

A dramatic photograph of a volcanic eruption. A massive, billowing plume of dark grey ash and smoke rises from the left side of the frame. In the upper right, a bright, glowing fireball of orange and yellow lava is visible, with a trail of sparks or ash falling from it. The background is a clear, pale blue sky. The overall scene is one of intense natural power and energy.

Energy Relationships in Chemical Reactions



Chapter 6 – Energy Relationships in Chemical Reactions

- The nature of energy and types of energy (6.1)
- Energy changes in chemical reactions (6.2)
- Introduction to thermodynamics (6.3)
- Calorimetry (6.5)
- Enthalpy of chemical reactions (6.4)
- Standard enthalpy of formation and reaction (6.6)

Chapter 6 – Energy Relationships in Chemical Reactions

- System and Surroundings (6.2)
- Internal Energy ΔU (6.2)
 - Work
 - Heat
 - First Law of Thermodynamics
 - State Functions
 - ΔU as a state function
- Enthalpy ΔH (6.3 to 6.6)
 - Exothermic and endothermic processes (6.4, 6.6)
 - Enthalpy and spontaneous change
 - Heat capacity (6.5)
 - Specific heat capacity (6.5)
 - Calorimetry
 - Enthalpy as a state function (6.4, 6.6)
 - Thermochemical cycles
 - $\Delta H_f \rightarrow \Delta H_{\text{rxn}}$





6.1 The nature of energy and types of energy

- *Radiant energy* comes from the sun and is earth's primary energy source
- *Thermal energy* is the energy associated with the random motion of atoms and molecules
- *Chemical energy* is the energy stored within the bonds of chemical substances
- *Nuclear energy* is the energy stored within the collection of neutrons and protons in the atom
- *Potential energy* is the energy available by virtue of an object's position

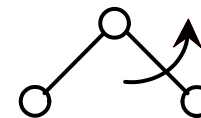
6.1 The nature of energy and types of energy

What are the forms of energy (*thinking in terms of particles*)?

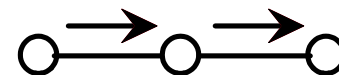
Translational ($E_{K, trans}$)



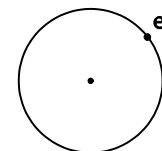
Rotational ($E_{K, rot}$)



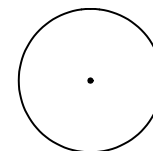
Vibrational ($E_{K, vib}$)



Electronic (E_{elec})



Nuclear (E_{nucl})



Scale

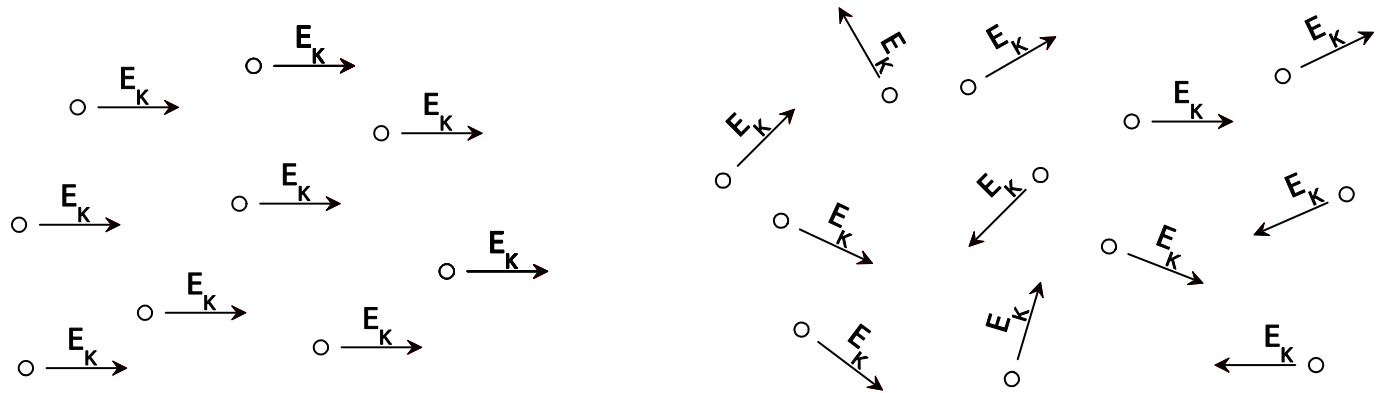


6.2 Energy changes in chemical reactions

- Key Definition:

- Energy

- The capacity to do work
- The capacity to direct energy change resulting from a process (or to move matter)



Work

Heat

6.2 Energy changes in chemical reactions

- Key Definition:

- Energy

Work + Heat

- Work is moving matter in a concerted fashion (work done by the system by moving matter)
- Heat is moving matter in a non-concerted fashion (work not done by the system, but matter still moved)

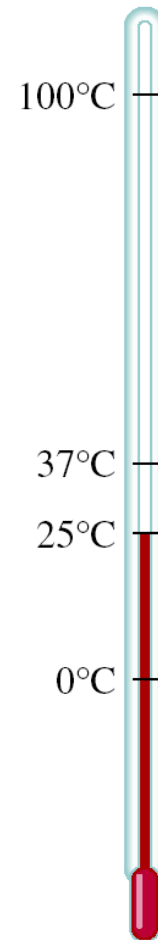


6.2 Energy changes in chemical reactions

Heat is the transfer of **thermal energy** between two bodies that are at different temperatures.

Temperature is a measure of the **thermal energy**.

Temperature \neq Thermal Energy





6.2 Energy changes in chemical reactions

- **Key Definitions:**
 - **System**
 - The specific part of the universe that is of interest to us (to study and understand).
 - **Surroundings**
 - The rest of the universe outside of the system
 - **Universe**
 - The system and the surroundings (everything)



6.2 Energy changes in chemical reactions

- **Key Definitions:**

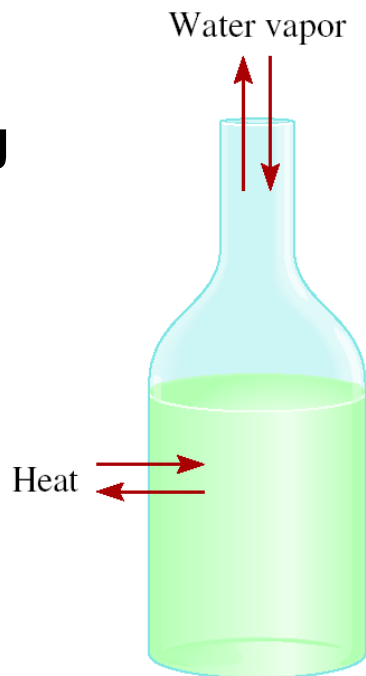
- **System**

- The specific part of the universe that is of interest to us (to study and understand).
- **Open**
 - Can mass and energy (usually in the form of heat) with its surroundings
- **Closed**
 - Allows the transfer of energy (usually heat) but not mass
- **Isolated**
 - Does not allow the transfer of either mass or energy

6.2 Energy changes in chemical reactions

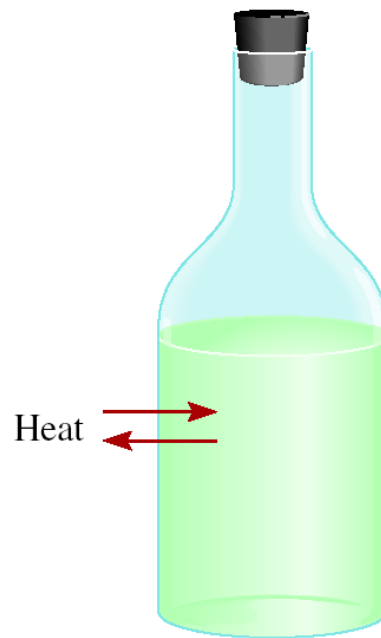
different systems

surrounding



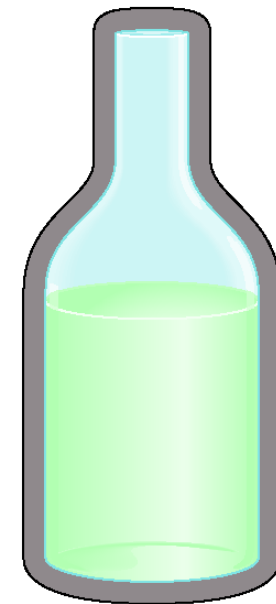
open

Exchange: mass & energy



closed

energy



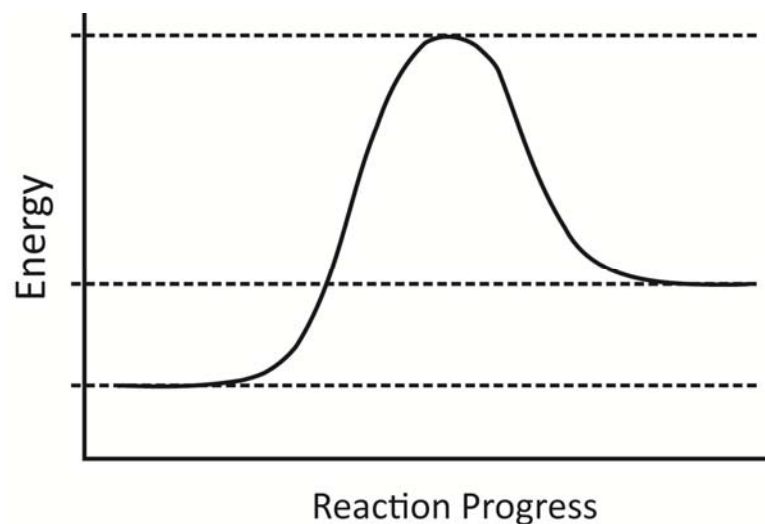
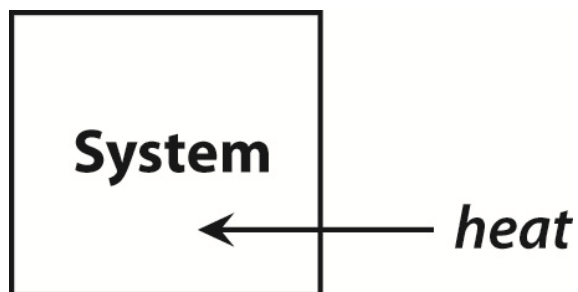
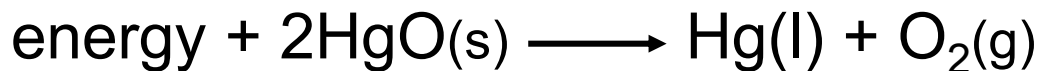
isolated

nothing

Figure 6.1, p. 180

6.2 Energy changes in chemical reactions

- System gains heat (transfer thermal energy from the surroundings to the system)
 - Heat is positive (wrt system)
 - **Endothermic**

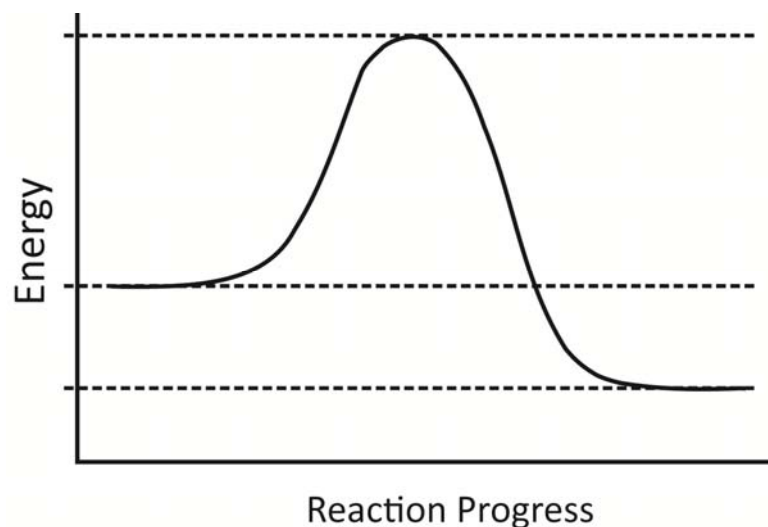
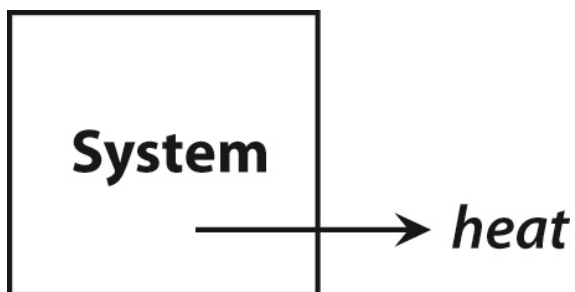
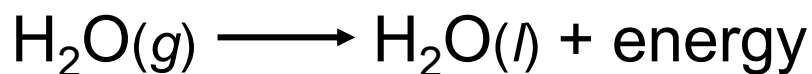
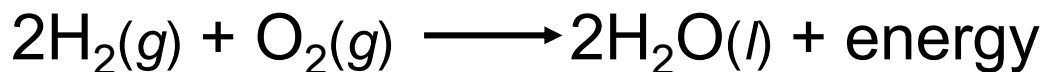


Scale



6.2 Energy changes in chemical reactions

- System loses heat (transfer thermal energy from the system to the surroundings)
 - Heat is negative (wrt system)
 - **Exothermic**



Scale





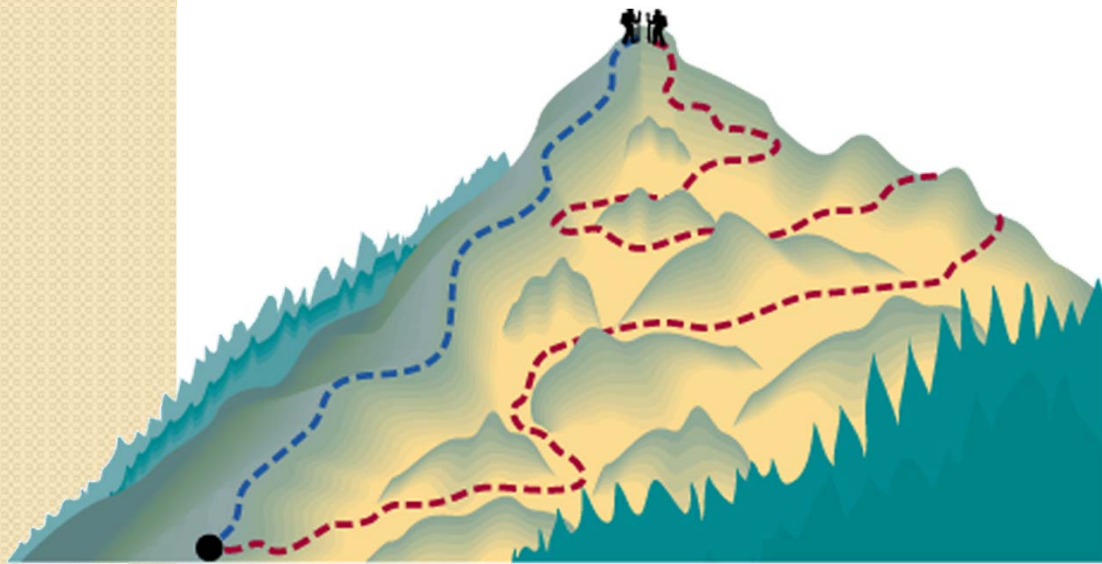
6.3 Introduction to thermodynamics

- **What is a thermodynamics?**
 - scientific study of the interconversion of heat and other kinds of energy
- **What is a state function?**
 - properties that are determined by the state of the system, regardless of how that condition was achieved.

6.3 Introduction to thermodynamics

State functions are properties that are determined by the state of the system, regardless of how that condition was achieved.

energy, pressure, volume, temperature



$$\Delta U = U_{final} - U_{initial}$$

$$\Delta P = P_{final} - P_{initial}$$

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

$$\Delta T = T_{final} - T_{initial}$$

Potential energy of **hiker 1** and **hiker 2** is the same even though they took different paths.

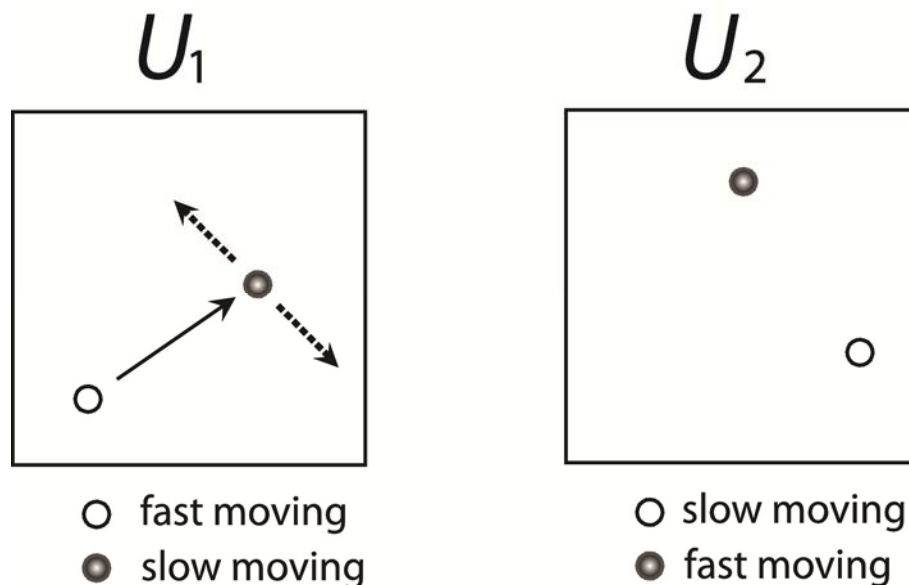


6.3 Introduction to thermodynamics

- What is the first law of thermodynamics?
 - In terms of the energy of the universe?
 - In terms of heat and work?
 - In terms of the energy of the system vs. the surroundings?

6.3 Introduction to thermodynamics

Internal Energy of a System



- U_1 vs. U_2 (not a particle basis but on a system basis)?
- For an isolated system; $U_1 = U_2$ or $\Delta U = U_2 - U_1 = 0$
- Cannot measure the internal energy of a system, but can measure the change in internal energy
- For chemical reactions: $\Delta U = U_{\text{products}} - U_{\text{reactants}}$



6.3 Introduction to thermodynamics

- What is the first law of thermodynamics?
 - In terms of the energy of the universe?
 - In terms of heat and work?
 - In terms of the energy of the system vs. the surroundings?

TABLE 6.1 Sign Conventions for Work and Heat

Process	Sign
Work done by the system on the surroundings	–
Work done on the system by the surroundings	+
Heat absorbed by the system from the surroundings (endothermic process)	+
Heat absorbed by the surroundings from the system (exothermic process)	–

- What is the law of conservation of energy?



6.5 Calorimetry

- Is heat a state function?
- How do we quantify heat for any system?
 - What is heat capacity (C)?
 - The amount of heat (q) required to raise the temperature of a **given quantity** of substance (m) by **one degree Celsius** for that substance.
- What are the units for heat capacity?
- What is the relationship between heat capacity and change in temperature?

6.5 Calorimetry

- How do we quantify heat for any pure substance?
 - What is specific heat (s)?
 - The amount of heat (q) required to raise the temperature of **one gram** of the substance **by one degree Celsius**
- What are the units for specific heat?
- What is the relationship between
 - Specific heat and change in temperature?
 - Specific heat and heat capacity?

Table 6.2

The Specific Heats of Some Common Substances

Substance	Specific Heat ($\text{J/g} \cdot ^\circ\text{C}$)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H ₂ O	4.184
C ₂ H ₅ OH (ethanol)	2.46

Table 6.2, p. 193

6.5 Calorimetry

Practice:

What was the initial temperature of water when 1 mol of iron at 550.0°C was placed in a 1.5 L water bath and both substances reached a final temperature of 28.25°C ?

The specific heat of iron is $0.444 \text{ J} \cdot \text{g}^{-1} \cdot ^{\circ}\text{C}^{-1}$

The specific heat of water is $4.18 \text{ J} \cdot \text{g}^{-1} \cdot ^{\circ}\text{C}^{-1}$

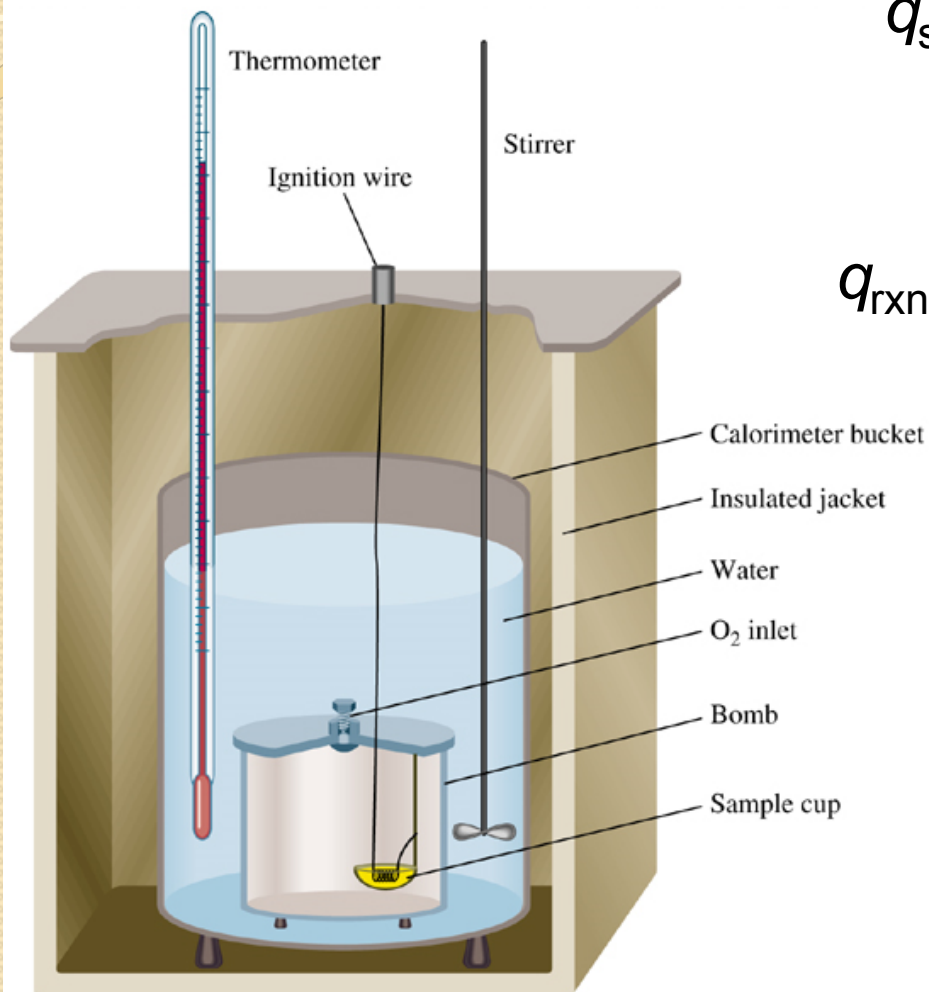




6.5 Calorimetry

- How do we measure heat (or calculate a heat capacity)?
 - What is calorimetry?
 - Different types:
 - Constant Volume
 - Constant Pressure

6.5 Calorimetry



No heat enters or leaves!

$$q_{\text{sys}} = q_{\text{water}} + q_{\text{bomb}} + q_{\text{rxn}}$$

$$q_{\text{sys}} = 0$$

$$q_{\text{rxn}} = -(q_{\text{water}} + q_{\text{bomb}}) = -q_{\text{cal}}$$

$$q_{\text{cal}} = C_{\text{cal}} \times \Delta t$$

Reaction at Constant V

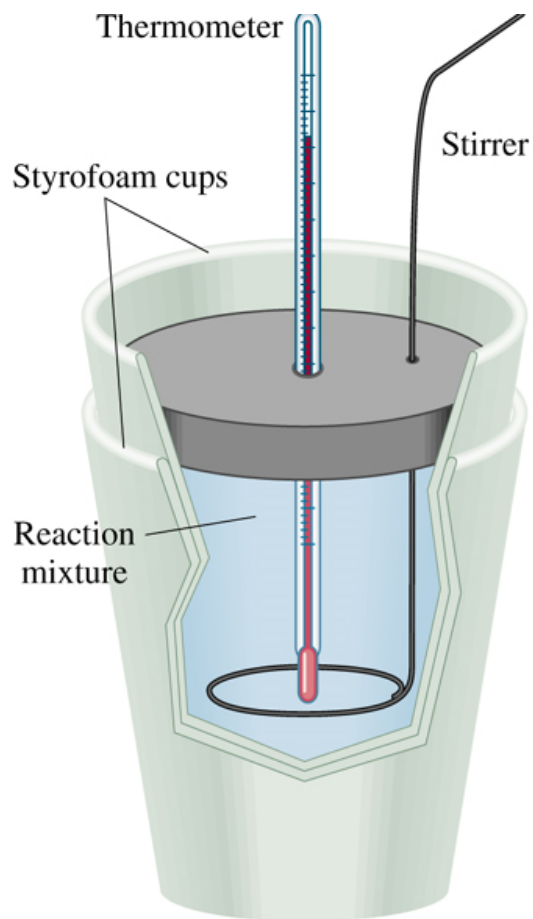


6.5 Calorimetry

Practice:

What is heat of combustion (in $\text{kJ} \cdot \text{mol}^{-1}$) for graphite when 1.850 g is combusted in a constant volume bomb calorimeter with the water at an initial temperature of $22.02\text{ }^{\circ}\text{C}$ and the final temperature of the water is $27.95\text{ }^{\circ}\text{C}$.

6.5 Calorimetry



$$q_{\text{sys}} = q_{\text{water}} + q_{\text{rxn}}$$

$$q_{\text{sys}} = 0$$

$$q_{\text{rxn}} = -q_{\text{water}}$$

$$q_{\text{water}} = m_{\text{water}} \times S_{\text{water}} \times \Delta t_{\text{water}}$$

Reaction at Constant P

No heat enters or leaves!

6.5 Calorimetry

TABLE 6.3 Heats of Some Typical Reactions Measured at Constant Pressure

Type of Reaction	Example	ΔH (kJ/mol)
Heat of neutralization	$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$	-56.2
Heat of ionization	$\text{H}_2\text{O}(l) \longrightarrow \text{H}^+(aq) + \text{OH}^-(aq)$	56.2
Heat of fusion	$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$	6.01
Heat of vaporization	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$	44.0*
Heat of reaction	$\text{MgCl}_2(s) + 2\text{Na}(l) \longrightarrow 2\text{NaCl}(s) + \text{Mg}(s)$	-180.2

*Measured at 25°C. At 100°C, the value is 40.79 kJ.



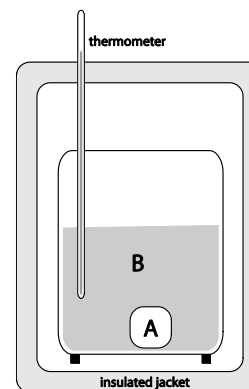
6.5 Calorimetry

Practice:

When 10.0 g of ammonium nitrate is dissolved in 100.0 mL of water and the temperature decreases from 25.0°C to 17.1°C. What is the molar heat of solution of ammonium nitrate?

Chapter 6 Calorimetry – Practice

A reaction occurs in a vessel (part A in the figure) which is submerged in water (part B in the figure) in a constant volume bomb calorimeter. If the observed temperature (on the thermometer) increases,



- A. the reaction is endothermic, since $q_{\text{cal}} = q_{\text{rxn}}$.
- B. the reaction is endothermic, since $q_{\text{cal}} = -q_{\text{rxn}}$.
- C. the reaction is exothermic, since $q_{\text{cal}} = q_{\text{rxn}}$.
- D. the reaction is exothermic, since $q_{\text{cal}} = -q_{\text{rxn}}$.

What is the standard molar enthalpy of solution for sodium chloride if 8.00 g of sodium chloride decreases the temperature of 74.90 g of water by 1.81 °C? Assume the heat transfer occurs only between the water and the reaction. The specific heat of water is $4.18 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1}$.

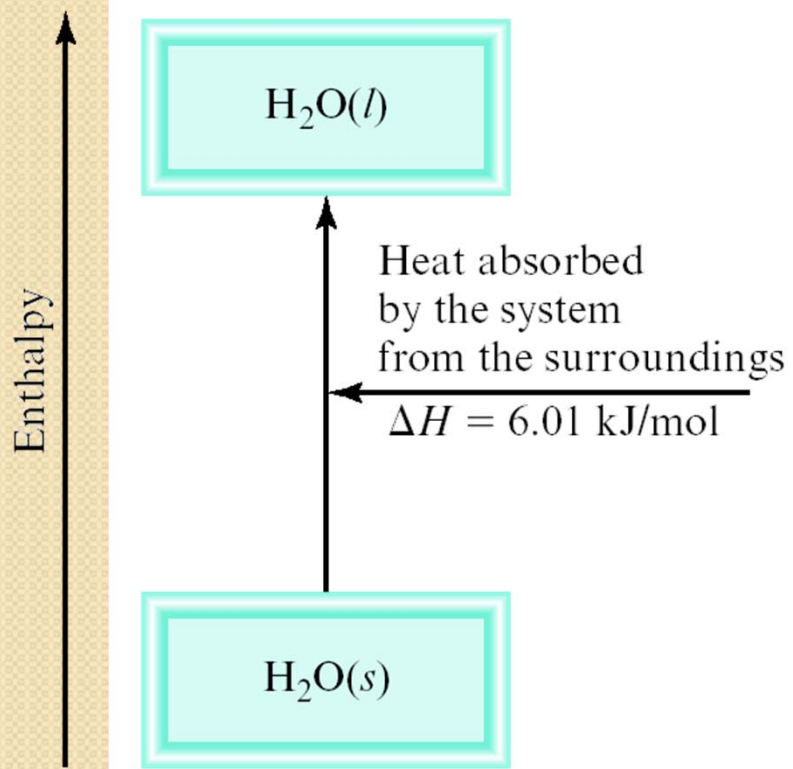
- A. 4140 kJ \cdot mol⁻¹
- B. 567 kJ \cdot mol⁻¹
- C. 4.14 kJ \cdot mol⁻¹
- D. 0.567 kJ \cdot mol⁻¹

6.4 and 6.6 Enthalpy

- What is enthalpy?
 - Heat content of a reaction or a quantity to describe the heat flow into or out of a system in a process that occurs at constant pressure
- Is enthalpy a state function?
 - What does this mean in terms of a reaction?
- Is enthalpy extensive?
 - What does this mean in terms of a reaction?
- How can we visualize this?
- How can we calculate this?
 - How are the methods the same/different?



Thermochemical Equations



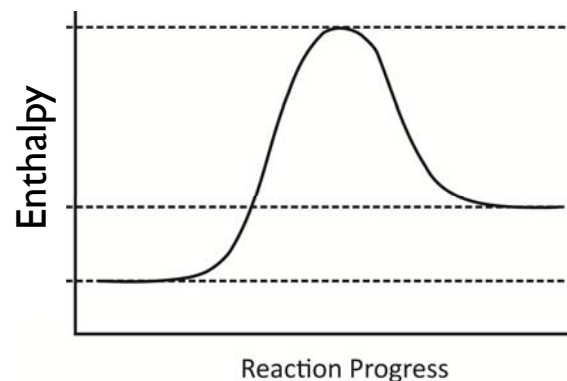
Is ΔH negative or positive?

System absorbs heat

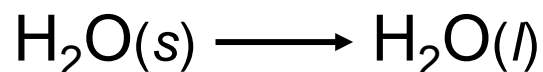
Endothermic

$$\Delta H < 0$$

$$H_{\text{reactants}} < H_{\text{products}}$$



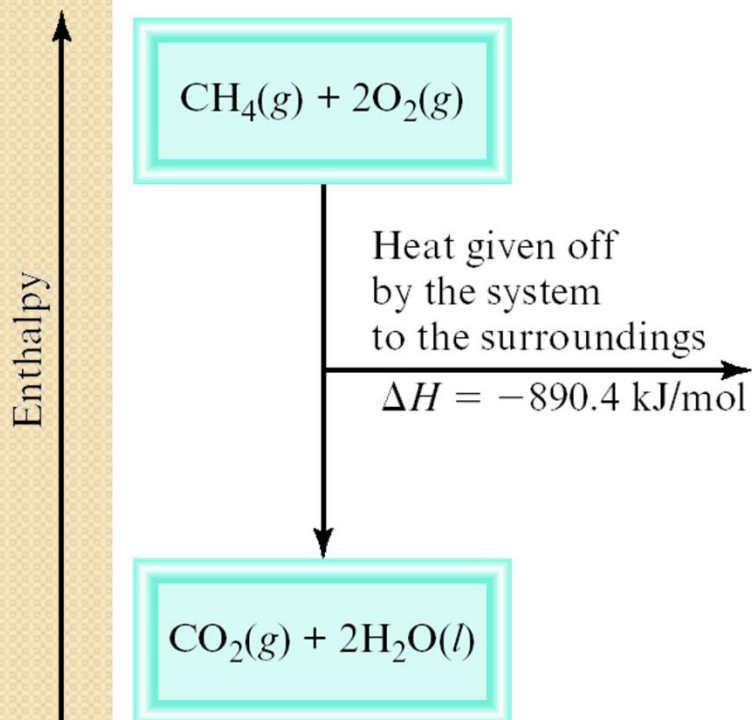
6.01 kJ are absorbed for every 1 mole of ice that melts at 0°C and 1 atm.



$$\Delta H = 6.01 \text{ kJ/mol}$$



Thermochemical Equations



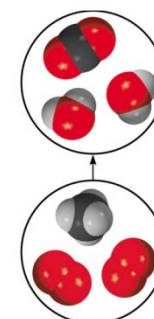
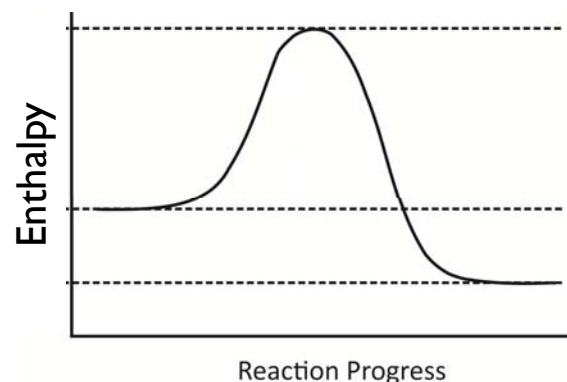
Is ΔH negative or positive?

System gives off heat

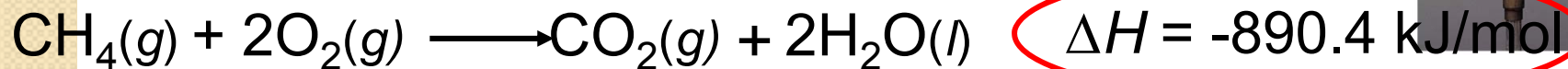
Exothermic

$$\Delta H < 0$$

$$H_{\text{reactants}} > H_{\text{products}}$$



890.4 kJ are released for every 1 mole of methane that is combusted at 25⁰C and 1 atm.





6.4 and 6.6 Enthalpy

- How are enthalpy and heat related?
- How are enthalpy and energy related?



6.4 and 6.6 Enthalpy

- What are the rules for enthalpy?
 1. Writing a thermochemical equation
 2. Direction of the equation (reactants vs. products)
 3. Extensive property – increasing or decreasing the amounts of products or reactants
 4. State property – one reaction or multiple reactions to an overall reaction

6.4 and 6.6 Enthalpy

- Key Definitions:
 - Standard conditions
 - Enthalpy of formation
 - Enthalpy of combustion
 - Enthalpy of solution
 - Enthalpy of vaporization (heat of vaporization)
 - Enthalpy of fusion (heat of fusion)

- What is an energy diagram?



6.4 and 6.6 Enthalpy

Table 6.3 Heats of Some Typical Reactions Measured at Constant Pressure

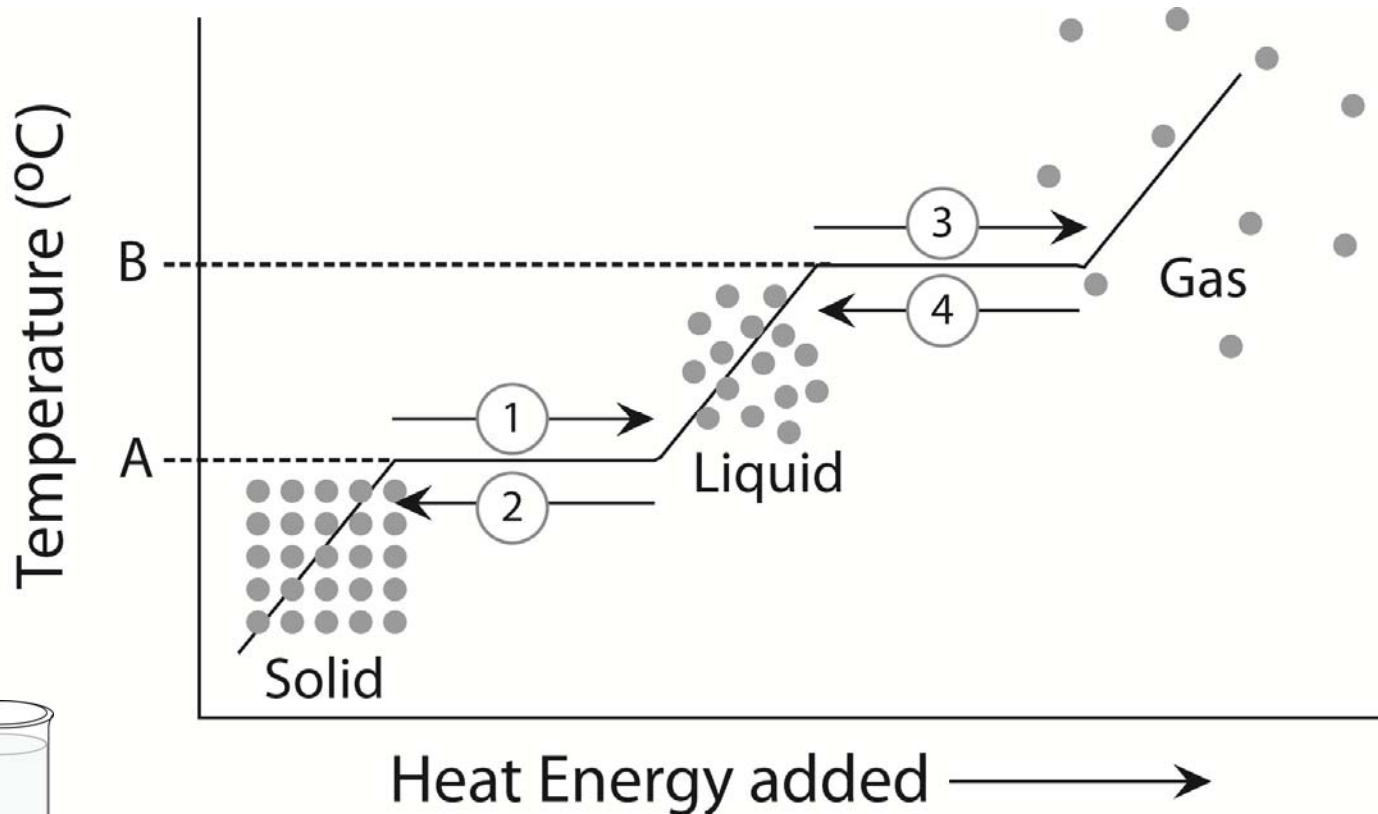
Type of Reaction	Example	ΔH (kJ)
Heat of neutralization	$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$	-56.2
Heat of ionization	$\text{H}_2\text{O}(l) \longrightarrow \text{H}^+(aq) + \text{OH}^-(aq)$	56.2
Heat of fusion	$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$	6.01
Heat of vaporization	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$	44.0*
Heat of reaction	$\text{MgCl}_2(s) + 2\text{Na}(l) \longrightarrow 2\text{NaCl}(s) + \text{Mg}(s)$	-180.2

*Measured at 25°C. At 100°C, the value is 40.79 kJ.



6.4 and 6.6 Enthalpy

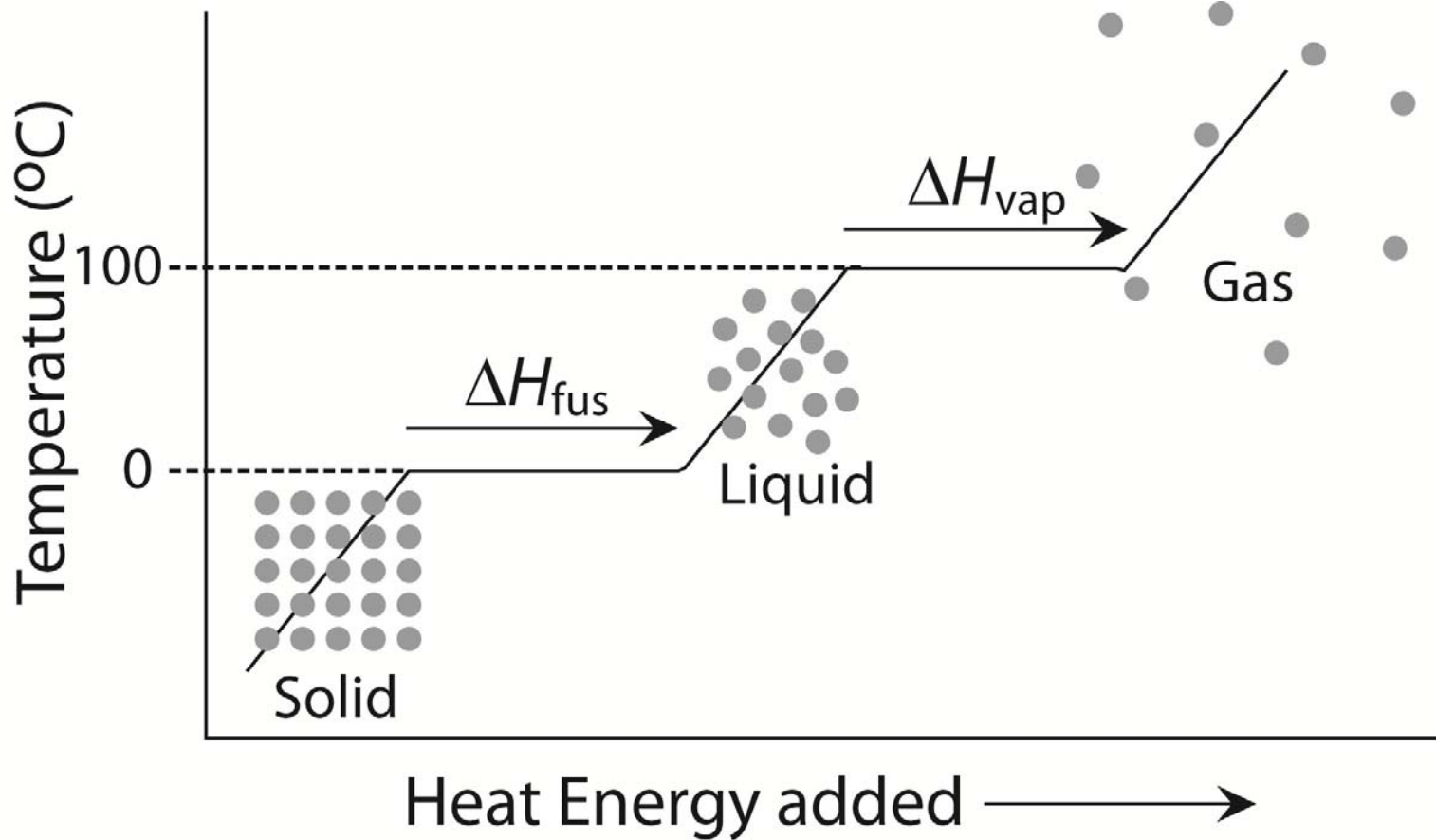
- What occurs at 1, 2, 3, and 4?
- How do we define this in terms of ΔH



Scale



6.4 and 6.6 Enthalpy

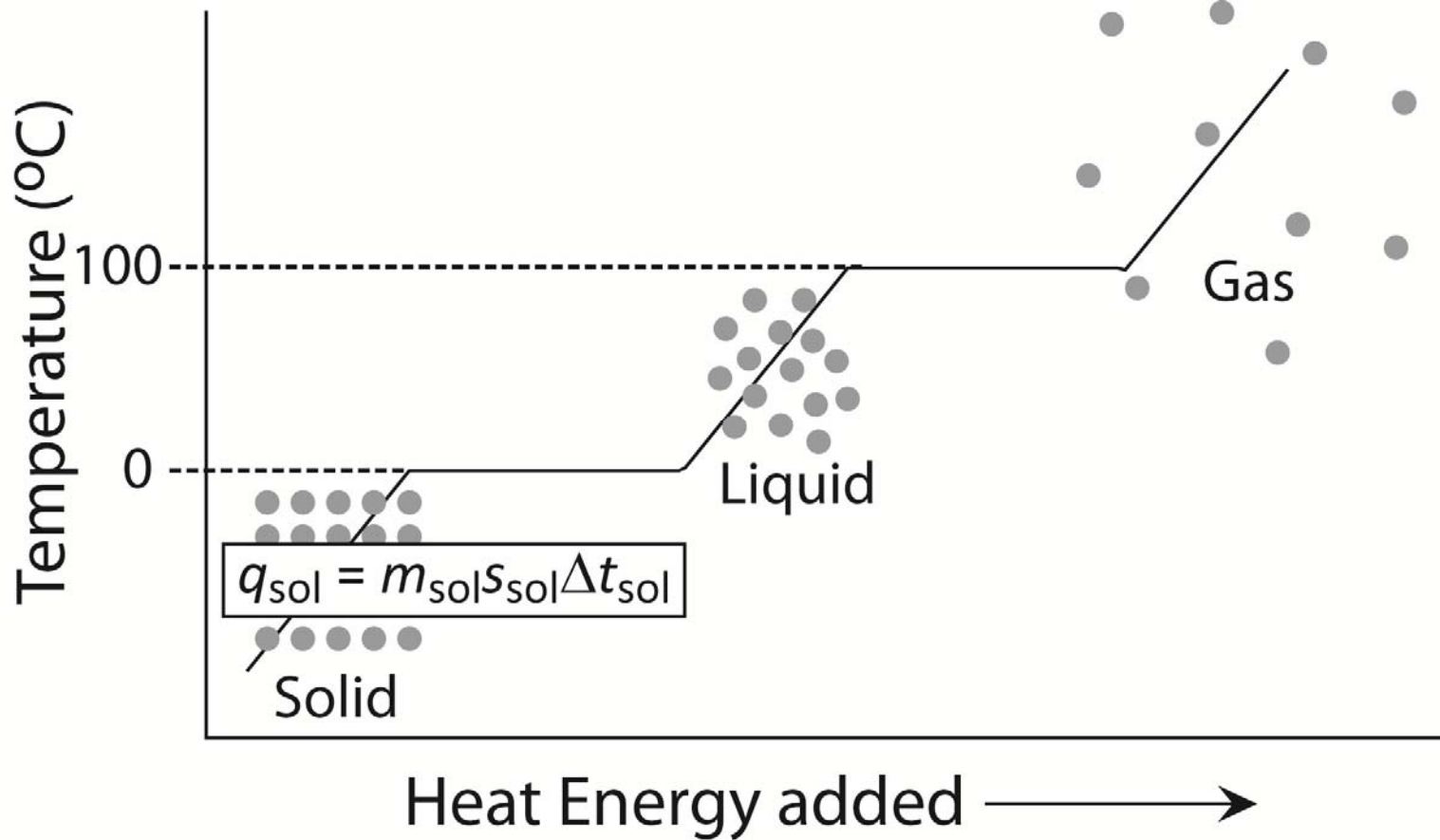


6.4 and 6.6 Enthalpy

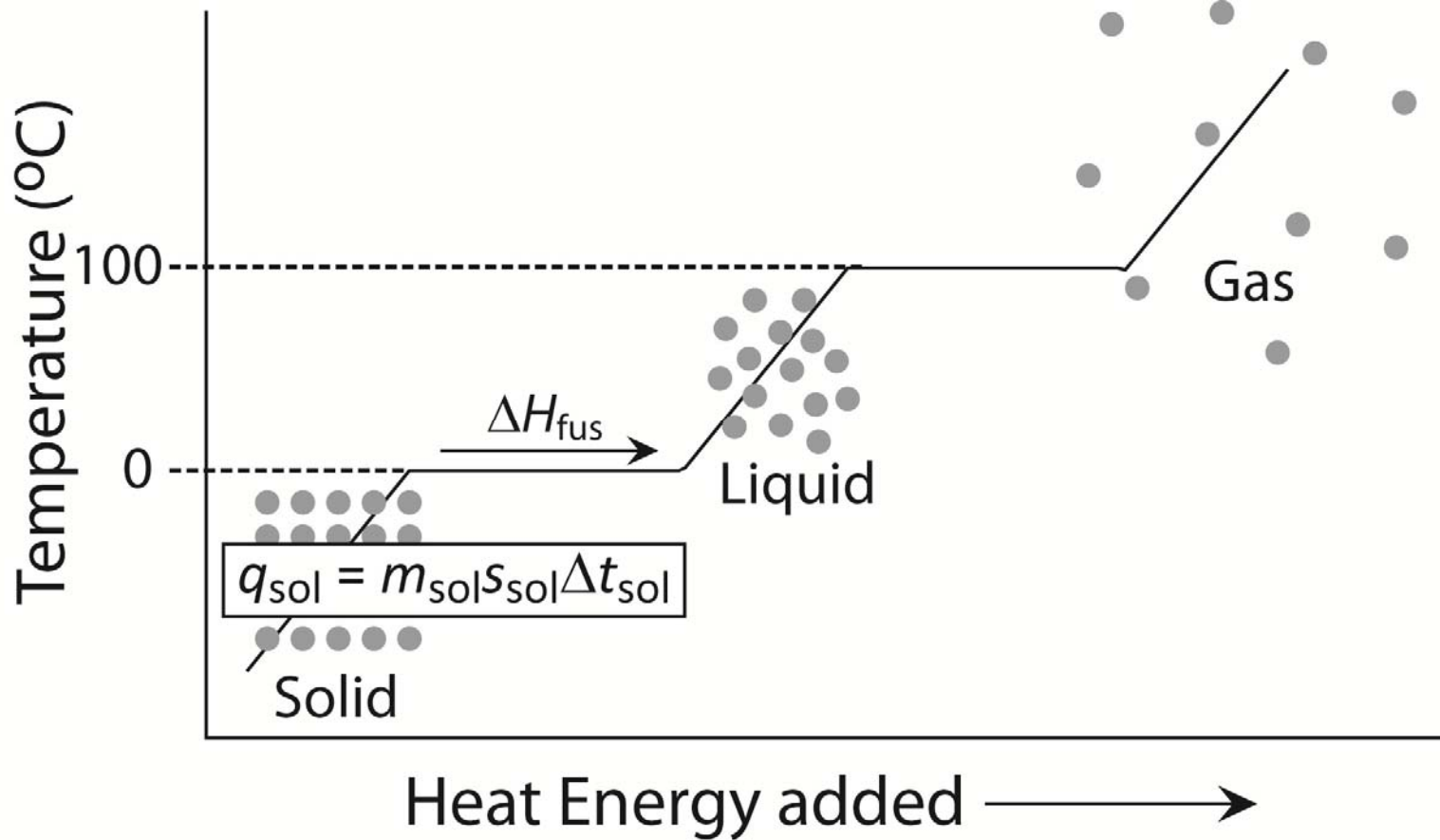
- How do we incorporate phase changes (melting, boiling) with warming of substances?
- What does this mean on a particle level?
- What is a heating or cooling curve?
- How do we calculate the amount of heat required to warm ice to steam or cool steam to ice?



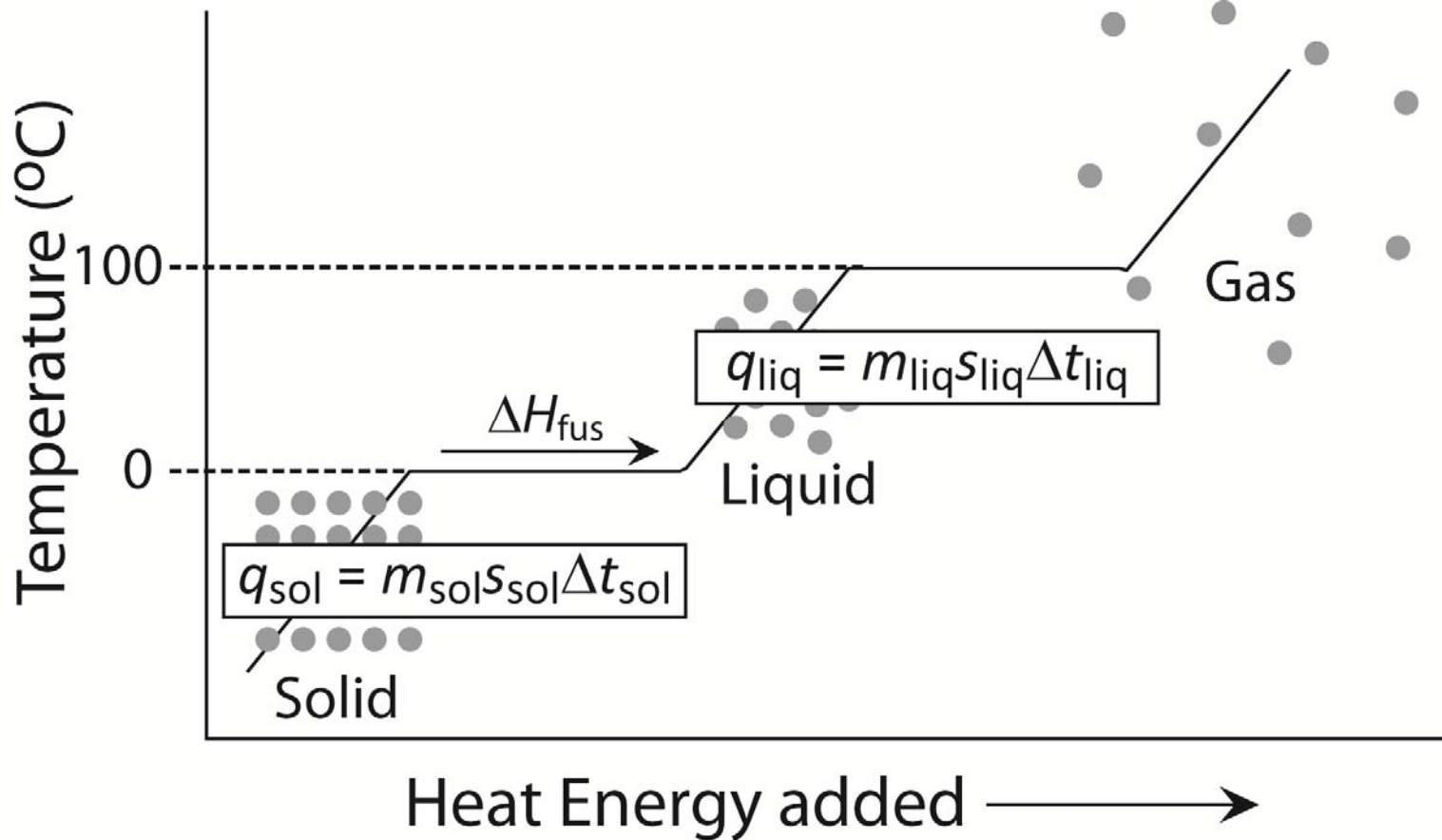
6.4 and 6.6 Enthalpy



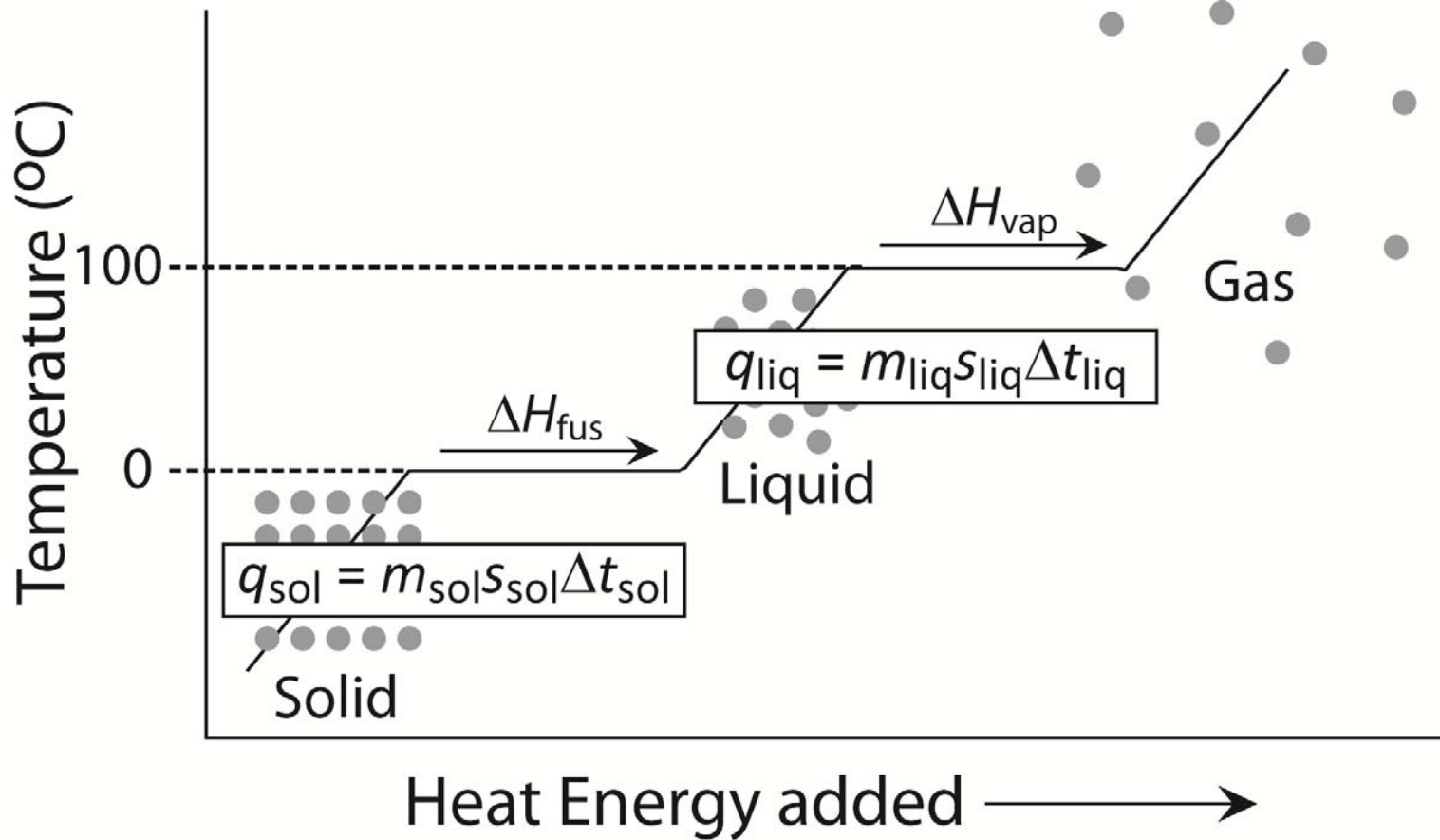
6.4 and 6.6 Enthalpy



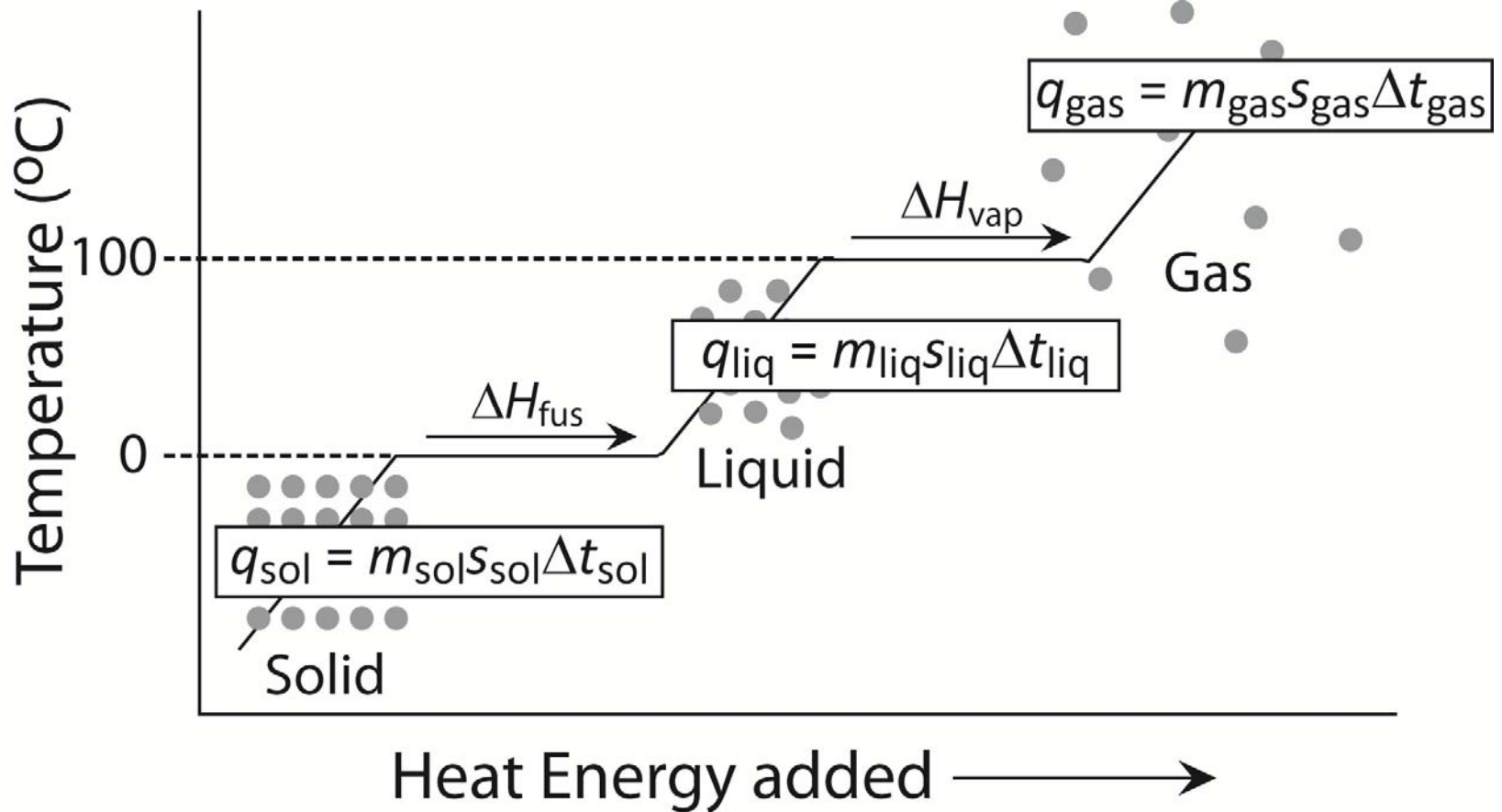
6.4 and 6.6 Enthalpy



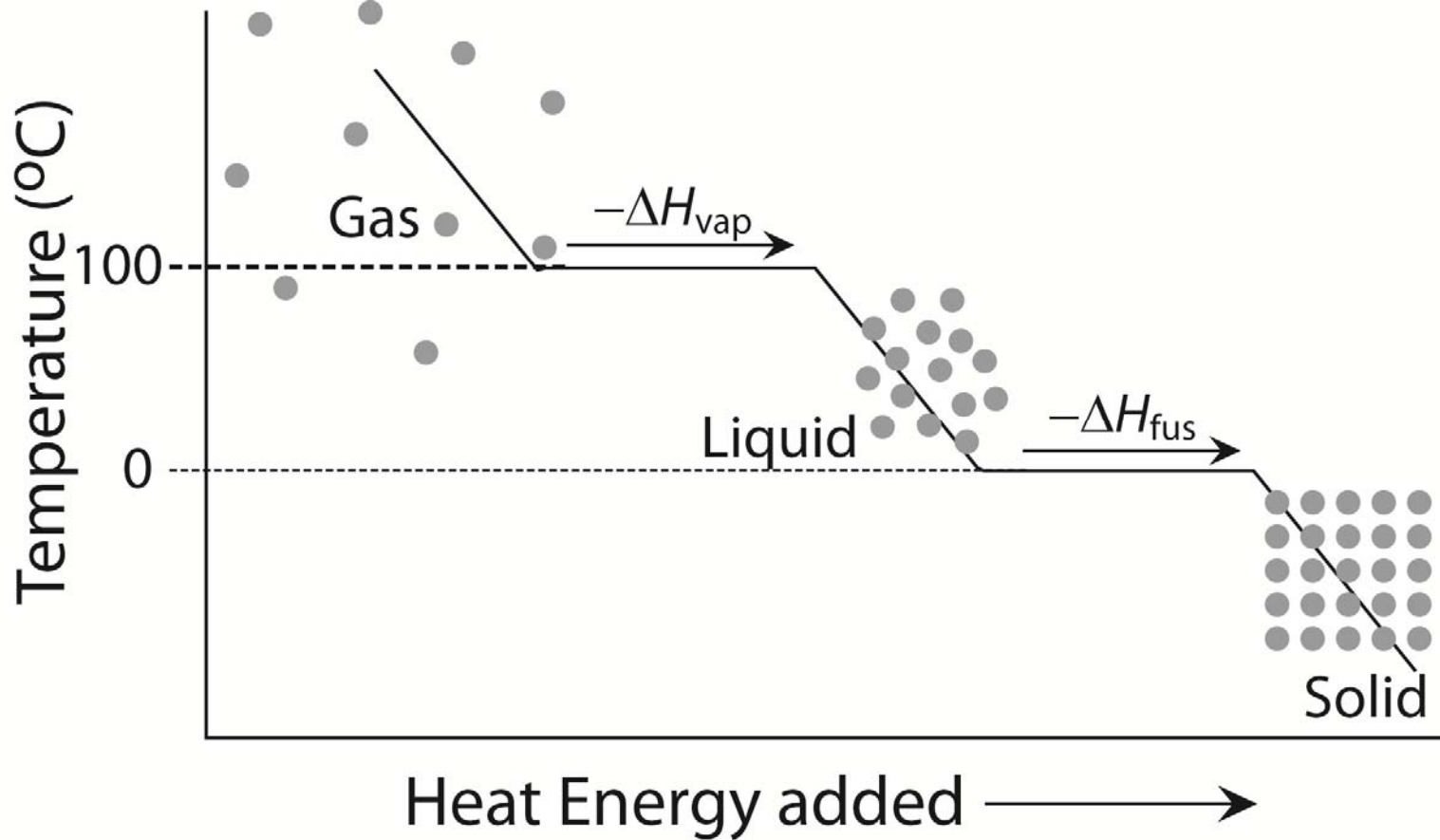
6.4 and 6.6 Enthalpy



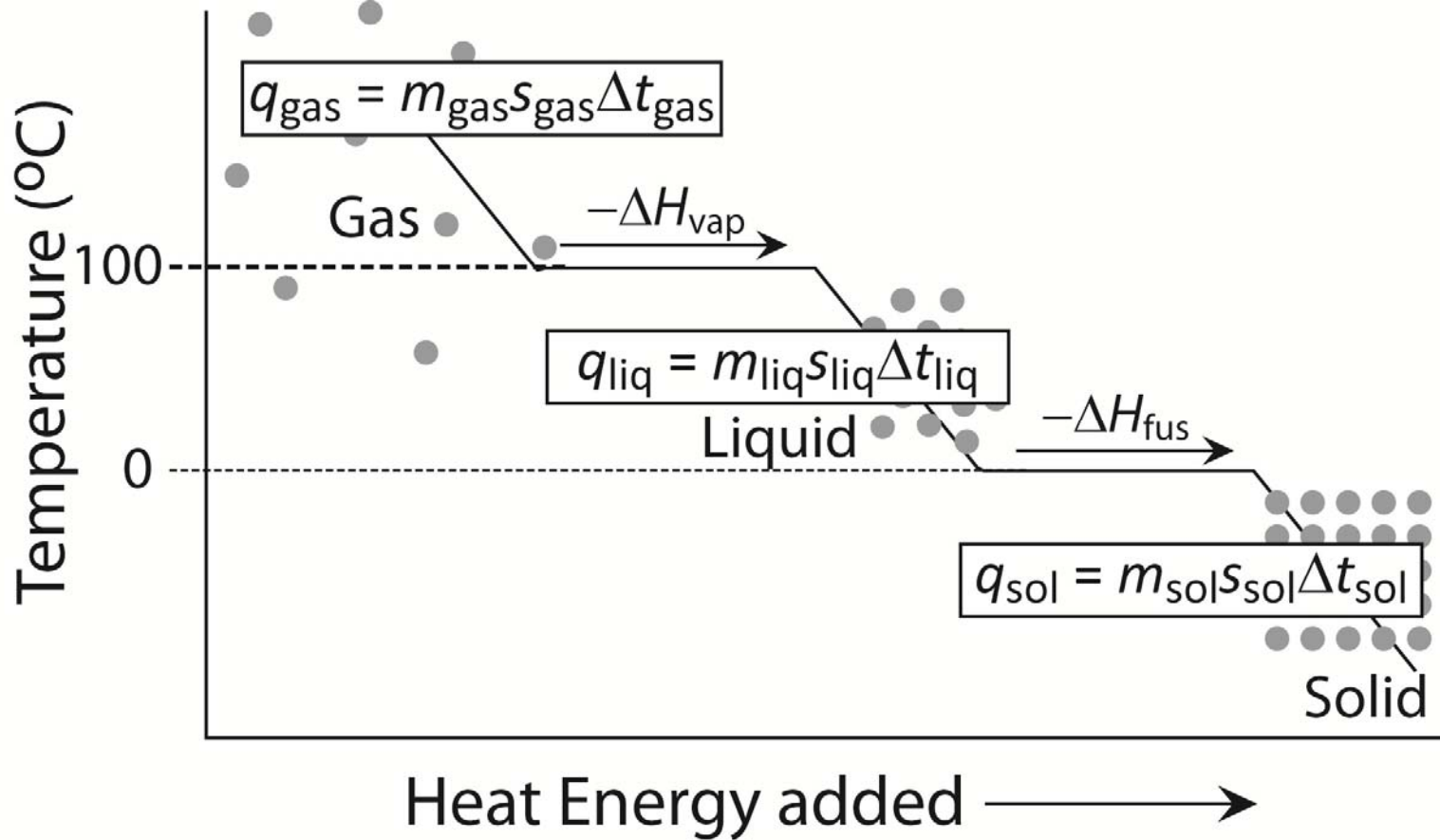
6.4 and 6.6 Enthalpy



6.4 and 6.6 Enthalpy



6.4 and 6.6 Enthalpy



6.4 and 6.6 Enthalpy

Practice:

What was the initial temperature of water when 100 g of ice at -20°C was placed in a 1.5 L water bath and both substances reached a final temperature of 28.25°C ?

The specific heat of ice is $2.06 \text{ J} \cdot \text{g}^{-1} \cdot ^{\circ}\text{C}^{-1}$

The specific heat of liquid water is $4.18 \text{ J} \cdot \text{g}^{-1} \cdot ^{\circ}\text{C}^{-1}$

The enthalpy of fusion for water is $6.0 \text{ kJ} \cdot \text{mol}^{-1}$



6.4 and 6.6 Enthalpy

- How do we measure change in enthalpy for a reaction?
 - Direct method
 - Indirect methods
 - Using a series of reactions (Hess's Law)
 - Using tables of data (enthalpy of formation)



Table 6.4 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
Ag(s)	0	H ₂ O ₂ (l)	-187.6
AgCl(s)	-127.04	Hg(l)	0
Al(s)	0	I ₂ (s)	0
Al ₂ O ₃ (s)	-1669.8	HI(g)	25.94
Br ₂ (l)	0	Mg(s)	0
HBr(g)	-36.2	MgO(s)	-601.8
C(graphite)	0	MgCO ₃ (s)	-1112.9
C(diamond)	1.90	N ₂ (g)	0
CO(g)	-110.5	NH ₃ (g)	-46.3
CO ₂ (g)	-393.5	NO(g)	90.4
Ca(s)	0	NO ₂ (g)	33.85
CaO(s)	-635.6	N ₂ O ₄ (g)	9.66
CaCO ₃ (s)	-1206.9	N ₂ O(g)	81.56
Cl ₂ (g)	0	O(g)	249.4
HCl(g)	-92.3	O ₂ (g)	0
Cu(s)	0	O ₃ (g)	142.2
CuO(s)	-155.2	S(rhombic)	0
F ₂ (g)	0	S(monoclinic)	0.30
HF(g)	-268.61	SO ₂ (g)	-296.1
H(g)	218.2	SO ₃ (g)	-395.2
H ₂ (g)	0	H ₂ S(g)	-20.15
H ₂ O(g)	-241.8	ZnO(s)	-347.98
H ₂ O(l)	-285.8	ZnS(s)	-202.9

†In thermodynamics, the standard pressure is defined as 1 bar, where 1 bar = 10⁵ Pa = 0.987 atm. Because 1 bar differs from 1 atm by only 1.3 percent, we will continue to use 1 atm as the standard pressure. Note that the normal melting point and boiling point of a substance are defined in terms of 1 atm.

6.4 and 6.6 Enthalpy

Practice:

What is the enthalpy of combustion for methane?

What volume of methane at 1 atm and 25°C is needed to heat 500 mL of water from 5°C to 95°C?

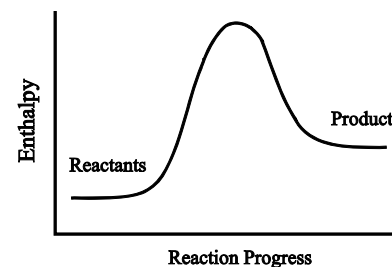
If the current price of natural gas is \$0.10 per cubic foot, (and we assume natural gas is all methane) how much does it cost to heat the water?



Chapter 6 Enthalpy – Practice

For the reaction energy diagram shown to the right, the reaction is

- A. exothermic with $\Delta H_{\text{reactants}} > \Delta H_{\text{products}}$.
- B. exothermic with $\Delta H_{\text{reactants}} < \Delta H_{\text{products}}$.
- C. endothermic with $\Delta H_{\text{reactants}} > \Delta H_{\text{products}}$.
- D. endothermic with $\Delta H_{\text{reactants}} < \Delta H_{\text{products}}$.



Which reaction corresponds to the reaction for the enthalpy of formation for methanol, $\text{CH}_3\text{OH}(\text{l})$?

- A. $2\text{CH}_3\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$
- B. $\text{CH}_3\text{OH}(\text{l}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
- C. $2\text{C}(\text{s, graphite}) + \text{O}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightarrow 2\text{CH}_3\text{OH}(\text{l})$
- D. $\text{C}(\text{s, graphite}) + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l})$

Chapter 6 Enthalpy – Practice

Hess's Law states when reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps. This is valid because change in enthalpy is

- A.** extensive.
- B.** a state function.
- C.** a type of energy.
- D.** equal to energy when no work is done.