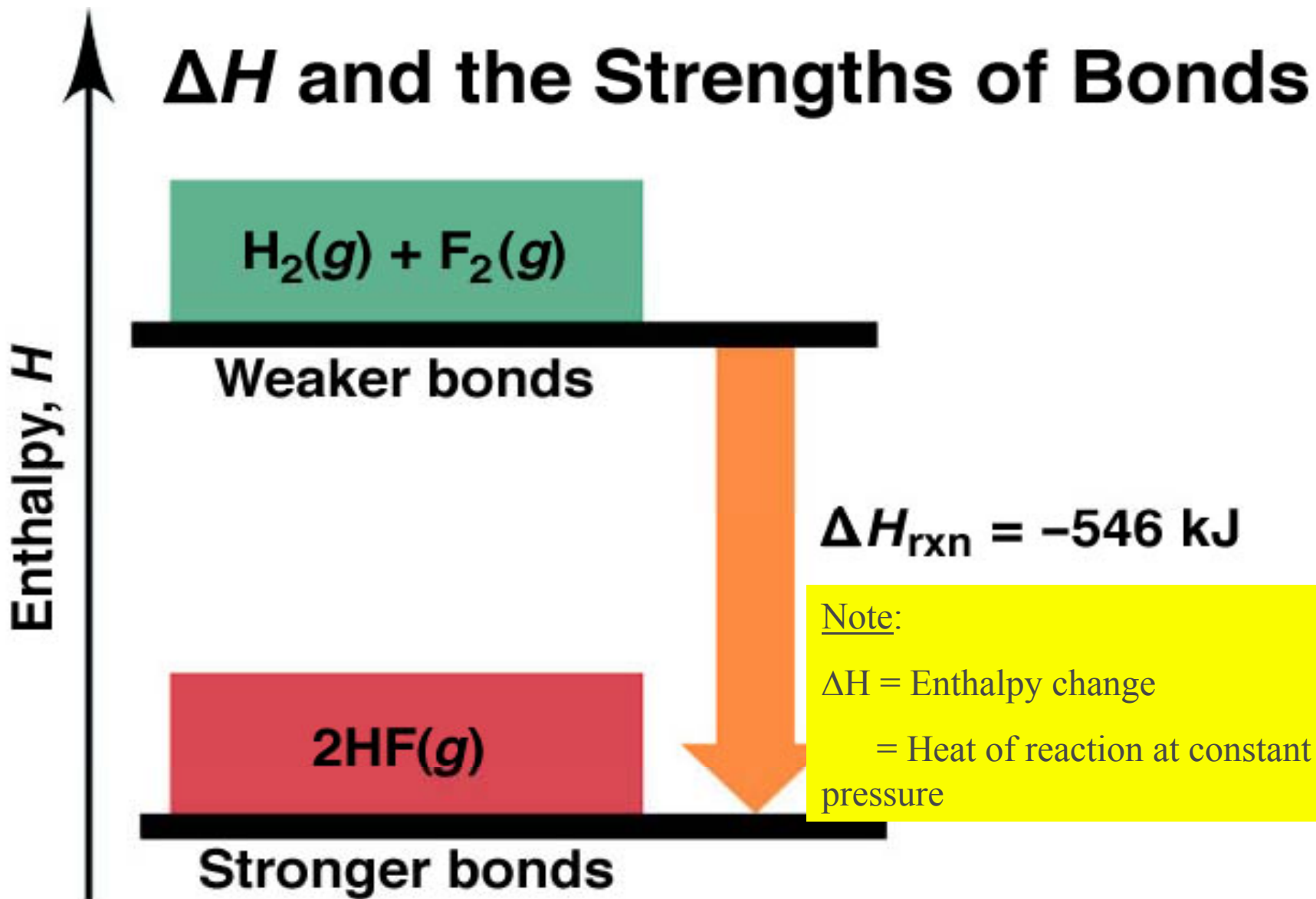= Heat of reaction at constant pressure

Fig. 6.10

Why is bond breaking Endothermic?

- **Bond breaking is like stretching a spring**
  - ➤ **Separates attracting things**
- **E_P increases, E_K decreases**
- **Temp drops...... Why?   Recall...**
  - » **Temp is a measure of E_K**
  - » **Total E_{system} = $E_{K(system)}$ + $E_{P(system)}$**

Why is Bond formation Exothermic?

- **Bond formation brings attracting things together**
    - » **It's like releasing a stretched spring**
- **E_P decreases, E_K increases**
- Temp increases...... Why?   Recall...
    - » Temp is a measure of KE
    - » **Total E_{system} = $E_{K(system)}$ + $E_{P(system)}$**

Table 6.2 Heats of Combustion (ΔH_{comb}) of Some Carbon Compounds

Name (Formula)	Structural Formula	Sum of C–C and C–H Bonds	Sum of C–O and O–H Bonds	ΔH_{comb} (kJ/mol)	ΔH_{comb} (kJ/g)
Two-carbon compounds					
Ethane (C_2H_6)	H–C–C–H (with H H above and H H below)	7	0	–1560	–51.88
Ethanol (C_2H_5OH)	H–C–C–O–H (with H H above and H H below)	6	2	–1367	–29.67
One-carbon compounds					
Methane (CH_4)	H–C–H (with H above and H below)	4	0	–890	–55.5
Methanol (CH_3OH)	H–C–O–H (with H above and H below)	3	2	–727	–22.7

(p. 235)

Heats of Combustion of Some Fats and Carbohydrates

Substance	$\triangle H_{comb}$(kJ/mol)
Fats	
Vegetable oil	37.0
Margarine	30.1
Butter	30.0
Carbohydrates	
Table sugar (sucrose)	16.6
Brown rice	14.9
Maple syrup	10.4

Measuring Heat in Chemical Reactions

- **Terms used.....**
  - » **System**
    - – Things studied (e.g. Reactants and Products)
  - » **Surroundings**
    - – Everything else
      - • Room, air, building, etc.
  - » **Boundary**
    - – What separates system from surroundings
      - • e.g. walls of reaction vessel

Methanol Cannon Demo

$$CH_3OH + 2.5\ O_2 \rightarrow CO_2 + 2\ H_2O + 726.4\ kJ$$

- » **System = ?**
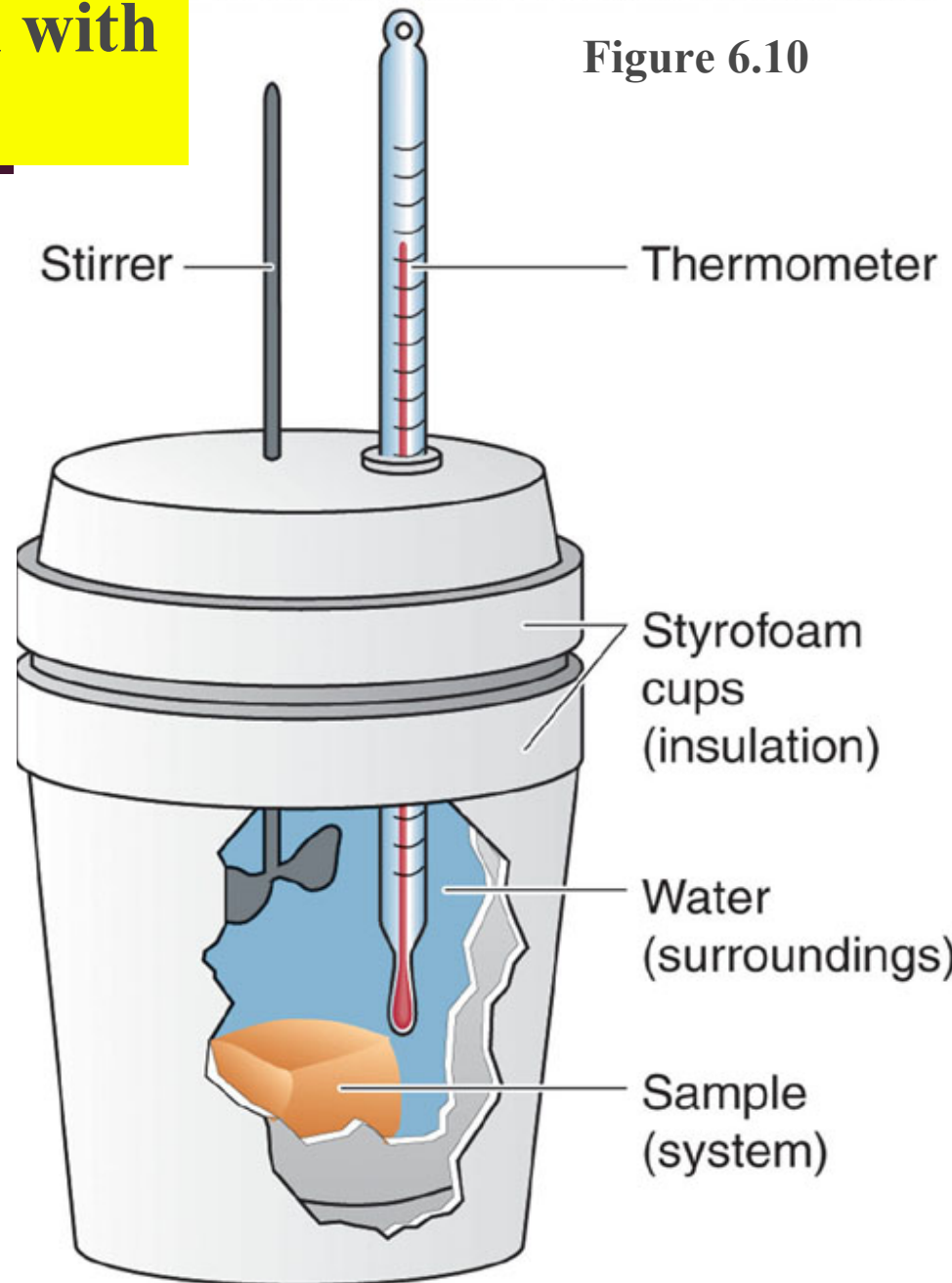- » **Surroundings = ?**
- » **Boundary = ?**

What happens to the E_P, E_K, and temp. of.....

- » System?
- » Surroundings and boundary?

Measuring Heats of Reaction with Coffee-cup calorimeter

Figure 6.10

A Calorimeter measures the amount of heat lost or absorbed in a reaction

1. The Reaction studied is the system
2. The water in the calorimeter is the surroundings
3. Calorimeter wall is the boundary (assume no heat lost or gained with the lab)

Stirrer

Thermometer

Styrofoam cups (insulation)

Water (surroundings)

Sample (system)

Calculating Heats of Reaction

$$q = (\text{Specific Heat})(\text{mass})(\Delta t)$$

- **q** = heat lost or gained in Joules
- **Specific Heat, C**
  - » Definition? Units: cal / g^{o}C
  - » An Intensive property: depends on the ID of the substance undergoing the temperature change
- **mass**
  - » mass in grams of the substance undergoing the temperature change
- $\Delta t = t_{final} - t_{initial}$ **Units:** temperature in Celsius

Table 6.4

Specific Heat Capacities of Some Elements, Compounds, and Materials

Substance	Specific Heat Capacity (J/g*K)	Substance	Specific Heat Capacity (J/g*K)
Elements		**Compounds**	
aluminum, Al	0.900	water, $H_2O(l)$	4.184
graphite,C	0.711	ethyl alcohol, $C_2H_5OH(l)$	2.46
iron, Fe	0.450	ethylene glycol, $(CH_2OH)_2(l)$	2.42
copper, Cu	0.387	carbon tetrachloride, $CCl_4(l)$	0.864
gold, Au	0.129	**Materials**	
Lead, Pb	0.128	wood	1.76
		cement	0.88
		glass	0.84
		granite	0.79
		steel	0.45

Practice Problems: Heats of Reaction

- **Calculate the amount of heat lost in kJ by a 250.0 g piece of copper at 100.0 ºC that is placed in water and cools to 30.0 ºC. How much heat is gained by the water?**

  » Ans. 6.77 kJ

- **If the mass of water was 200.0 g, what was its initial temperature?**

  » Ans. 21.9 ºC

- **Repeat the question if Fe was used instead of Cu.**

  » Ans. 7.87 kJ; Initial water temp = 20.6 ºC

Another Example: Heat of Reaction

- **Identify an unknown metal from the following data. It takes 96.0 J to raise the temperature of 75.0 g of this substance 10.0 ºC.**

  » Ans.   Pb or Au

Practice makes perfect........

- **Calculate the heat of solution of an unknown salt in J/g from the following data. 100.0 g of water at 22.0 ºC were placed in a coffee cup calorimeter. 10.0 g of the salt were dissolved in the water. The highest temperature reached by the solution was 24.0 ºC.**
  - » Ans.   Heat of soln = -83.7 j/g
- **Calculate the heat of solution of this salt in kJ/mol if the formula mass of the salt is 56.0 g/mol**
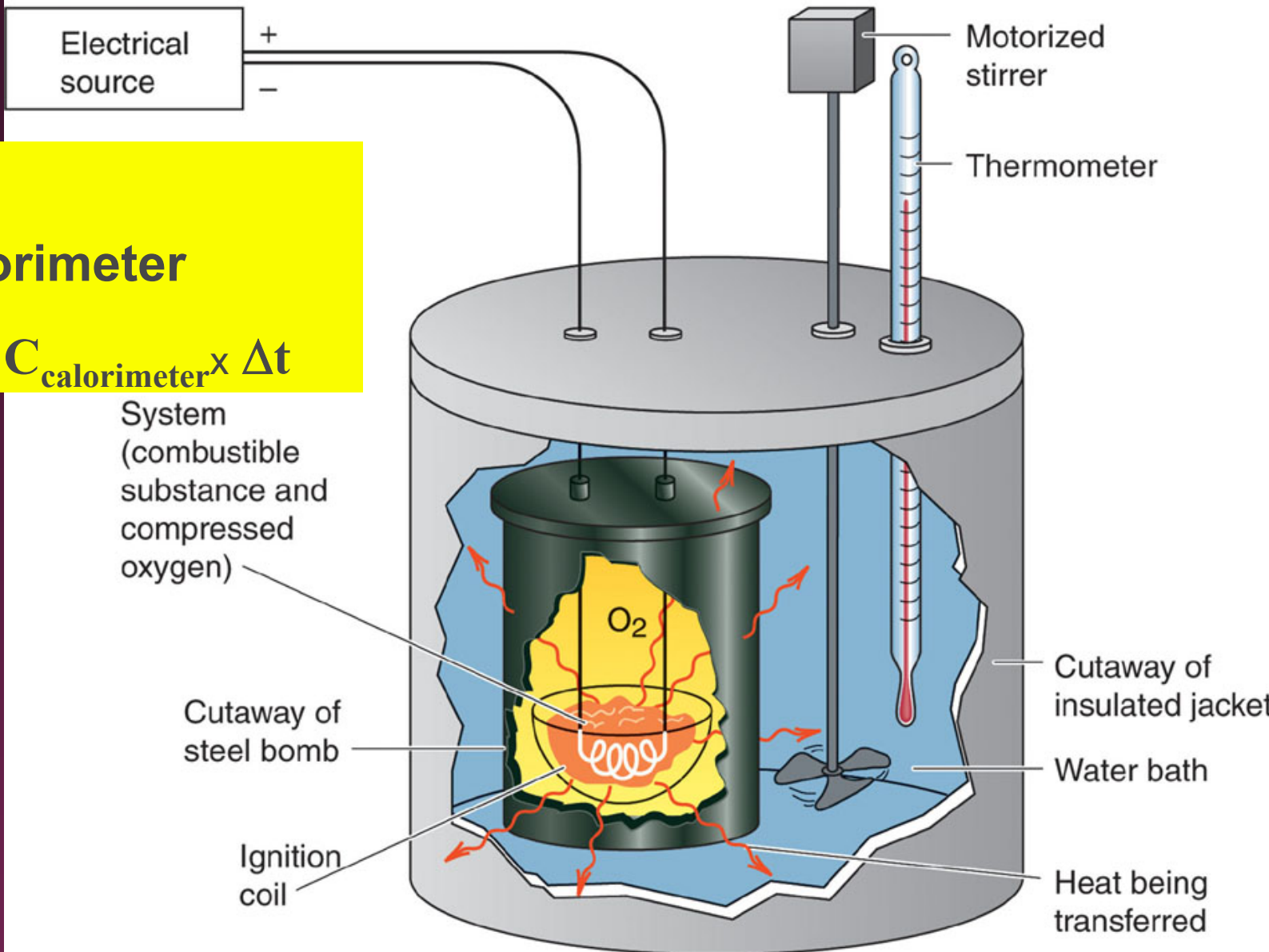 - » Ans   -4.69 kJ/mol

Electrical source

\+

\−

Motorized stirrer

Thermometer

Figure 6.11

Bomb calorimeter

$$q_{calorimeter} = C_{calorimeter} \times \Delta t$$

System (combustible substance and compressed oxygen)

O_2

Cutaway of steel bomb

Ignition coil

Cutaway of insulated jacket

Water bath

Heat being transferred

PROBLEM: A manufacturer claims that its new dietetic dessert has "fewer than 10 Calories per serving." To test the claim, a chemist at the Department of Consummer Affairs places one serving in a bomb calorimater and burns it in O_2(the heat capacity of the calorimeter = 8.15kJ/K). The temperature increases 4.937^{0}C. Is the manufacturer's claim correct?

PLAN: $- q_{sample} = q_{calorimeter}$

SOLUTION:

$q_{calorimeter}$ = heat capacity x ΔT

= 8.151kJ/K x 4.937K

= 40.24kJ

$$40.24kJ \quad \frac{kcal}{4.18kJ} \quad = 9.62kcal \text{ or Calories}$$

The manufacturer's claim is true.

Constant Volume Calorimetry
e.g. Bomb Calorimeters

- **Calculate the heat of combustion for methanol in kJ/mol if <u>3.200g CH$_3$OH</u> are combusted in a bomb calorimeter with a <u>heat capacity of 9.43</u> kJ/^{o}C causing the temperature of the calorimeter to increase by <u>7.75 ^{o}C</u>.**

  ✓Ans. 731 kJ/mol

Heat and Work in Energy Changes

- **Energy is transferred to or from a system as <u>heat</u> and/or <u>work</u>**
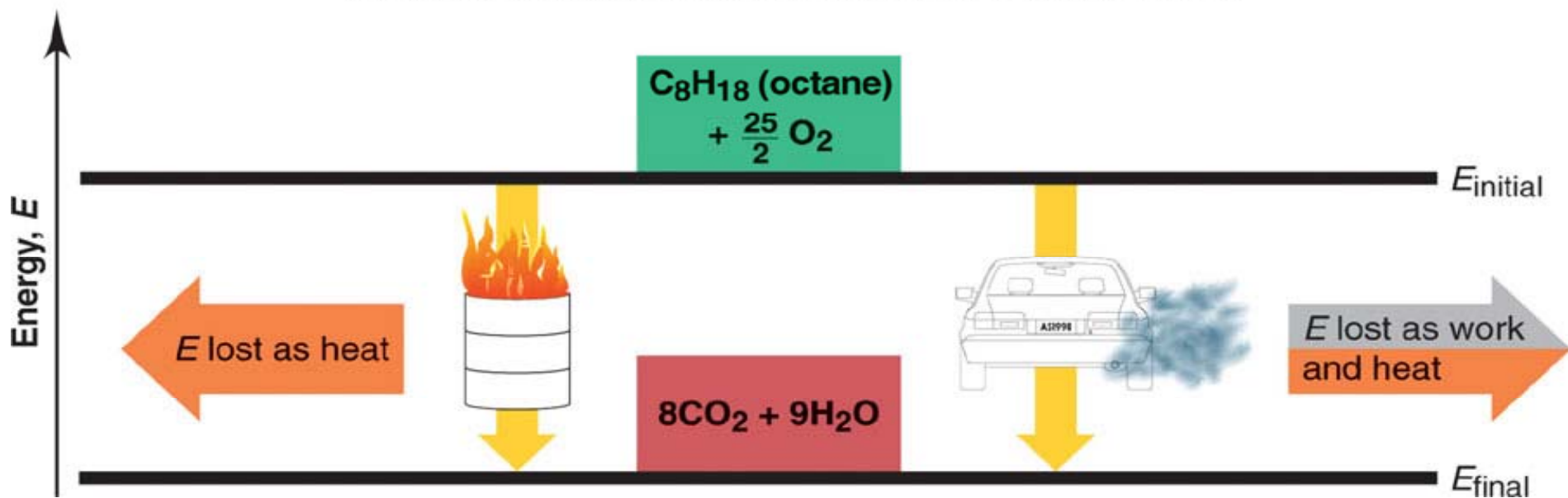
$$\Delta E = q + w$$

- **Heat, q**
  - ❖ **Thermal energy transferred between a system and its surroundings due to the temperature differences between the two.**
  - ❖ **Heat flows from warm to cool objects**
- **Work, w**
  - ❖ **Energy transferred when an object is moved by force**

Fig. 6.6   Two different paths for the energy change of a system

Energy, E

C_8H_{18} (octane) + $\frac{25}{2}$ O_2

$E_{initial}$

E lost as heat

$8CO_2 + 9H_2O$

E lost as work and heat

E_{final}

$\Delta E = q$

$\Delta E = q + w$

(since w = 0)

A system transferring energy only as *Heat*

Fig. 6.3 $\Delta E = q$ since w = 0

A   *E* lost as heat

B   *E* gained as heat
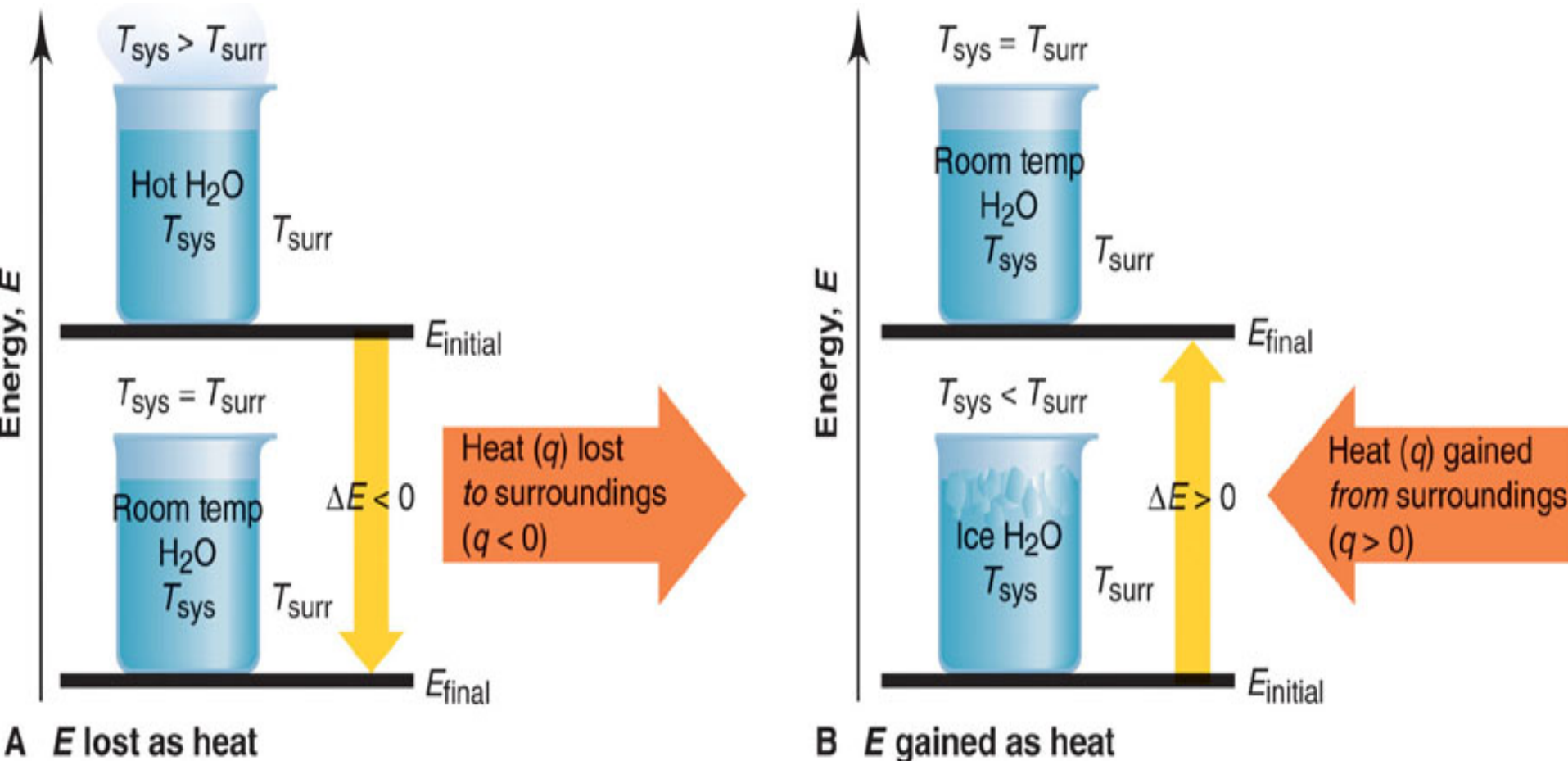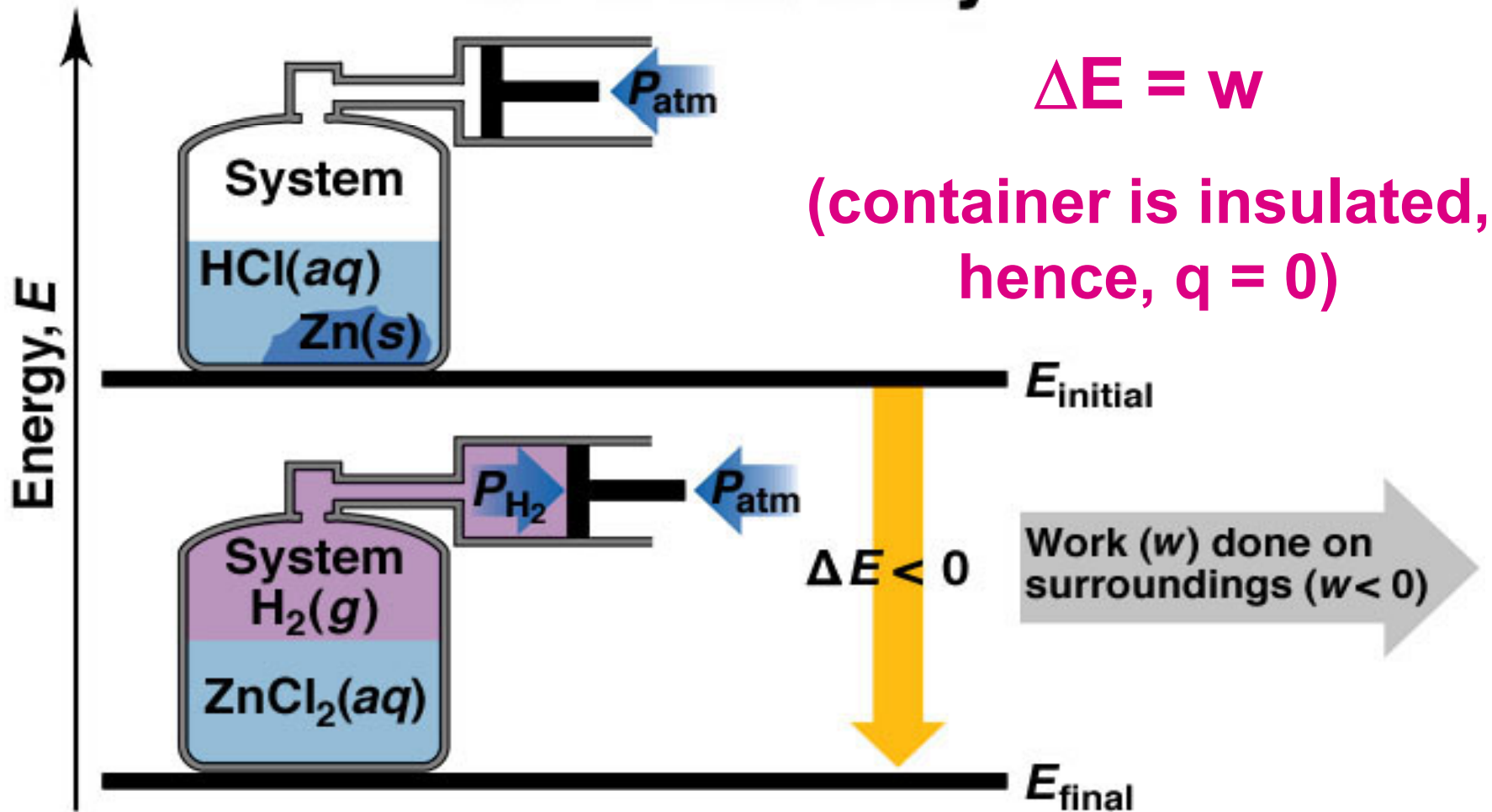
Fig. 6.4

Pressure-Volume Work

Surroundings

P

P

P

System

ΔV

System

Initial state

$w = -P\Delta V$

Final state

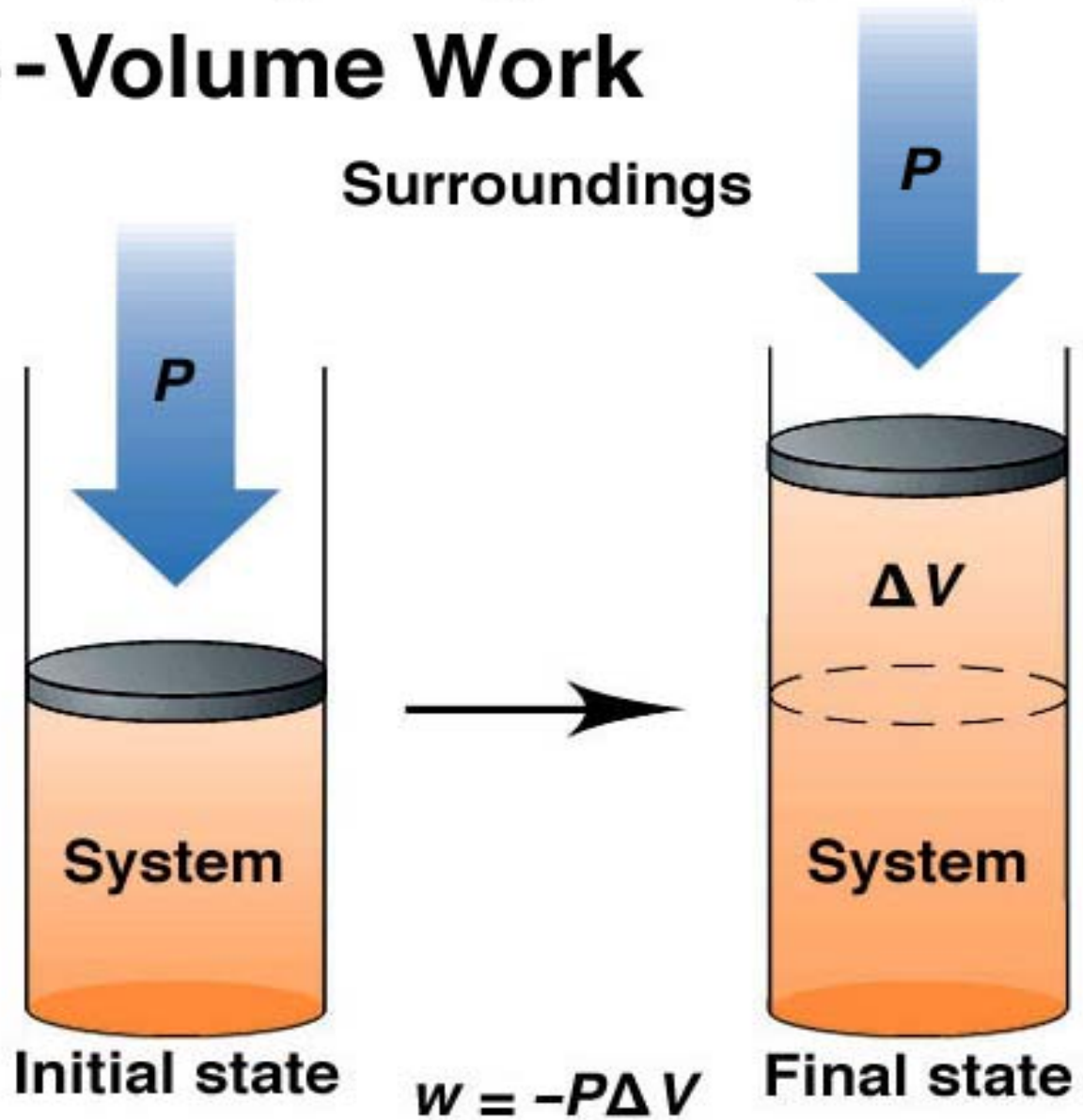## Fig. 6.7

Determining the Change in Internal Energy of a System

PROBLEM: When gasoline burns in a car engine, the heat released causes the products CO_2 and H_2O to expand, which pushes the pistons outward. Excess heat is removed by the car's cooling system. If the expanding gases do 451J of work on the pistons and the system loses 325J to the surroundings as heat, calculate the change in energy (ΔE) in J, kJ, and kcal.

PLAN: Define system and surrounds, assign signs to q and w and calculate ΔE. The answer should be converted from J to kJ and then to kcal.

SOLUTION:

$q = - 325J$ $w = - 451J$

$\Delta E = q + w =$ $-325J + (-451J) =$ $-776J$

$-776J$ $\dfrac{kJ}{10^3 J}$ $= 0.776kJ$ $0.776kJ$ $\dfrac{kcal}{4.18kJ}$ $= 0.776kcal$

6-10

Table 6.1   The Sign Conventions* for q, w and ΔE

q	$+$	w	$=$	ΔE
$+$		$+$		$+$
$+$		$-$		depends on *sizes* of q and w
$-$		$+$		depends on *sizes* of q and w
$-$		$-$		$-$

* For q: + means system <u>gains</u> heat; - means system <u>loses</u> heat.

* For w: + means word done <u>on</u> system; - means work done <u>by</u> system.

Reactions at Constant Volume
e.g. Bomb Calorimeters

- **Only energy changes, $\triangle E$, can be measured**
  - » Absolute energies can never be measured.....Why?
- **Recall: $\triangle E = q + w$**
  - » **q = heat energy; w = work performed**
- **Volume is constant in bomb calorimeter**
  - » **Therefore, w = 0**
- Thus... $\triangle E = q_v$
  - » Therefore....**all energy is released as heat at since it is not possible to perform work**

ΔH = Enthalpy Change
Heat of Reaction at Constant Pressure

- Most reactions occur at constant pressure, not at constant volume

- At constant pressure some of the energy produced by a reaction is used to do work.

- Therefore, <u>not all the energy of a rxn is released as heat</u>

- Since some E is used to do work:

$$\Delta E > \Delta H$$

(See the next slide for the proof)

ΔH = Enthalpy Change
Heat of Reaction at Constant Pressure

$\Delta H = q_p$ = heat of rxn at constant pressure

$\Delta E = q + w$ or $\Delta E = q_p + w$ or $\Delta E = \Delta H + w$

$\Delta H = \Delta E - w$

This means.....the heat of a reaction at constant pressure is less than the energy change of the rxn by the amount of work performed

The Meaning of Enthalpy

$$w = -P\Delta V$$

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

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

$$\Delta H \approx \Delta E \text{ in}$$

1. Reactions that do not involve gases.

2. Reactions in which the number of moles of gas does not change.

3. Reactions in which the number of moles of gas <u>does</u> change but q is >>> $P\Delta V$.

Some Important Types of Enthalpy Change

heat of combustion (ΔH_{comb})
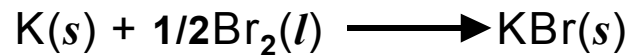
$$C_4H_{10}(l) + 13/2\,O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(g)$$

heat of formation (ΔH_f)

$$K(s) + 1/2\,Br_2(l) \longrightarrow KBr(s)$$

heat of fusion (ΔH_{fus})

$$NaCl(s) \longrightarrow NaCl(l)$$

heat of vaporization (ΔH_{vap})

$$C_6H_6(l) \longrightarrow C_6H_6(g)$$

Thermochemical Equations

$$N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g) \quad \Delta H^o = -92.2 \text{ kJ}$$
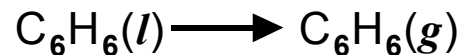
- Thermochemical equations always include physical states of reactants and products

- ΔH^o = Standard Heat (Enthalpy) of Rxn

  Enthalpy change Measured @

  Standard conditions: **25 °C and 1 atm. pressure**

- ΔH^o Depends on moles of reactants

ΔH = Enthalpy Change or Heat of Rxn

- **Enthalpy changes are State Functions**
  - » **Depend only on starting and ending points, not on the route taken**

    e.g. Seattle $\rightarrow$ NY

Hess's Law: The overall enthalpy change of a reaction that occurs in steps is equal to the sum of the standard enthalpy changes of the individual steps

$$A + B + D \rightarrow G + H \qquad \Delta H^o = ???$$

Steps:

1) $A + B \rightarrow C$ $\qquad \Delta H^o = -20. \text{ kJ}$

2) $C + D \rightarrow E + F$ $\qquad \Delta H^o = +35 \text{ kJ}$

3) $E + F \rightarrow G + H$ $\qquad \Delta H^o = -10. \text{ kJ}$

$$A + B + D \rightarrow G + H \qquad \Delta H^o = +5 \text{ kJ}$$

Rules for Manipulating Thermochemical Equations

- **Change the sign of ΔH^o if you reverse the equation**

- **Cancel formulas only if they are of the same physical state**

- **If you multiple or divide the coeficients of the equation, do so to ΔH^o too**
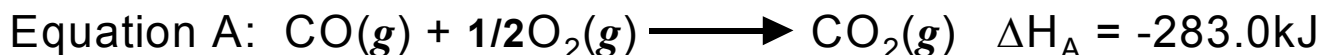
PROBLEM: Two gaseous pollutants that form auto exhaust are CO and NO. An environmental chemist is tudying ways to convert them to less harmful gases through the following equation:
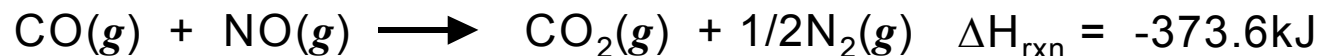
$$CO(g) + NO(g) \longrightarrow CO_2(g) + 1/2N_2(g) \quad \Delta H = ?$$

Given the following information, calculate the unknown ΔH:

Equation A: $CO(g) + \mathbf{1/2}O_2(g) \longrightarrow CO_2(g) \quad \Delta H_A = -283.0kJ$

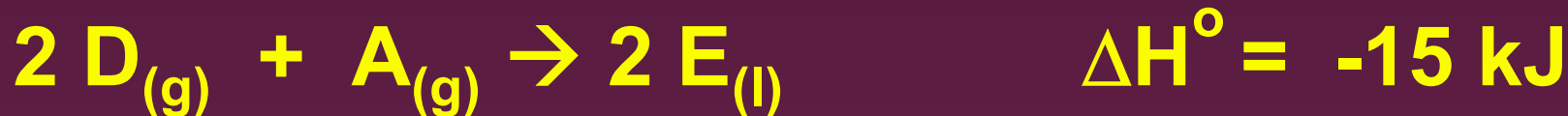Equation B: $N_2(g) + O_2(g) \longrightarrow 2NO(g) \quad \Delta H_B = 180.6kJ$

PLAN: Equations A and B have to be manipulated by reversal and/or multiplication by factors in order to sum to the first, or target, equation.

SOLUTION: Multiply Equation B by 1/2 and reverse it.

$$CO(g) + \mathbf{1/2}O_2(g) \longrightarrow CO_2(g) \quad \Delta H_A = -283.0kJ$$

$$NO(g) \longrightarrow 1/2N_2(g) + 1/2O_2(g) \quad \Delta H_B = -90.6kJ$$

$$CO(g) + NO(g) \longrightarrow CO_2(g) + 1/2N_2(g) \quad \Delta H_{rxn} = -373.6kJ$$

Another Example....

$A_{(g)}$ + 2 B $_{(g)}$ → 2 C$_{(s)}$ ΔH^{o} = ????

$C_{(s)}$ → $C_{(l)}$ ΔH^{o} = +5 kJ

2 D$_{(g)}$ + A$_{(g)}$ → 2 E$_{(l)}$ ΔH^{o} = -15 kJ

C$_{(l)}$ + D$_{(g)}$ → B$_{(g)}$ + E$_{(l)}$ ΔH^{o} = +35 kJ
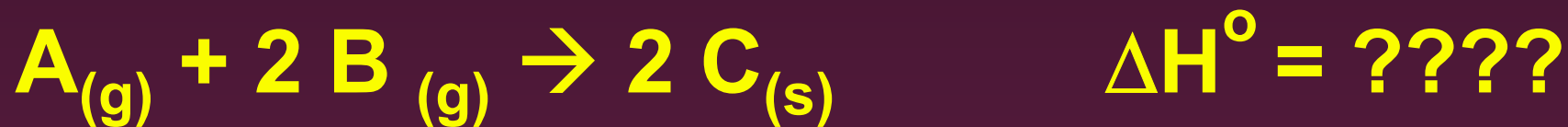
Ans. ΔH^{o} = -95 kJ

Writing Thermochemical Equations for ΔH_f^o

- ΔH_f^o = Standard enthalpy of formation

  » Enthalpy change associated with the formation of **one mole** of a substance from its **constituent elements**

- ΔH_f^o are used to calculate standard enthalpies of reaction, ΔH_{rxn}^o

  $\Delta H_{rxn}^o = \Sigma \Delta H_f^o \text{ Products} \quad - \quad \Sigma \Delta H_f^o \text{ Reactants}$

PROBLEM: Write balanced equations for the formation of 1 mol of the following compounds from their elements in their standard states and include ΔH^0_f.
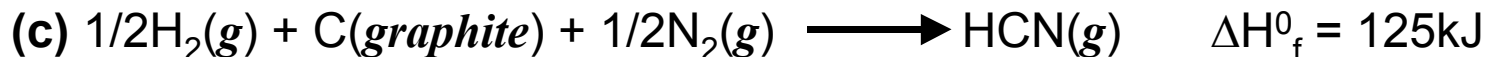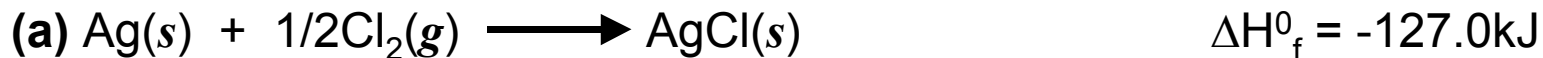
(a) Silver chloride, AgCl, a solid at standard conditions.

(b) Calcium carbonate, $CaCO_3$, a solid at standard conditions.

(c) Hydrogen cyanide, HCN, a gas at standard conditions.

PLAN: Use the table of heats of formation for values.

SOLUTION:

(a) $Ag(s) + 1/2Cl_2(g) \longrightarrow AgCl(s)$ $\Delta H^0_f = -127.0kJ$

(b) $Ca(s) + C(\textbf{\textit{graphite}}) + 3/2O_2(g) \longrightarrow CaCO_3(s)$ $\Delta H^0_f = -1206.9kJ$

(c) $1/2H_2(g) + C(\textbf{\textit{graphite}}) + 1/2N_2(g) \longrightarrow HCN(g)$ $\Delta H^0_f = 125kJ$

Practice
Writing Formation Equations

Write the thermochemical formation equations for

1. Sulfuric acid, H_2SO_4, $\Delta H_f^o = -833.32$ kJ
2. Methanol, CH_3OH, $\Delta H_f^o = -238.6$ kJ
3. Ethanol, CH_3CH_2OH, $\Delta H_f^o = -277.63$ kJ

Using ΔH_f^o to Calculate Standard Enthalpies of Reaction, ΔH^o

- $\Delta H^o_{rxn} = \Sigma \Delta H_f^o$ **Products** - $\Sigma \Delta H_f^o$ **Reactants**
  - → ΔH_f^o for all elements = 0
  - → Tables of ΔH_f^o can be found on page 240 and Appendix B (Silberberg 3ed)

PROBLEM: Nitric acid, whose worldwide annual production is about 8 billion kg, is used to make many products, including fertilizer, dyes, and explosives. The first step in the industrial production process is the oxidation of ammonia:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

Calculate ΔH^0_{rxn} from ΔH^0_f values.

PLAN: Look up the ΔH^0_f values and use Hess's Law to find ΔH_{rxn}.

SOLUTION: $\Delta H_{rxn} = \Sigma\, m\Delta H^0_f \text{ (products)} - \Sigma\, n\Delta H^0_f \text{ (reactants)}$

$\Delta H_{rxn} = [4(\Delta H^0_f\, NO(g) + 6(\Delta H^0_f\, H_2O(g)] - [4(\Delta H^0_f\, NH_3(g) + 5(\Delta H^0_f\, O_2(g)]$

$= (4mol)(90.3kJ/mol) + (6mol)(-241.8kJ/mol) -$

$[(4mol)(-45.9kJ/mol) + (5mol)(0kJ/mol)]$

$\Delta H_{rxn} = -906kJ$

Practice: Calculating Heats of Reaction from Standard Heats of Formation

1. **Which has a larger Standard Heat of Combustion, methanol, CH_3OH, or ethanol, C_2H_5OH? Use standard enthalpies of formation to calculate the standard heat of combustion for each alcohol.**

2. **Compare your value for methanol with the result from the bomb calorimeter, slide 44. Why the difference?**

Table 6.5 Selected Standard Heats of Formation at 25⁰C(298K)

Formula	ΔH^0_f(kJ/mol)	Formula	ΔH^0_f(kJ/mol)	Formula	ΔH^0_f(kJ/mol)
calcium		$Cl_2(g)$	0	silver	
Ca(s)	0	HCl(g)	-92.3	Ag(s)	0
CaO(s)	-635.1			AgCl(s)	-127.0
$CaCO_3$(s)	-1206.9	hydrogen			
		H(g)	218	sodium	
carbon		$H_2(g)$	0		
C(graphite)	0			Na(s)	0
C(diamond)	1.9	nitrogen		Na(g)	107.8
CO(g)	-110.5	$N_2(g)$	0	NaCl(s)	-411.1
$CO_2(g)$	-393.5	$NH_3(g)$	-45.9		
$CH_4(g)$	-74.9	NO(g)	90.3	sulfur	
CH_3OH(l)	-238.6			S_8(rhombic)	0
HCN(g)	135	oxygen		S_8(monoclinic)	2
CS_s(l)	87.9	$O_2(g)$	0	$SO_2(g)$	-296.8
		$O_3(g)$	143	$SO_3(g)$	-396.0
chlorine		$H_2O(g)$	-241.8		
Cl(g)	121.0	H_2O(l)	-285.8		

Using the Heat of Reaction (ΔH_{rxn}) to Find Amounts

PROBLEM: The major source of aluminum in the world is bauxite (mostly aluminum oxide). Its thermal decomposition can be represented by

$$Al_2O_3(s) \longrightarrow 2Al(s) + \textbf{3/2}O_2(g) \qquad \Delta H_{rxn} = 1676kJ$$

If aluminum is produced this way, how many grams of aluminum can form when $1.000 \times 10^3 kJ$ of heat is transferred?

PLAN:

SOLUTION:

heat(kJ)

1676kJ=2mol Al

mol of Al

x *M*

g of Al

$$1.000 \times 10^3 kJ \times \frac{2mol\ Al}{1676kJ} \quad \frac{26.98g\ Al}{1mol\ Al}$$

$$= 32.20g\ Al$$

Figure 6.12

Summary of the relationship between amount (mol) of substance and the heat (kJ) transferred during a reaction.

AMOUNT (mol) of compound A

molar ratio from balanced equation

AMOUNT (mol) of compound B

ΔH_{rxn} **(kJ/mol)**

HEAT (kJ) gained or lost