

# Thermochemistry: Energy Changes in Reactions

## Chapter 5

- Thermodynamics – The study of energy and its transformations
- Thermochemistry – The study of the relation between chemical reactions and changes in heat energy

# Heat

- energy transferred between two objects as a result of the temperature difference between them.

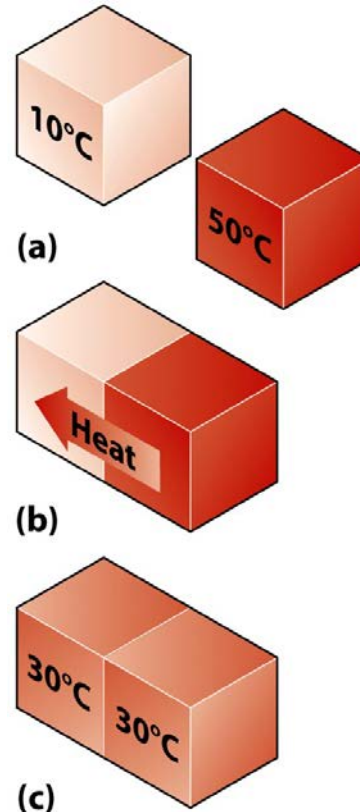
# Temperature

- A measure of kinetic energy

# Heat Transfer

The process of heat energy flowing from one object into another.

Will reach thermal equilibrium.



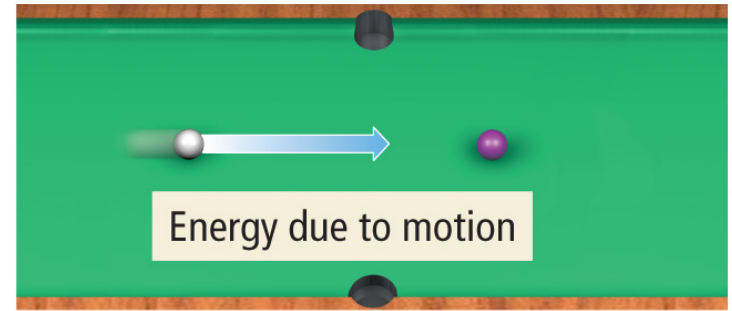
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# Types of Energy

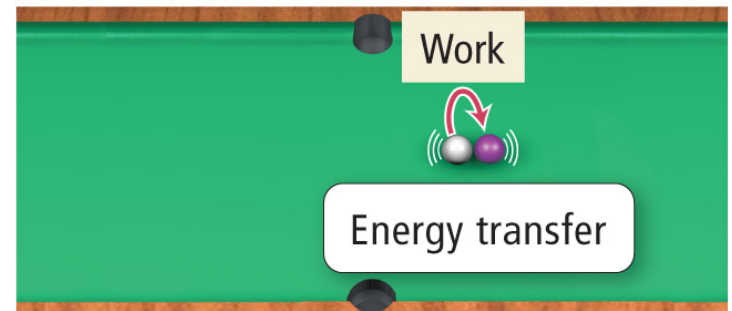
- Potential Energy –
  - Energy of position
- To a chemist –
  - The energy to be derived from a chemical reaction
  - Due to new atomic interactions

# Kinetic Energy

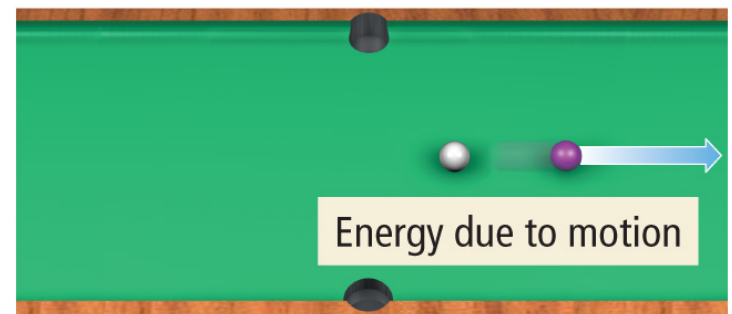
- energy of motion
- thermal energy is kinetic
- 
- $\frac{1}{2} mv^2$



(a)

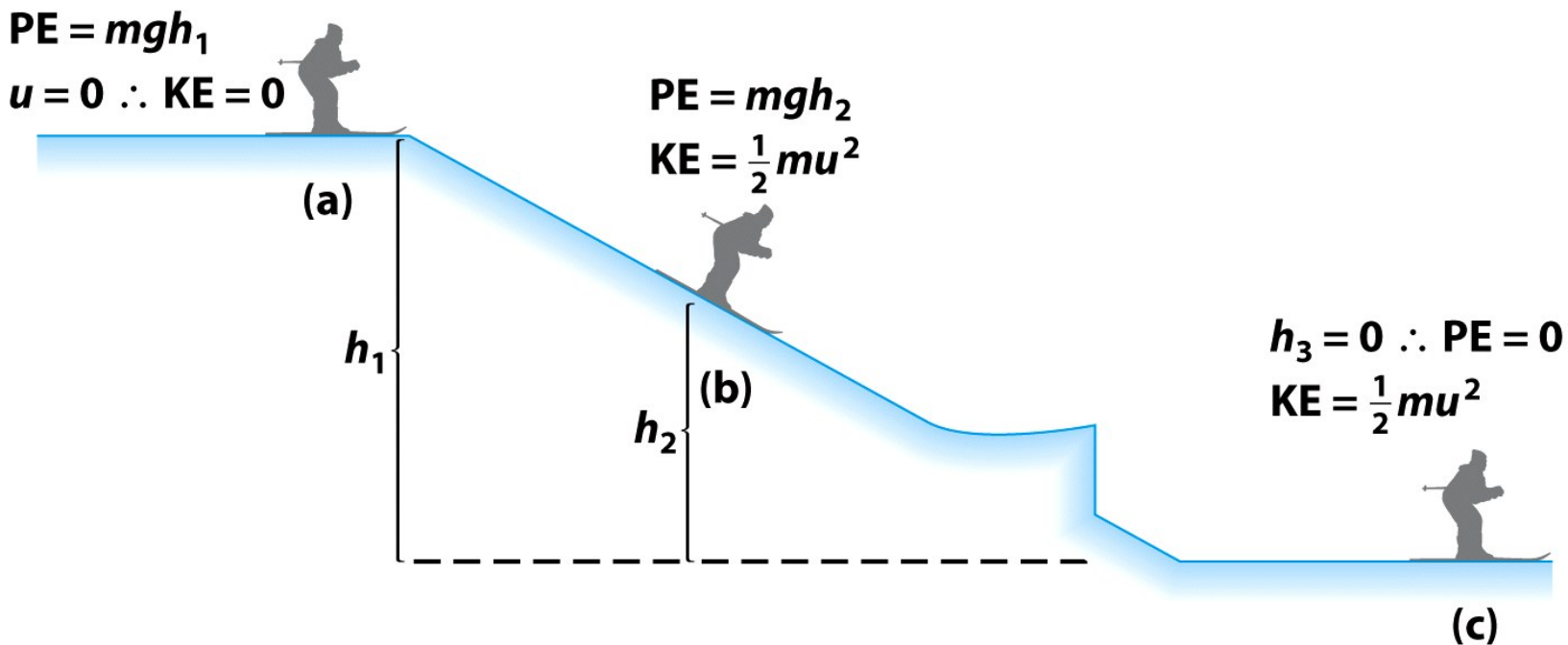


(b)



(c)

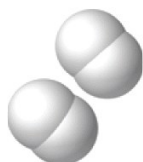
# Energy can be converted from one form to another



# Conversion of potential energy to kinetic energy



Chemistry: The Science in Context 2/e Figure 5.7a  
Reed Saxon/AP Images



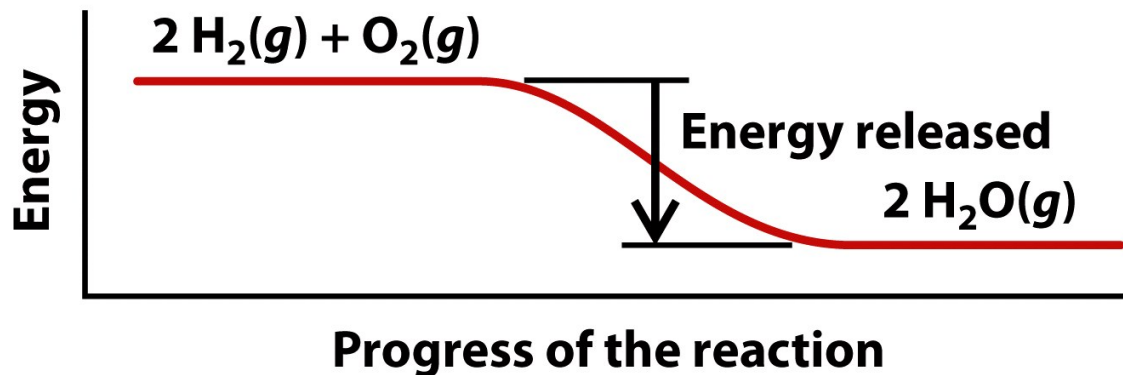
+



→



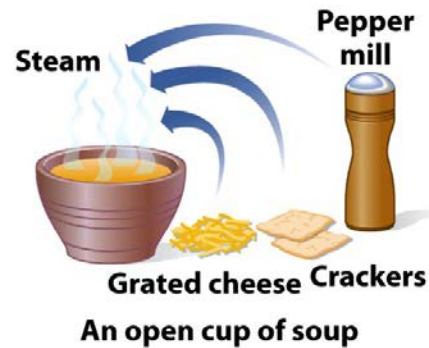
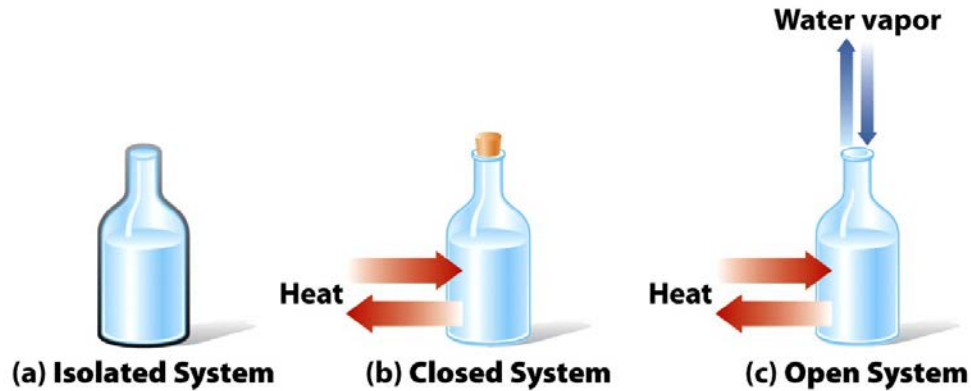
+ energy



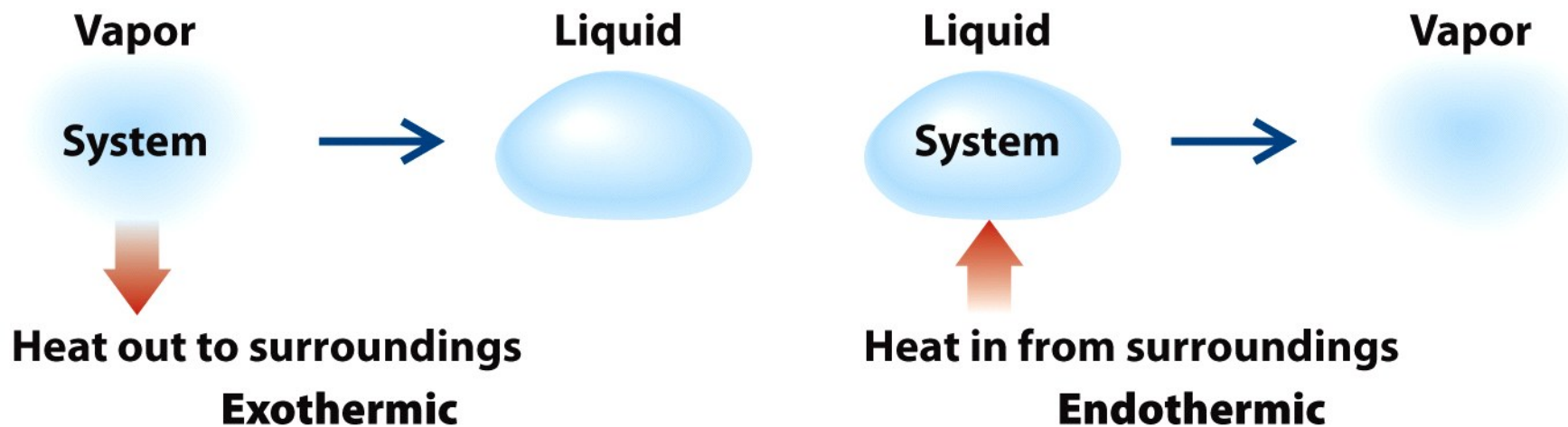
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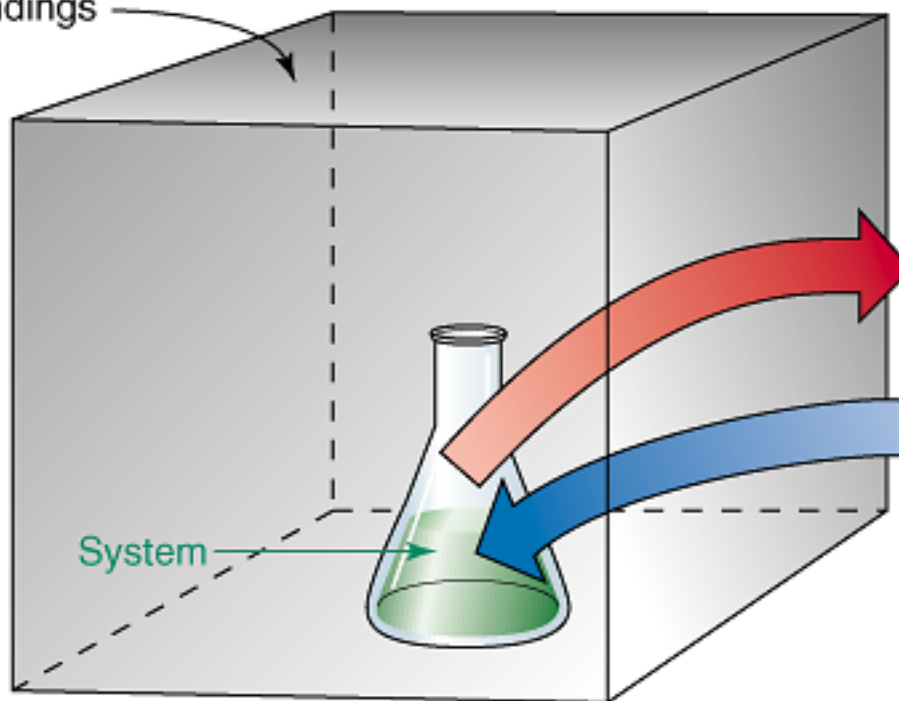
# Systems, Surroundings, and the Flow of Energy



- In an Exothermic process, heat flows from a system into its surroundings.
- In an Endothermic process, heat flows from the surroundings into the system



Surroundings



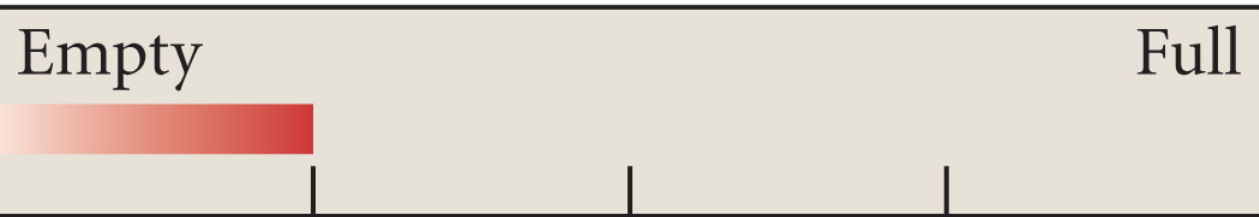
System

Energy out of system  
to surroundings: - sign

Energy into system  
from surroundings: + sign



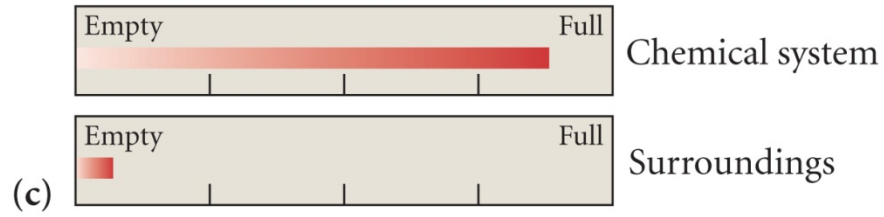
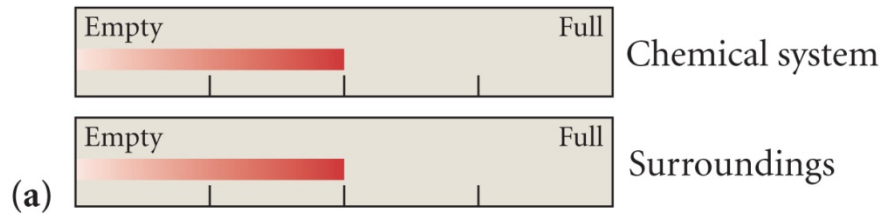
Chemical system



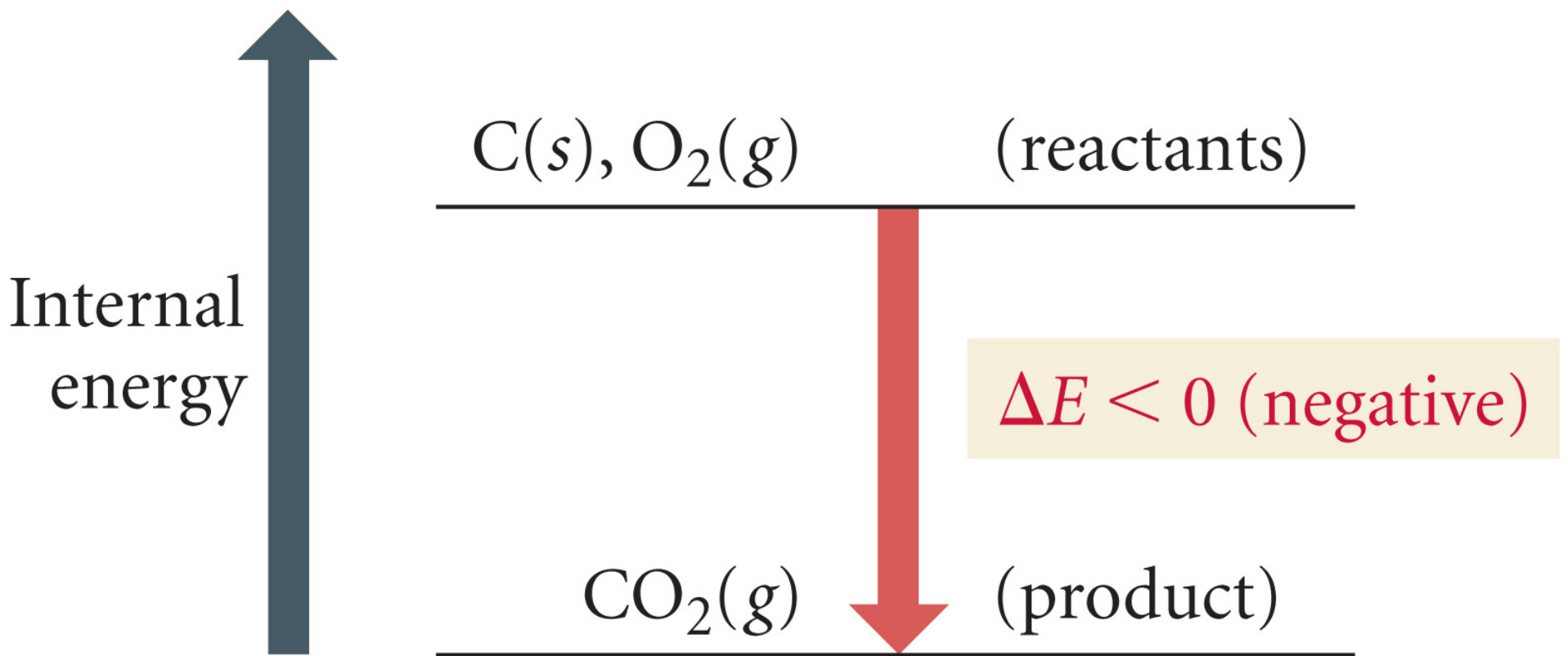
Surroundings

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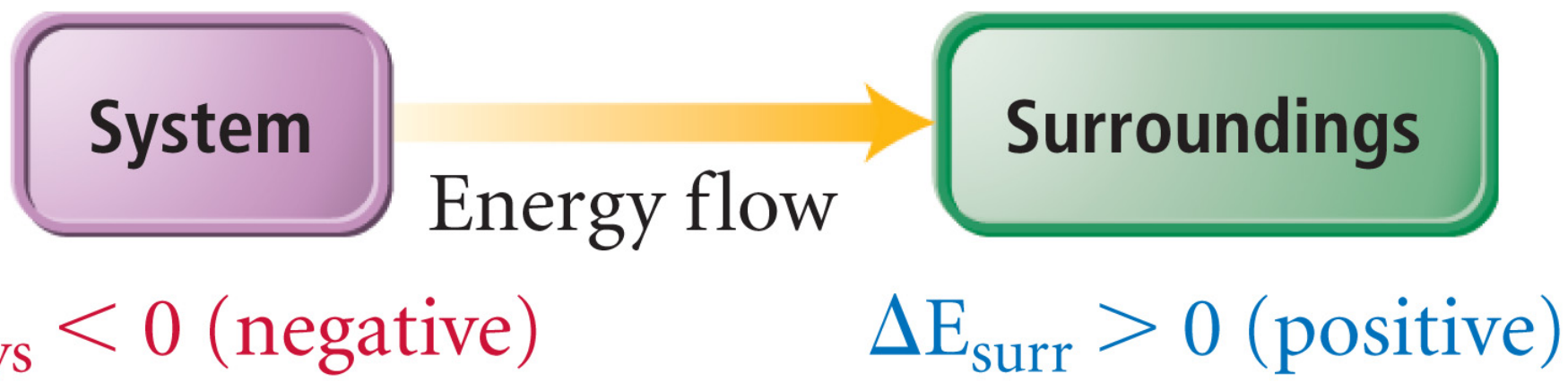
Which of the pictures at the right represents the energy gauge for the system above when the  $\Delta E_{\text{system}}$  is negative?



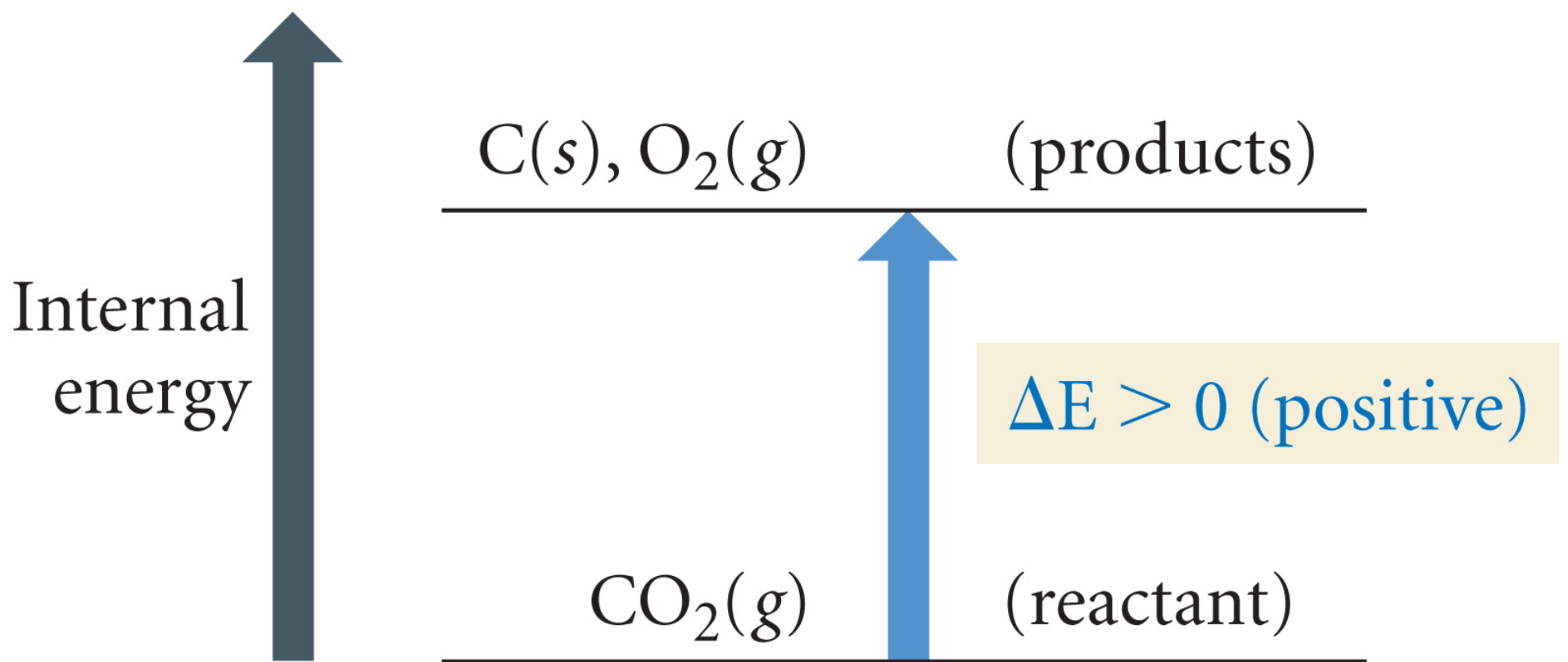
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$$\Delta E_{\text{sys}} > 0 \text{ (positive)}$$

$$\Delta E_{\text{surr}} < 0 \text{ (negative)}$$

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# 1st Law of Thermodynamics

- The energy of the universe is constant.
- i.e. the energy of the universe is conserved

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

- $-\Delta E$  if energy leaves system
- $+\Delta E$  if energy enters system
  
- Note the  $E$  of a system doesn't depend on how system got there -- i.e. it is a state function

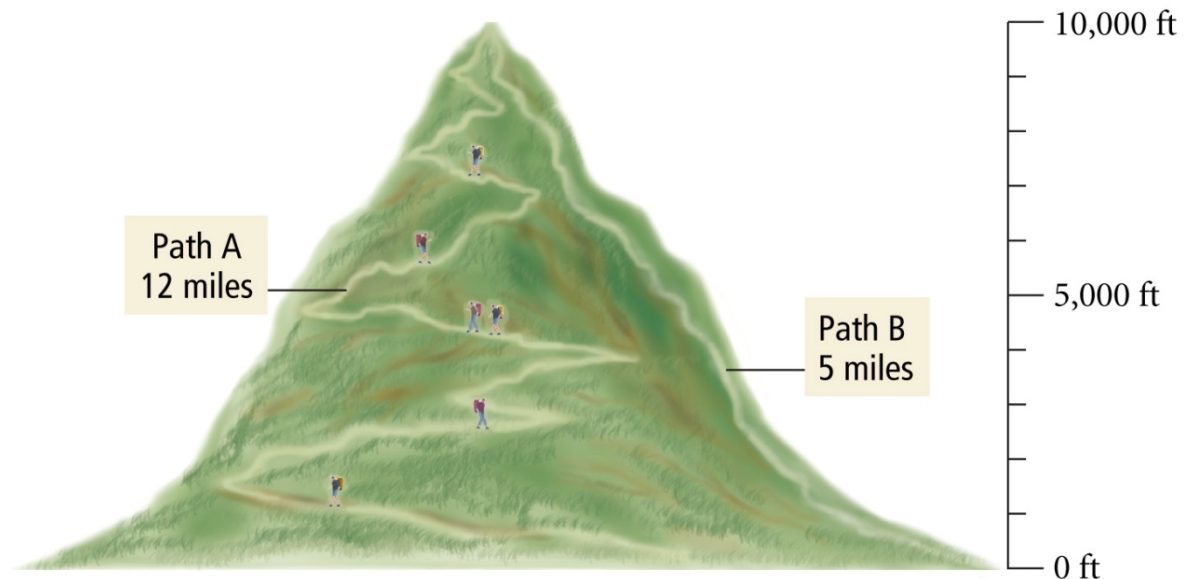


# State Function

- A function or property whose value depends only on the present state (condition) of the system, not on the path used to arrive at that condition.

## A State Function

Change in altitude depends only on the difference between the initial and final values, not on the path taken.

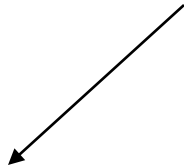


# Energy Units

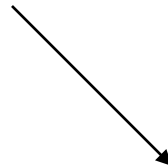
- Traditional unit – calorie
  - 1 calorie = energy to increase temperature of water by 1°C
  - 1 Calorie = food Calorie = 1kcal
- SI unit – joule
  - 4.184 joule = 1 cal

# Energy can be either work or heat

$$\Delta E = q + w$$

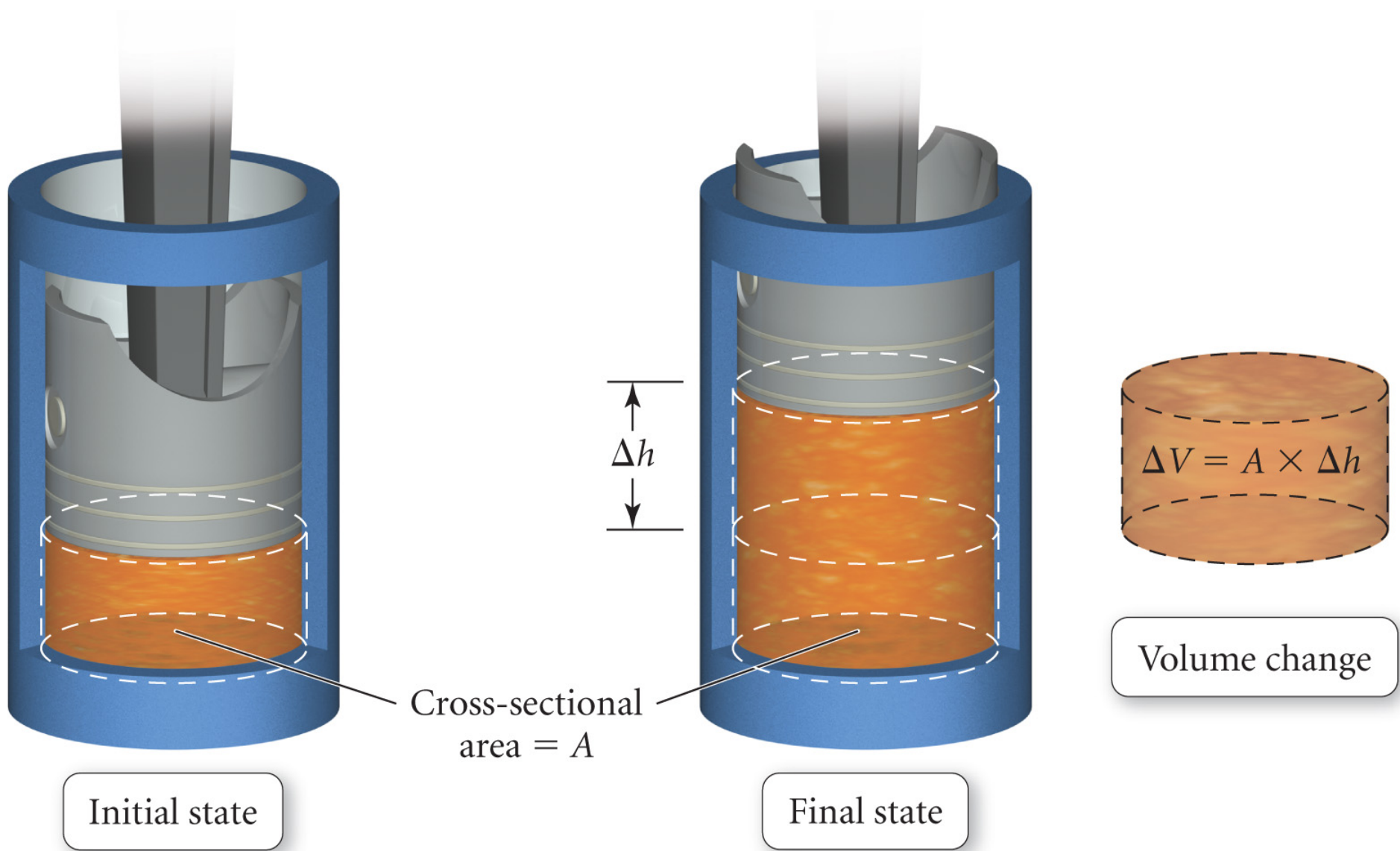


Heat gain or loss



Work done =  $-P\Delta V$

Matches our earlier convention that  $E_{\text{in}}$  is + and  $E_{\text{out}}$  is -



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Sample exercise 5.4

$$E = q + w = q - PV$$

At constant pressure this becomes

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

Define

$$H = E + PV$$

Or at constant pressure

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

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

$$\Delta H = \Delta E + P\Delta V = (q_p - P\Delta V) + P\Delta V = q_p$$

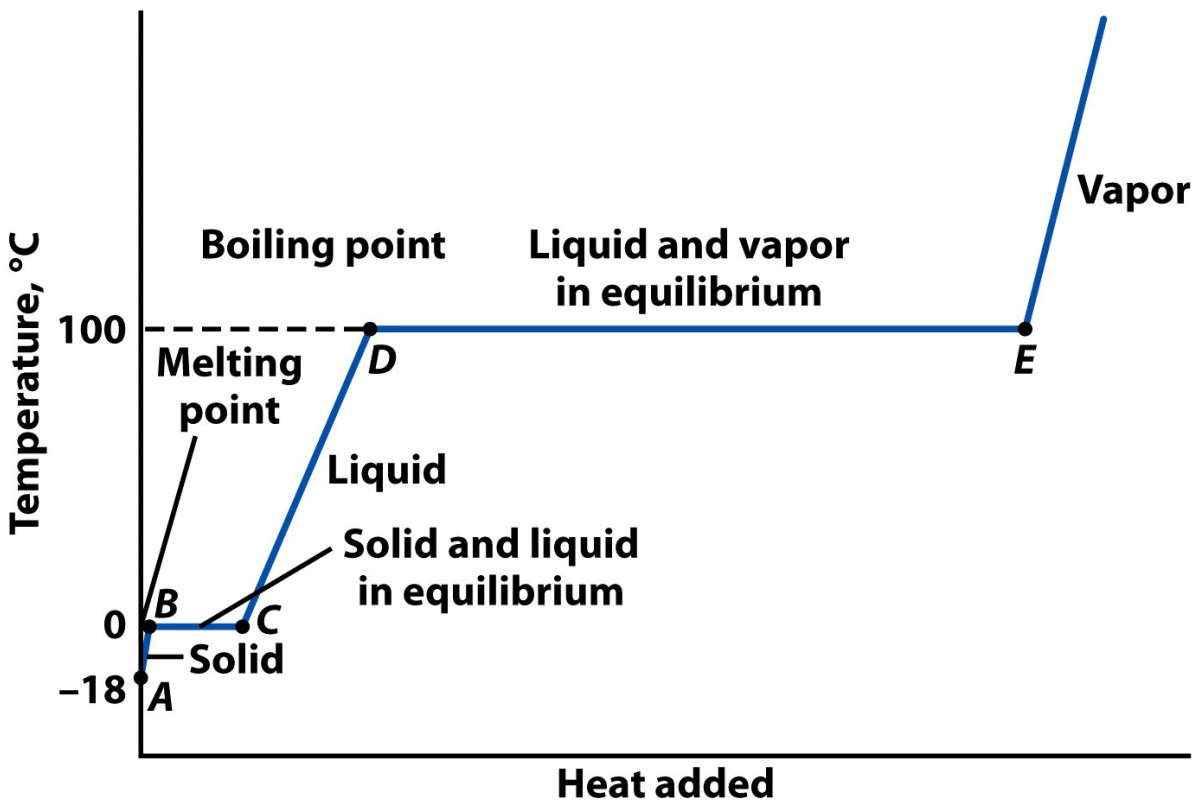
# Enthalpy

- $\Delta H = q_p = \Delta E + P\Delta V$
- $\Delta H = H_{\text{final}} - H_{\text{initial}}$
- $= H_{\text{products}} - H_{\text{reactants}}$

Sample exercises 5.5, 5.6  
HW 5.31 – 5.40



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Quantity of heat supplied

$$\text{Specific Heat Capacity or Specific Heat (C)} = \frac{q}{m \times \Delta T}$$

Tells how much heat is required to change the temp of a substance.

Temperature change  
(always  $T_f - T_i$ )

Some specific heats are

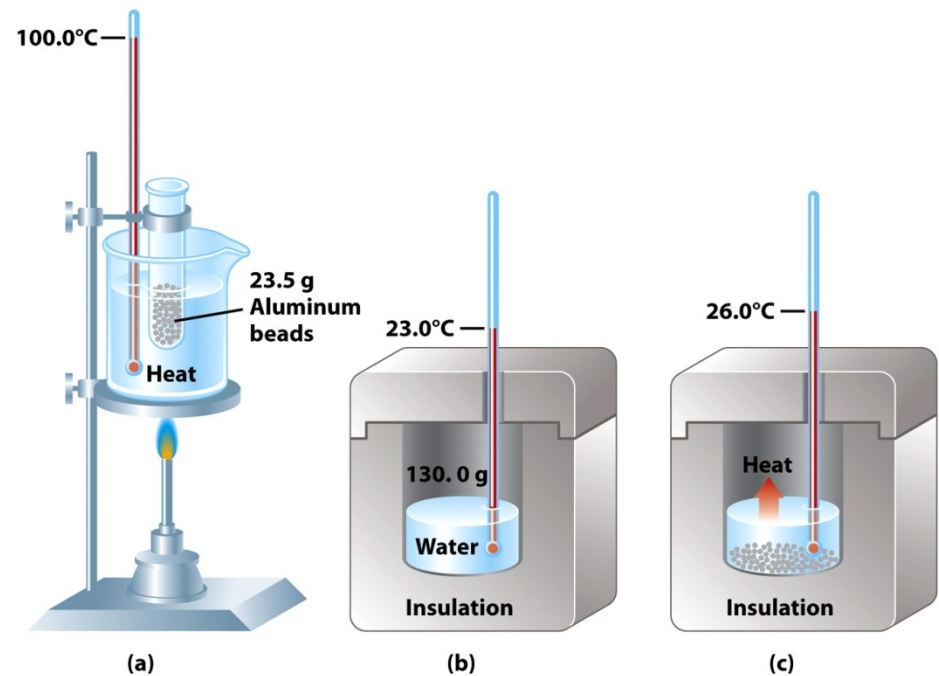
Al 0.902 J/g °K

Cu 0.385 J/g °K

H<sub>2</sub>O 4.184 J/g °K

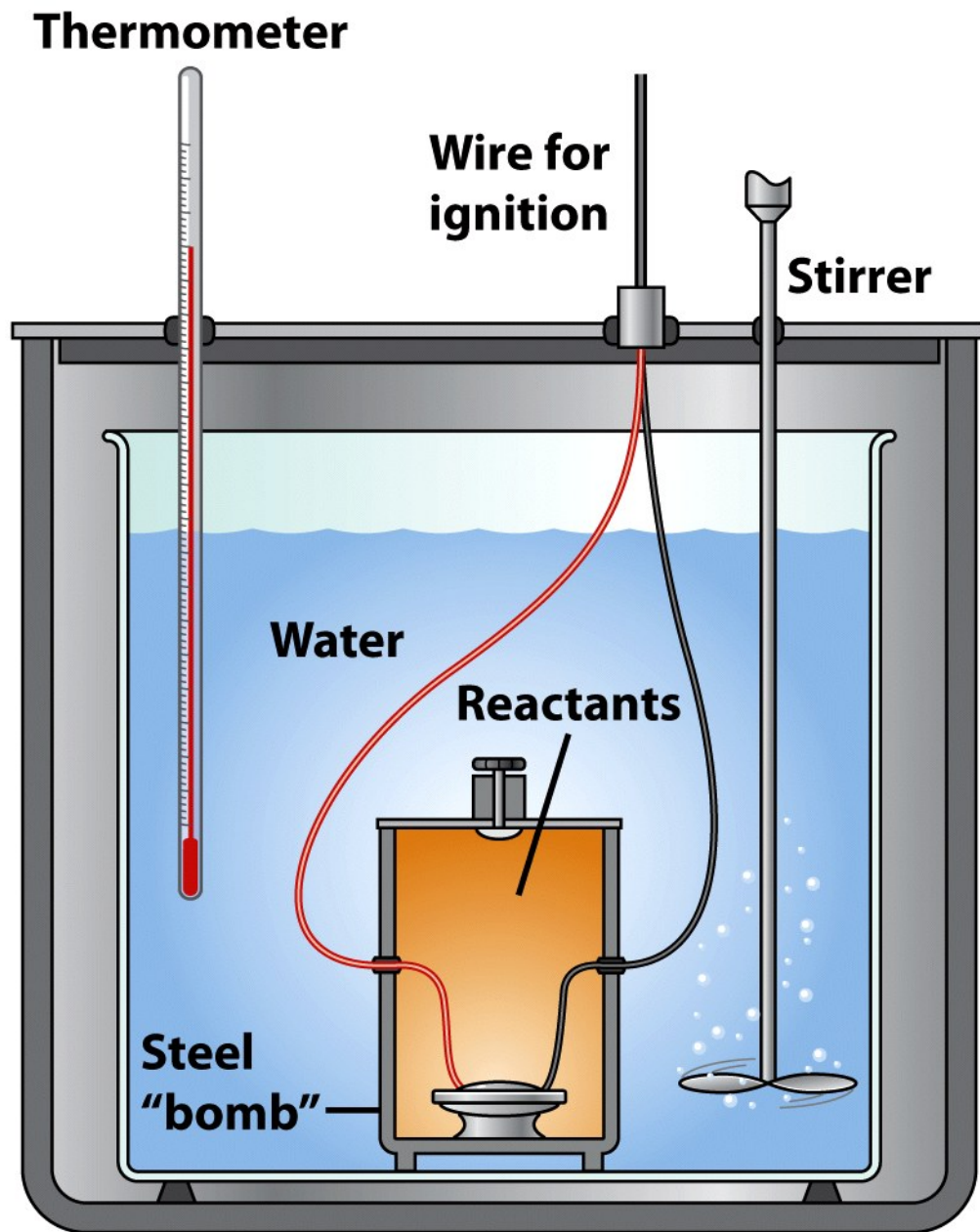


A 55.0 g piece of metal was heated in boiling water to a temperature of  $99.8^{\circ}\text{C}$  and dropped into an insulated beaker with 225 mL of water ( $d = 1.00 \text{ g/ml}$ ) at  $21.0^{\circ}\text{C}$ .



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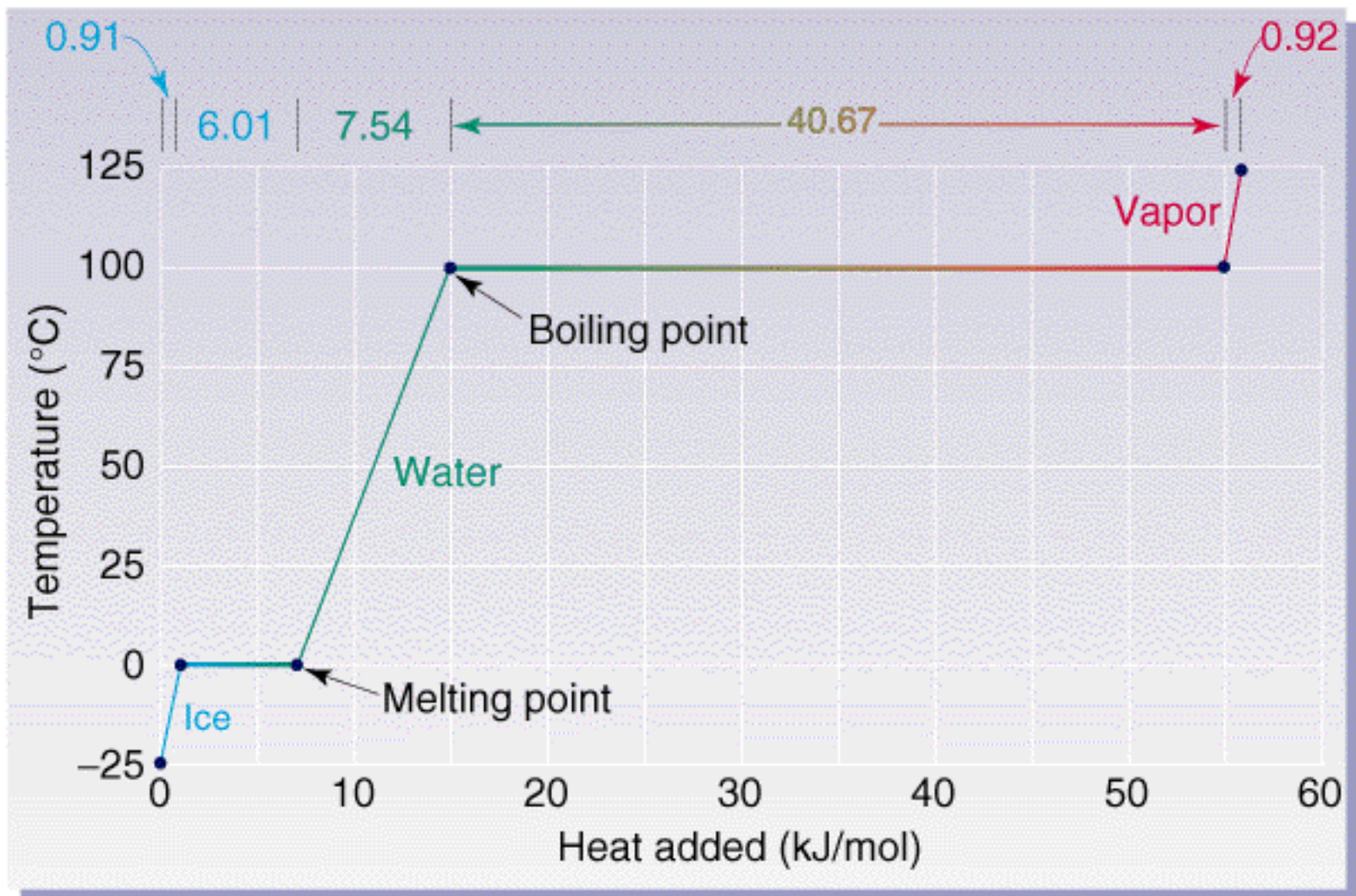
The final temperature of the metal and water is  $23.1^{\circ}\text{C}$ . Calculate the specific heat of the metal assuming that no heat was lost to the surroundings.



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- Octane,  $C_8H_{18}$ , a primary constituent of gasoline, burns in air.
- $C_8H_{18}(l) + 25/2 O_2(g) \longrightarrow 8 CO_2(g) + 9 H_2O(l)$
- Suppose that a 1.00 g sample of octane is burned in a calorimeter that contains 1.20 kg of water. The temperature of the water and the bomb rises from  $25.00^\circ C$  to  $33.20^\circ C$ . If the specific heat of the bomb,  $C_{\text{bomb}}$ , is known to be  $837 J/^\circ C$ , calculate the molar heat of reaction of  $C_8H_{18}$ .

Sample exercise 5.10, 5.11  
HW 5.57 – 5.72



A quantity of ice at  $0^{\circ}\text{C}$  is added to 90.0 g of water at  $80^{\circ}\text{C}$ . After the ice melted, the temperature of the water was  $25^{\circ}\text{C}$ . How much ice was added?

- specific heat of ice                      2.06 J/g $^{\circ}\text{C}$                       37.1 J/mol $^{\circ}\text{C}$
- specific heat of water                      4.184 J/g $^{\circ}\text{C}$                       75.4 J/mol $^{\circ}\text{C}$
- specific heat of steam                      2.0 J/g $^{\circ}\text{C}$                       36 J/mol $^{\circ}\text{C}$
- heat of fusion                      333 J/g                      6.01 kJ/mol
- heat of vaporization                      2260 J/g                      40.7 kJ/mol

- 50.0 g of ice at  $-20.0\text{ }^{\circ}\text{C}$  are added to 342.0 g of water at  $86.0\text{ }^{\circ}\text{C}$ . What will be the final temperature of the sample?

- |                          |                              |                               |
|--------------------------|------------------------------|-------------------------------|
| • specific heat of ice   | 2.06 J/g $^{\circ}\text{C}$  | 37.1 J/mol $^{\circ}\text{C}$ |
| • specific heat of water | 4.184 J/g $^{\circ}\text{C}$ | 75.4 J/mol $^{\circ}\text{C}$ |
| • specific heat of steam | 2.0 J/g $^{\circ}\text{C}$   | 36 J/mol $^{\circ}\text{C}$   |
| • heat of fusion         | 333 J/g                      | 6.01 kJ/mol                   |
| • heat of vaporization   | 2260 J/g                     | 40.7 kJ/mol                   |

Sample exercise 5.7, 5.8, 5.9  
HW #5.41 – 5.56

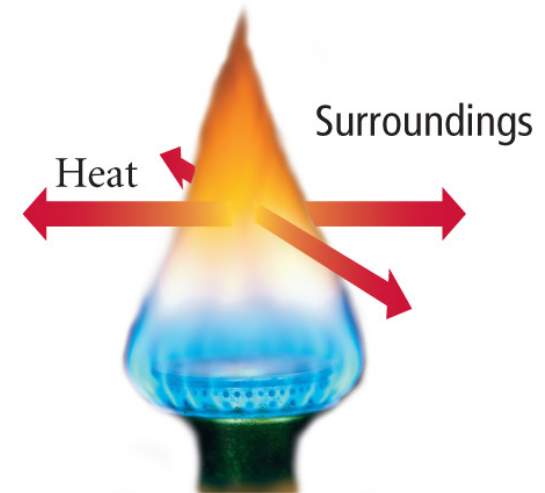
- A 33.14 g sample of copper and aluminum was heated to 119.25°C and dropped into a calorimeter containing 250.0 g of water at 21.00°C. The temperature rose to 23.05°C. Assuming no heat was lost to the surroundings, what is the percent copper in the sample?

# Enthalpy

- Enthalpy transferred out of reactants → exothermic →  $\Delta H = -$
- Enthalpy transferred into products → endothermic →  $\Delta H = +$



Endothermic

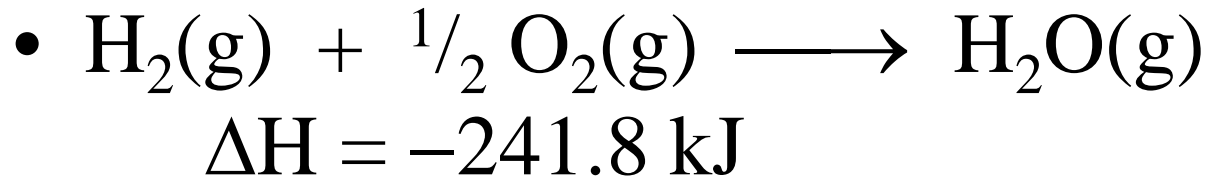
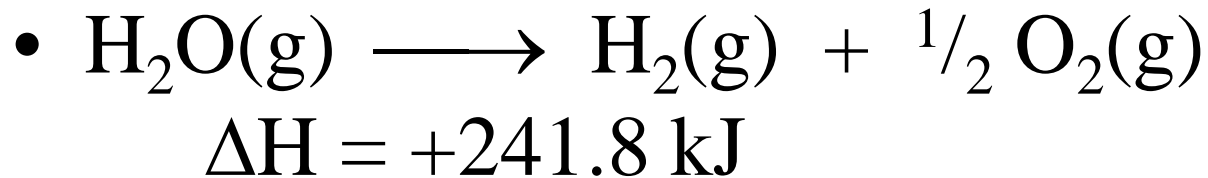


Exothermic



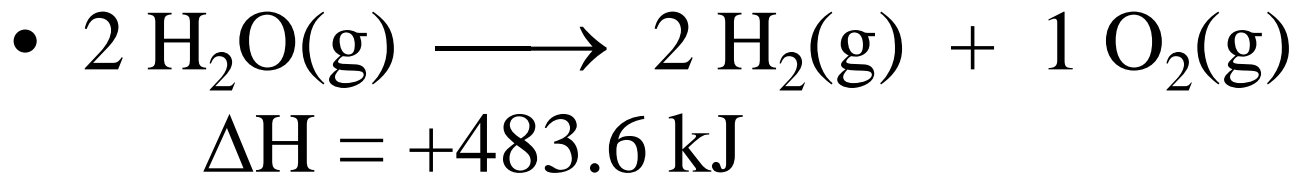
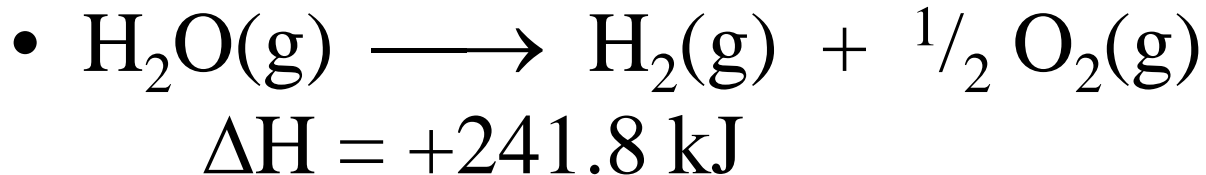
# Enthalpy

- $\Delta H_{\text{forward}} = -\Delta H_{\text{reverse}}$  (For reversible reactions)



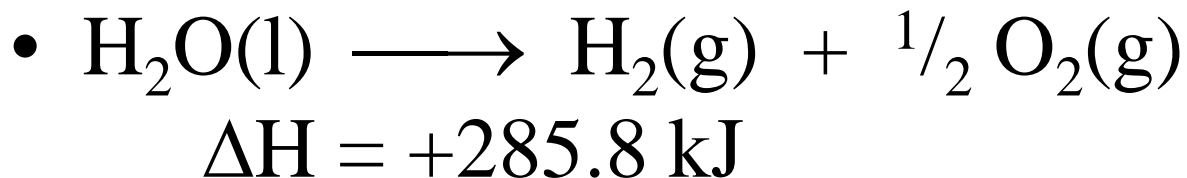
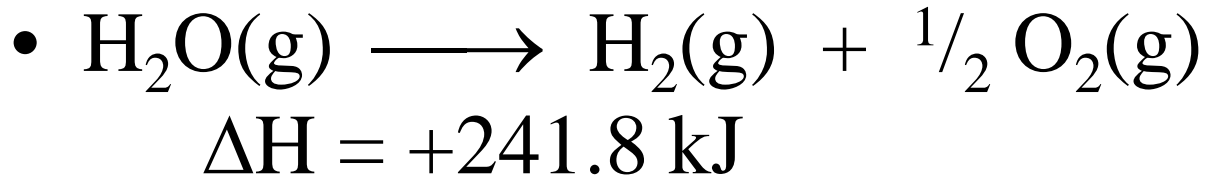
# Enthalpy

- The  $\Delta H$  is proportional to the amount of substance undergoing change.



# Enthalpy

- The physical state of reactants and products is important.

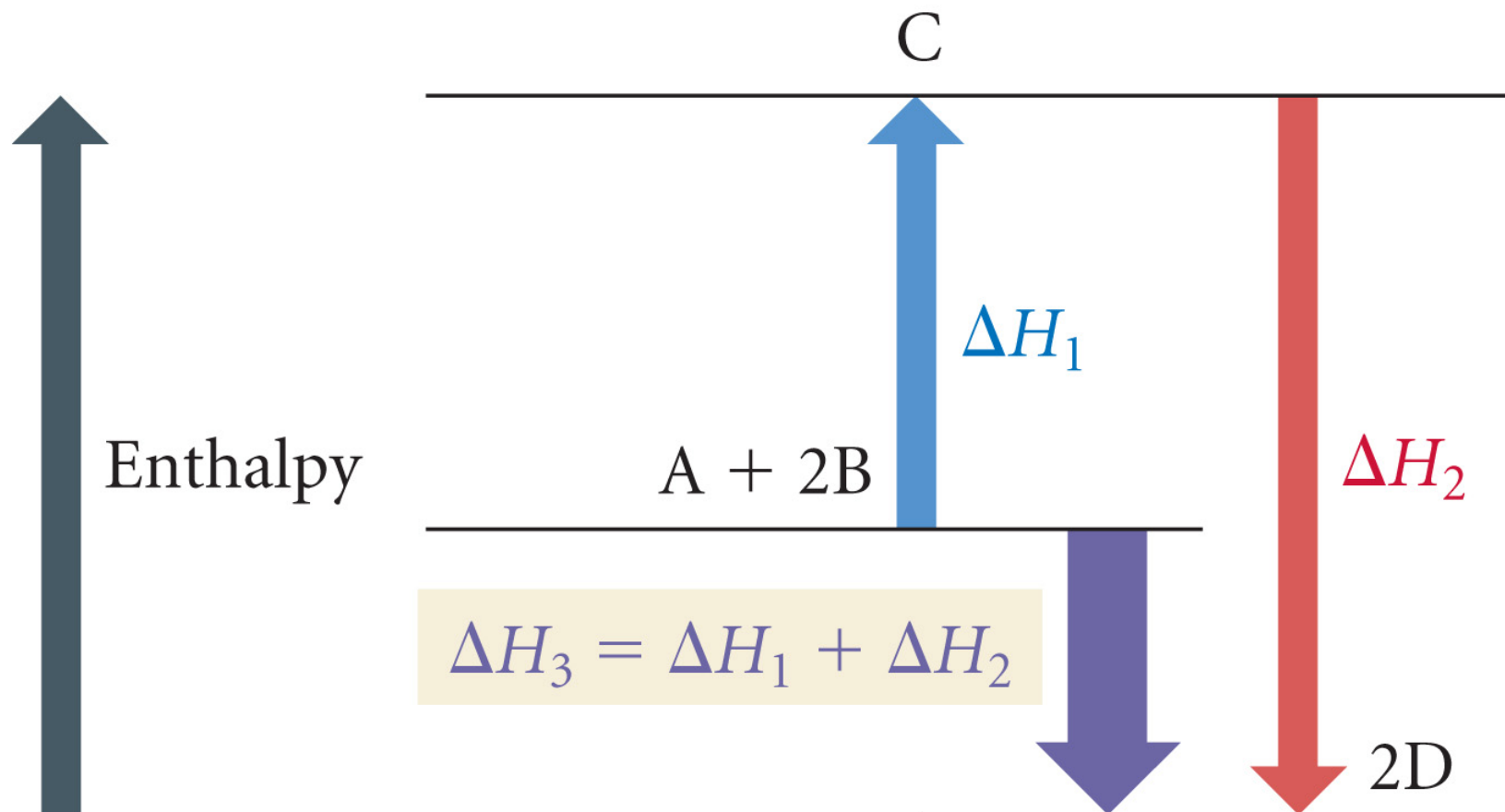


# Enthalpy

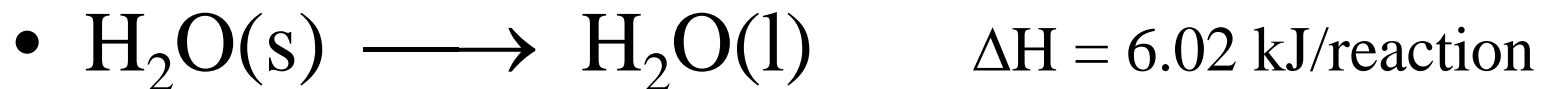
- Enthalpy is a state function -- it doesn't matter how you go from one place to another -- enthalpy and enthalpy changes are the same!!
- The  $\Delta H$  value is the same no matter how you get from  $A \rightarrow B$

# Hess's Law

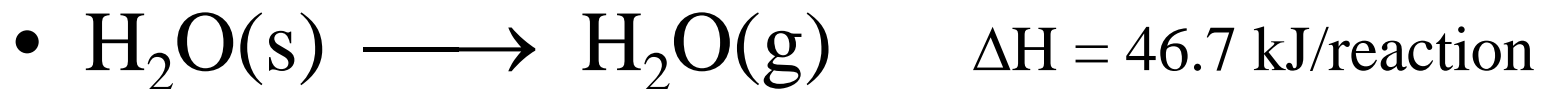
The change in enthalpy for a stepwise process is the sum of the enthalpy changes of the steps.

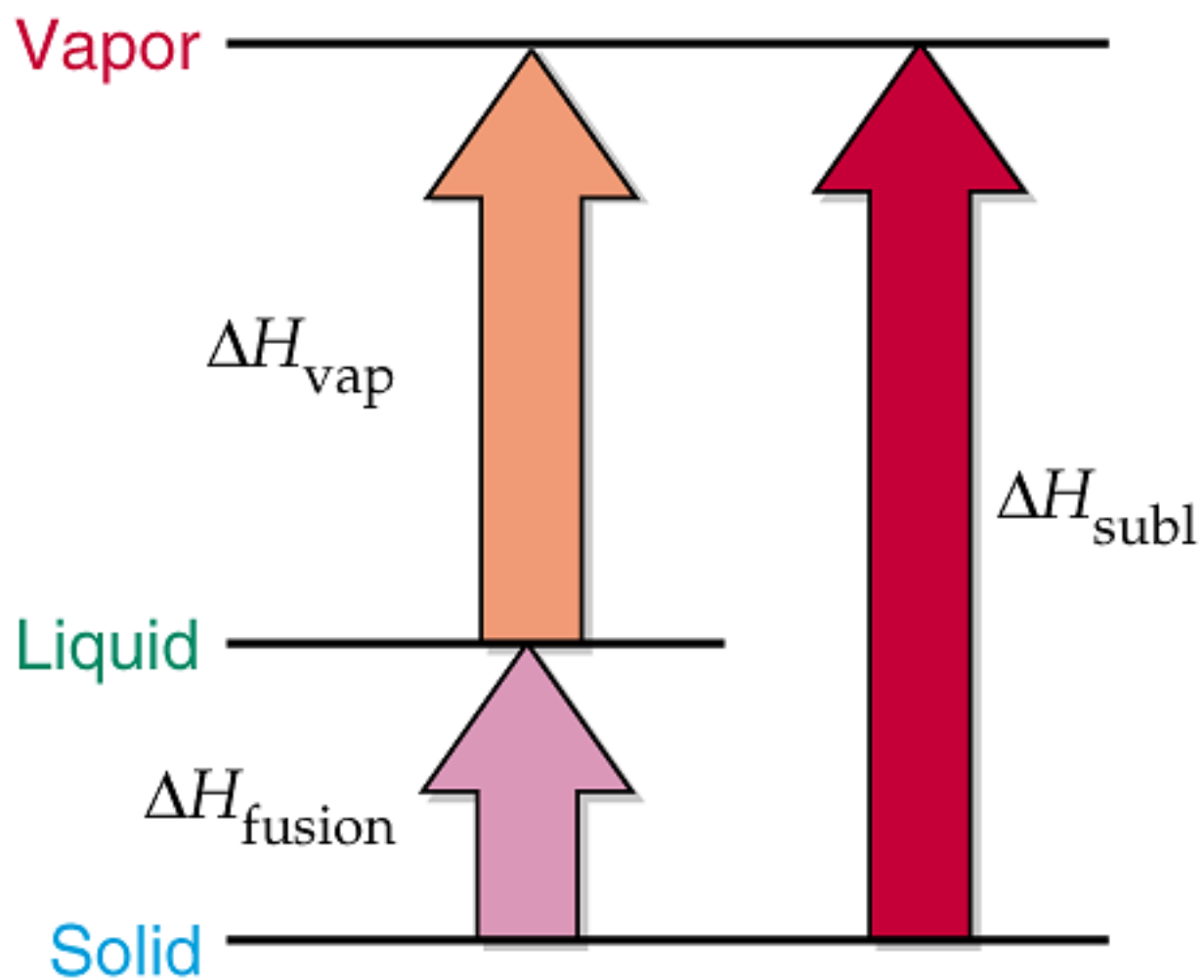


Determine the  $\Delta H$  for the sublimation of ice to water vapor at  $0^\circ\text{C}$ .



- -----

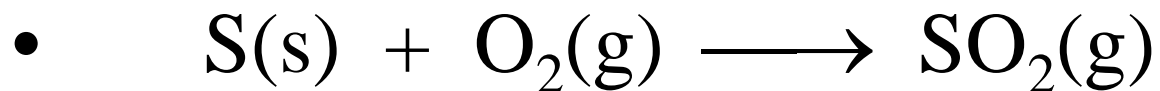




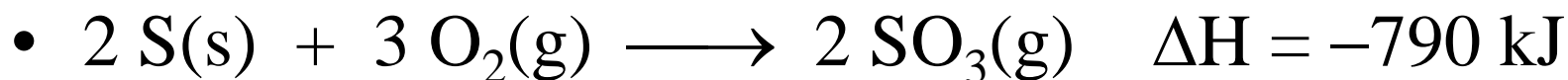
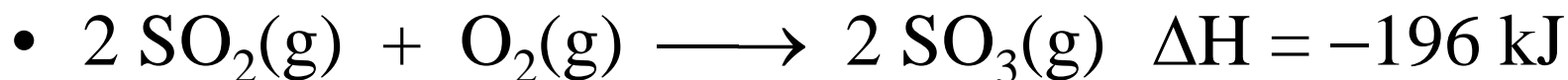
- Calculate the enthalpy change for the formation of methane, CH<sub>4</sub>, from solid carbon (as graphite) and hydrogen gas.
- $$\text{C(s)} + 2 \text{H}_2(\text{g}) \longrightarrow \text{CH}_4(\text{g})$$
- The enthalpies for the combustion of graphite, hydrogen gas and methane are given.
- $$\text{C(s)} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) \quad -393.5 \text{ kJ}$$
- $$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O(l)} \quad -285.8 \text{ kJ}$$
- $$\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O(l)} \quad -890.3 \text{ kJ}$$



- Calculate the enthalpy change for the reaction



- given



# Standard Heat of Formation

- The enthalpy change,  $\Delta H_f^\circ$ , for the formation of 1 mol of a substance in the standard state from the most stable forms of its constituent elements in their standard states.



superscript  $^\circ$  means  
standard state  
25°C and 1 atm pressure

subscript f means formation  
from most stable elements

Sample exercise 5.14

**TABLE 6.5** Standard Enthalpies of Formation,  $\Delta H_f^\circ$ , at 298 K

Formula	$\Delta H_f^\circ$ (kJ/mol)	Formula	$\Delta H_f^\circ$ (kJ/mol)	Formula	$\Delta H_f^\circ$ (kJ/mol)
<i>Bromine</i>		C <sub>3</sub> H <sub>8</sub> O( <i>l</i> , isopropanol)	−318.1	<i>Oxygen</i>	
Br( <i>g</i> )	111.9	C <sub>6</sub> H <sub>6</sub> ( <i>l</i> )	49.1	O <sub>2</sub> ( <i>g</i> )	0
Br <sub>2</sub> ( <i>l</i> )	0	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> ( <i>s</i> , glucose)	−1273.3	O <sub>3</sub> ( <i>g</i> )	142.7
HBr( <i>g</i> )	−36.3	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ( <i>s</i> , sucrose)	−2226.1	H <sub>2</sub> O( <i>g</i> )	−241.8
<i>Calcium</i>		<i>Chlorine</i>		H <sub>2</sub> O( <i>l</i> )	−285.8
Ca( <i>s</i> )	0	Cl( <i>g</i> )	121.3	<i>Silver</i>	
CaO( <i>s</i> )	−634.9	Cl <sub>2</sub> ( <i>g</i> )	0	Ag( <i>s</i> )	0
CaCO <sub>3</sub> ( <i>s</i> )	−1207.6	HCl( <i>g</i> )	−92.3	AgCl( <i>s</i> )	−127.0
<i>Carbon</i>		<i>Fluorine</i>		<i>Sodium</i>	
C( <i>s</i> , graphite)	0	F( <i>g</i> )	79.38	Na( <i>s</i> )	0
C( <i>s</i> , diamond)	1.88	F <sub>2</sub> ( <i>g</i> )	0	Na( <i>g</i> )	107.5
CO( <i>g</i> )	−110.5	HF( <i>g</i> )	−273.3	NaCl( <i>s</i> )	−411.2
CO <sub>2</sub> ( <i>g</i> )	−393.5	<i>Hydrogen</i>		Na <sub>2</sub> CO <sub>3</sub> ( <i>s</i> )	−1130.7
CH <sub>4</sub> ( <i>g</i> )	−74.6	H( <i>g</i> )	218.0	NaHCO <sub>3</sub> ( <i>s</i> )	−950.8
CH <sub>3</sub> OH( <i>l</i> )	−238.6	H <sub>2</sub> ( <i>g</i> )	0	<i>Sulfur</i>	
C <sub>2</sub> H <sub>2</sub> ( <i>g</i> )	227.4	<i>Nitrogen</i>		S <sub>8</sub> ( <i>s</i> , rhombic)	0
C <sub>2</sub> H <sub>4</sub> ( <i>g</i> )	52.4	N <sub>2</sub> ( <i>g</i> )	0	S <sub>8</sub> ( <i>s</i> , monoclinic)	0.3
C <sub>2</sub> H <sub>6</sub> ( <i>g</i> )	−84.68	NH <sub>3</sub> ( <i>g</i> )	−45.9	SO <sub>2</sub> ( <i>g</i> )	−296.8
C <sub>2</sub> H <sub>5</sub> OH( <i>l</i> )	−277.6	NH <sub>4</sub> NO <sub>3</sub> ( <i>s</i> )	−365.6	SO <sub>3</sub> ( <i>g</i> )	−395.7
C <sub>3</sub> H <sub>8</sub> ( <i>g</i> )	−103.85	NO( <i>g</i> )	91.3	H <sub>2</sub> SO <sub>4</sub> ( <i>l</i> )	−814.0
C <sub>3</sub> H <sub>6</sub> O( <i>l</i> , acetone)	−248.4	N <sub>2</sub> O( <i>g</i> )	81.6		



$\Delta H_f^\circ$ 's

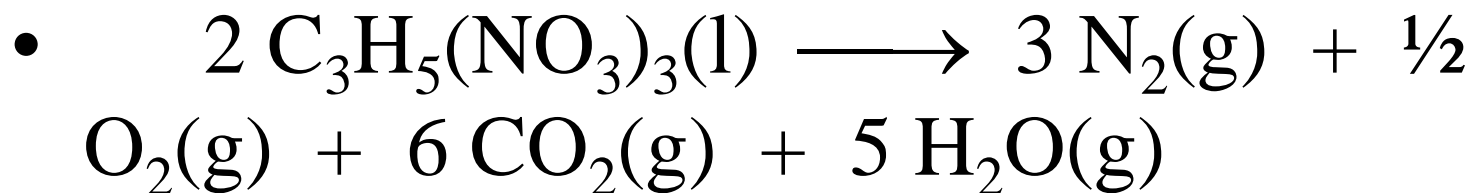
$\Delta H_{\text{rxn}}^\circ$

$$\Delta H_{\text{rxn}}^\circ = \sum n_p \Delta H_f^\circ (\text{products}) - \sum n_r \Delta H_f^\circ (\text{reactants})$$

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- Benzene,  $C_6H_6$ , is an important hydrocarbon. Calculate its enthalpy of combustion; that is, find the value of  $\Delta H^\circ$  for the following reaction.
- $C_6H_6(l) + 15/2 O_2(g) \longrightarrow 6 CO_2(g) + 3 H_2O(l)$
- Given
- $\Delta H_f^\circ [C_6H_6(l)] = +49.0 \text{ kJ/mol}$
- $\Delta H_f^\circ [CO_2(g)] = -393.5 \text{ kJ/mol}$
- $\Delta H_f^\circ [H_2O(l)] = -285.8 \text{ kJ/mol}$

- Nitroglycerin is a powerful explosive, giving four different gases when detonated.



- Given the enthalpy of formation of nitroglycerin,  $\Delta H_f^\circ$ , is  $-364 \text{ kJ/mol}$ , calculate the energy liberated when  $10.0 \text{ g}$  of nitroglycerin is detonated.

# Enthalpies from Bond Energies

- Calculate the enthalpy of formation of water vapor from bond energies.

- 



- (The experimental value is  $-241.8\text{kJ/mol}$ )

**TABLE 7.1 Average Bond Dissociation Energies,  $D$  (kJ/mol)\***

H—H	436*	C—H	410	N—H	390	O—H	460	F—F	159*
H—C	410	C—C	350	N—C	300	O—C	350	Cl—Cl	243*
H—F	570*	C—F	450	N—F	270	O—F	180	Br—Br	193*
H—Cl	432*	C—Cl	330	N—Cl	200	O—Cl	200	I—I	151*
H—Br	366*	C—Br	270	N—Br	240	O—Br	210	S—F	310
H—I	298*	C—I	240	N—I	—	O—I	220	S—Cl	250
H—N	390	C—N	300	N—N	240	O—N	200	S—Br	210
H—O	460	C—O	350	N—O	200	O—O	180	S—S	225
H—S	340	C—S	260	N—S	—	O—S	—		
Multiple covalent bonds †									
C=C	611	C≡C	835	C=O	732	O=O	498*	N≡N	945*

\* Bond dissociation energies for diatomic molecules are exact.

† We'll discuss multiple covalent bonds in Section 7.5.



- Oxygen difluoride,  $\text{OF}_2$ , is a colorless, very poisonous gas that reacts rapidly and exothermically with water vapor to produce  $\text{O}_2$  and HF. Calculate the  $\Delta H^\circ_f$  for  $\text{OF}_2$ .
- $$\text{OF}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow 2 \text{HF}(\text{g}) + \text{O}_2(\text{g})$$
$$\Delta H^\circ_{\text{rxn}} = -318 \text{ kJ}$$
- The heats of formation for  $\text{H}_2\text{O}(\text{g})$  and  $\text{HF}(\text{g})$  are  $-241.8 \text{ kJ/mol}$  and  $-271.1 \text{ kJ/mol}$  respectively.

# Energy Units

- 1 calorie = 4.184 J
- 1 food calorie = 1 Cal = 1 kcal = 1000 cal
- Given the reaction below for the combustion of glucose to form carbon dioxide and water, calculate the Calories/g for carbohydrates.
- $$\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{O}_2(\text{g}) \rightarrow 6 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l})$$
$$\Delta H_{\text{rxn}} = -2801.6 \text{ kJ}$$

- M & M candies consist of 70% carbohydrates, 21% fat, and 4.6% protein as well as other ingredients that do not have caloric value. What quantity of energy is generated if 47.9 g of M&Ms (1 small package) were burned in a bomb calorimeter? How long will a I need to walk to use up the value of the M&Ms if 1 hour of walking uses up 400 Cal?

- 4 Cal/g carbs
- 4 Cal/g protein
- 9 Cal/g fat

# Stoichiometry using Enthalpy

- Consider the following reaction:
- $2 \text{Na(s)} + \text{Cl}_2(\text{g}) \longrightarrow 2 \text{NaCl(s)} \quad \Delta H = -821.8 \text{ kJ}$
- Is the reaction exothermic or endothermic?
- Calculate the amount of heat transferred when 8.0 g of Na(s) reacts according to this reaction.

- We generally expect that reactions evolving heat should proceed spontaneously and those that absorb heat should require energy to occur.
  - Mix barium hydroxide and ammonium chloride



# Entropy

- The amount of randomness, or molecular disorder, in a system.
- $S$  = more positive to indicate greater disorder.

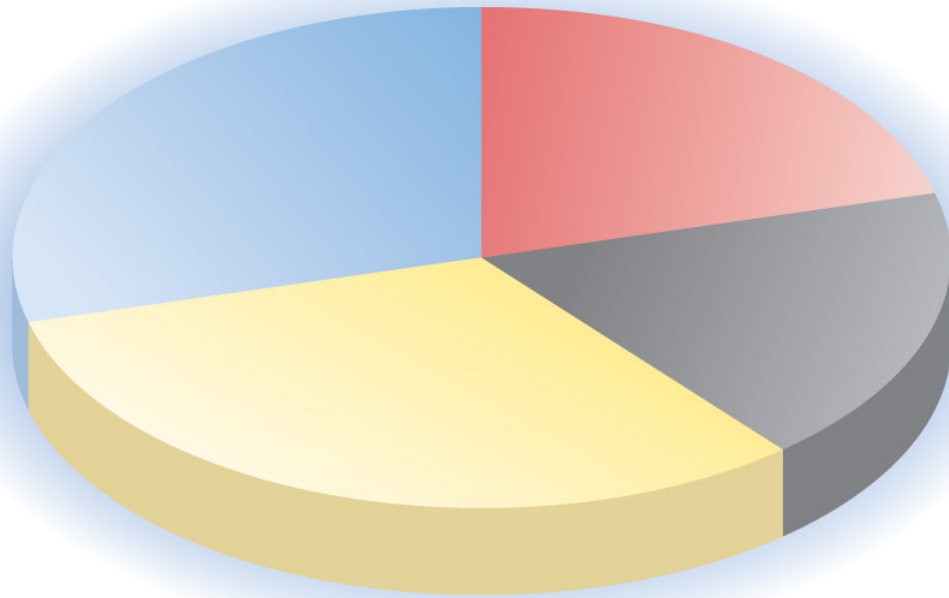
# Gibbs Free Energy, $\Delta G$

- Determines whether a reaction is spontaneous and at what temperature it becomes spontaneous.
- Spontaneous -- A process that proceeds on its own with out any continuous external influence.

$$\Delta G = \Delta H - T\Delta S$$

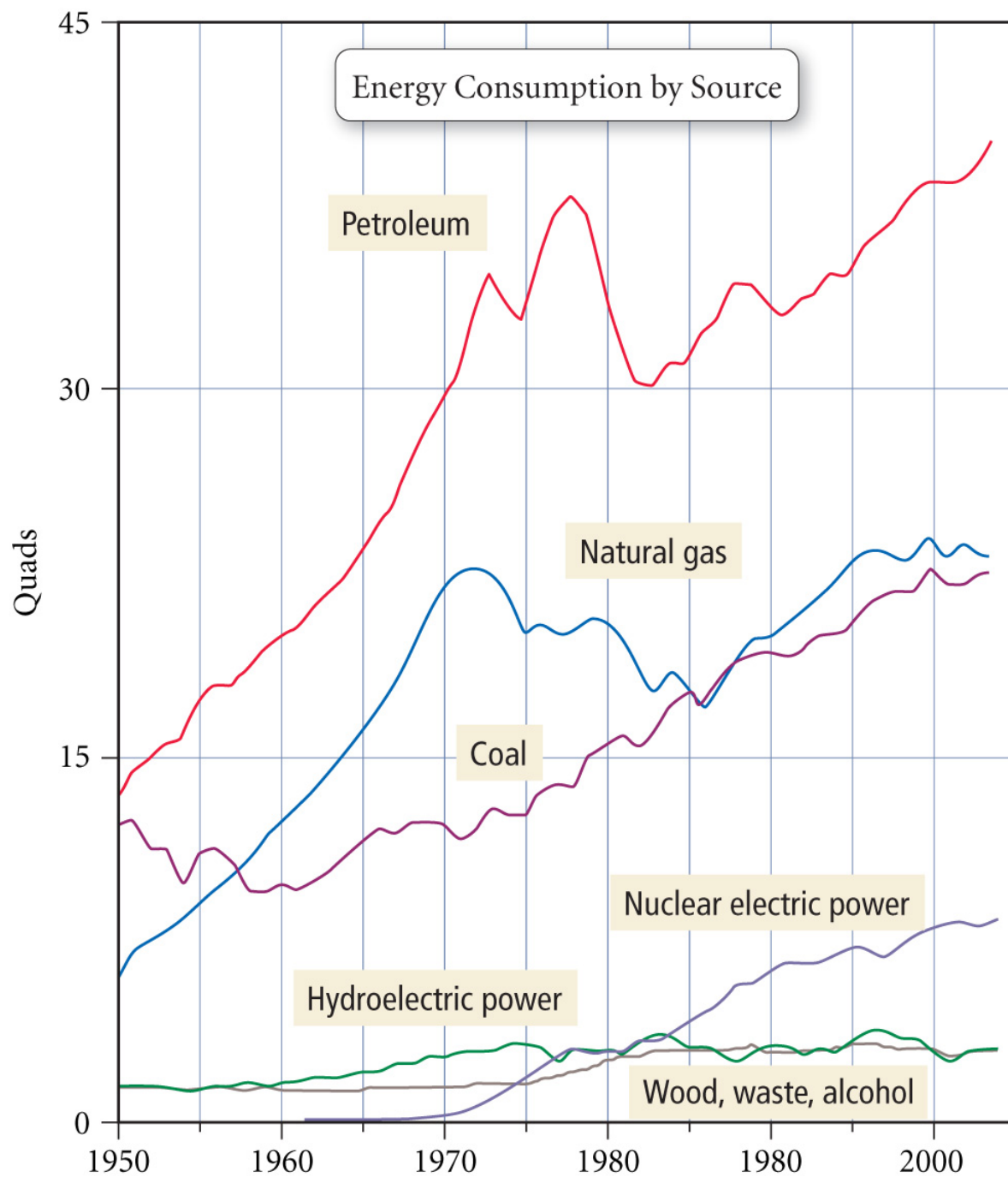
- If  $\Delta H = +$  and  $\Delta S = -$  never spontaneous  
 $\Delta G = +$
- If  $\Delta H = -$  and  $\Delta S = +$  always spontaneous  
 $\Delta G = -$
- If  $\Delta H = +$  and  $\Delta S = +$  or if  $\Delta H = -$  and  $\Delta S = -$   
temperature determines spontaneity
  - At T where  $\Delta G = -$  reaction is spontaneous
  - At T where  $\Delta G = +$  reaction is nonspontaneous





- Residential: 21%
- Commercial: 18%
- Industrial: 32%
- Transportation: 29%

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# Atmospheric Carbon Dioxide

