

# Calculations In Chemistry



## Modules 21 and 22

### Phase Changes, Energy, and ( $\Delta H$ )

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## Module 21 — Energy Calculations

**Timing:** Begin this module when you are assigned problems which involve *phase changes* or calculations involving *joules* or *calories*.

**Prerequisites:** This module for the most part does not require many prior topics. You should be able to do most of the calculations if you have completed Modules 2, 4, 5, and 8.

### Lesson 21A: Phases and Energy

#### Three Phases

In first-year chemistry, we are initially concerned with *three phases* for pure substances: **solid**, **liquid**, and **gas**.

In covalently bonded molecules, the forces that hold the atoms together within the molecule are relatively strong, but there are also relatively weak forces of attraction between molecules. These weak attractions mean that molecules are a bit “sticky:” they tend to attract each other somewhat like two weak but attracting magnets (these weak molecular attractions are electrical, but the behavior is similar).

In the solid phase, molecules **vibrate**, but the weak attractions between molecules hold the molecules in a crystal structure where they are limited in the extent to which they can **rotate**, and they can **translate** (move from place to place) only very slightly.

In their liquid phase, the molecules gain some freedom: they can vibrate, rotate, and translate. However, the liquid phase molecules are still very close together: they have minimal space between them. This is why solids and liquids do not compress (or compress only very slightly) when pressure is applied.

In the gas phase, molecules are separated by a considerable distance. In a gas at room temperature, the distance between molecules is typically about 10 times the diameter of the molecule. This means that 99.9% of the gas is empty space. Gases can be compressed because the empty space between the molecules can be reduced.

In a gas, the molecules remain weakly attractive. If a gas is highly compressed, or if its temperature is lowered (which slows down the speed at which the molecules move), the stickiness of the molecules becomes a larger factor. All gases condense into a liquid or a solid at some point as pressure is increased and temperature is decreased.

#### Three Phase Changes

In chemistry, a **chemical change** is defined as a process in which atoms rearrange to form new substances. A **physical change** is one in which characteristics of a substance change, but the substance does not change: it keeps the same chemical formula. A phase change is one example of a physical change.

There are *six* types of **phase changes** among the three phases, but most of these are familiar. The following terms are used to describe phase changes.

- **For solid/liquid changes:** Solids **melt** (or **fuse**) to become liquids; liquids **freeze** (or **solidify**) to become solids.

- **For liquid/gas changes:** Liquids **boil** or **evaporate** to form gases; gases **condense** to become liquids.
- **For solid/gas changes:** Solids **sublime** to become gases. In the reverse process, gases can undergo **deposition** to form solids.

**Sublimation** is a phase change that is less commonly encountered at room temperature and pressure, but you may be familiar with dry ice (solid carbon dioxide) or moth crystals (*para*-dichlorobenzene). At room conditions, these solids do not pass through a liquid phase as they convert from the solid to the gas phase.

Vapor **deposition** can be observed when water vapor forms ice crystals on a car windshield that is below 0°Celsius.

### Melting and Freezing

For a pure substance, the temperature at which it melts (its **melting point**) will *equal* the temperature at which it solidifies.

For pure substances: **Melting Point  $\equiv$  Freezing Point**

For pure substances, under atmospheric pressures that are at or near standard pressure, melting occurs at a *characteristic* temperature that can be used to identify the substance. However, even small amounts of impurity in a substance will weaken its crystal structure and cause it to melt and freeze at a lower temperature.

### Vapor Pressure

Nearly every liquid or solid has a measurable tendency for its particles to become gas particles. At the surface of a liquid or solid, vibrating neutral particles can break free and become part of the vapor above the liquid or solid. The *evaporation* of liquids at temperatures far below their boiling points is one example of this tendency.

The gas molecules that leave a solid or liquid create a gas pressure called the vapor pressure (see Lesson 18D). Vapor pressure can be *measured* by placing a liquid or solid in a vacuum, allowing the system to reach equilibrium at a given temperature, then measuring the gas pressure in the container. However, the vapor pressure of a liquid or solid is a *characteristic* property: a measure of the tendency of the particles of the substance to enter the gas phase. At a given temperature, the vapor pressure of a solid or liquid has the same value whether it is in a sealed container or not.

Vapor pressures are typically much higher for liquids than for solids, and vapor pressure is therefore a factor that has a larger impact on the behavior of liquids than solids.

Vapor pressure is measured in pressure units, and vapor pressure increases with increasing temperature. A liquid will **boil** at any temperature at which its **vapor pressure** equals the atmospheric pressure above it.

### Boiling Temperature and Pressure

**Boiling points** are characteristic temperatures which can be used to identify a substance. A **normal** boiling point is recorded at *standard* pressure (one atmosphere).

Boiling points must be recorded at a known pressure because liquids boil at a temperature that depends on the surrounding atmospheric pressure. A liquid will boil at a temperature

higher than its *normal* boiling point if the atmospheric pressure above it is higher than standard pressure. It will boil at a temperature lower than its normal boiling point if the pressure on the liquid is lower than standard pressure.

This means that there are three ways to boil a liquid: you can heat the liquid so that its vapor pressure rises to equal atmospheric pressure, or you can lower the lower pressure above the liquid, such as by using a bell jar and a vacuum pump, or you can do both.

### **Boiling Water**

Atmospheric pressure is generally lower at a high altitude than at sea level. This means that at high elevations, when you heat a liquid, its vapor pressure will equal atmospheric pressure at a lower temperature. The liquid will therefore boil at a lower temperature at high altitude than at sea level.

- Water boils at 100°C if the pressure above the water is 101 kPa = 760 torr = 1 atm. = standard pressure, which is about the average atmospheric pressure on a fair weather day at sea level. However, water boils at about 95° C under the lower atmospheric pressure typically found in locations one mile above sea level (such as Denver, Colorado). At high altitude, it takes more time to “hard boil” an egg than at sea level because the boiling water around the egg is not as hot.
- At 20.° C, water has a vapor pressure of 17.5 torr (see Lesson 18D). A *vacuum pump* can reduce the atmospheric pressure in a bell jar to below 17 torr, and water this partial vacuum will boil at room temperature (25° C).
- In a *pressure cooker*, boiling water is at higher temperature than boiling water at room pressure, and the changes required to “cook” food occur more quickly.

Boiling temperatures are affected by relatively small changes in the surrounding air pressure, such as those caused by altitude changes. Melting points are substantially changed only by much larger changes in pressure.

### **Boiling versus Evaporating**

Boiling is not the same as evaporating. Evaporation is a surface phenomenon. Measurable evaporation will occur from all liquids (and many solids) at any temperature. A liquid *boils* only when gas bubbles can form below the surface of the liquid and not just at its edges.

**Practice A:** Answer these questions, then, before going on to the next section, practice until you can answer the questions from memory.

1. Name the three phases. Name six different types of phase changes.
2. Which phases of matter can be significantly compressed in volume? Why?
3. Which has a higher temperature:
  - a. The melting point or the freezing point of a pure substance?
  - b. The melting point of a substance that is pure, or one that has impurities?
4. By definition, when does a liquid boil?
5. State three ways to boil a liquid.

- At what temperature does water boil at an atmospheric pressure of 101 kPa?
- At approximately what temperature does water boil in a city that is one mile above sea level? What explains the difference from the boiling temperature at sea level?
- Why does it take longer to hard-boil an egg at a high altitude?

## Energy

Chemistry is primarily concerned with matter and energy. In chemistry, matter and energy can be considered to be separate entities. Matter has mass and can be described in terms of particles such as protons, neutrons, and electrons. Energy has no mass. Sunlight, heat, and radio waves are a few examples of the many forms of energy.

A fundamental principle of chemistry is the **Law of Conservation of Energy**: energy can neither be created nor destroyed. However, during chemical or physical processes, energy can be *transferred* between substances, and to and from the environment. Energy can also change its *form*.

There are many forms of energy, but they can generally be divided into two types:

- kinetic** energy, defined as energy of *motion*, and
- potential** energy, defined as *stored* energy.

When a substance loses energy, the energy can do **work** as defined in physics (such as moving a piston against resistance), or energy can be transferred as heat to the environment around the substance. A substance can gain energy when work adds energy to the substance, such as by compressing a gas, or when the environment supplies heat to the substance.

## Kinetic Energy

Kinetic energy is energy of motion. The kinetic energy of an object is calculated by the equation

$$\text{KE} = \frac{1}{2} (\text{mass})(\text{velocity})^2$$

This equation means that if particle B has twice the mass of particle A but is moving at the same speed, Particle B has *twice* as much kinetic energy. If Particle C has the same mass as particle A but is moving twice as fast as Particle A, it has *four times* as much kinetic energy.

**Temperature** is a measure of the *average* kinetic energy of particles. When the temperature of particles goes up, their average kinetic energy increases. For this to occur, since the particles of a substance cannot change their mass, they must, on average, *move faster*.

**Practice B:** Answer, and be able to answer from memory, these questions.

- Define kinetic energy, in words, then using symbols in an equation.
- Batter #2 hits a baseball with a bat twice as heavy as Batter #1, swinging at the same speed. How much more energy will Batter #2 impart to the ball than Batter #1?
- Batter #3 hits the ball with the same bat as Batter #1, but swings twice as fast. How much more energy will Batter #3 impart to the ball than Batter #1?

#### 4. Define temperature.

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### Potential Energy

Potential energy is stored energy. Lifting an object against gravity is one way to add stored energy in an object. If the object returns to its former lower position, it must release that added energy.

- To raise a hammer, you must add energy. The energy is *stored* in the raised hammer as energy of position. If the hammer fall down to its original position, it must release the energy used to raise it. It can do so by creating *heat* where it hits. The hammer can also do *work*, such as driving nails. Heat, work, and energy of position are simply different forms of energy.
- The evaporation of water due to the absorption of radiation from the sun can store energy. One mechanism for this storage of energy is the transfer of water out of oceans (by evaporation) and into mountain streams (as rain). Lifting the water to a higher position stores energy from the sun in the water. As the water in rivers falls back toward sea level, the energy released in falling can be harnessed to spin turbines that create electricity. This electrical energy can be converted to light or heat, or can be used by electric motors to do work.

In chemical processes, forms of energy that can be stored and released include heat energy (including the energy stored in plants during photosynthesis) and electrical energy (as in rechargeable batteries). Compressing a gas can also store energy in a chemical system. When a compressed gas moves a piston against resistance, the potential energy stored in the gas is converted to work, another form of energy.

### Energy and Particle Attractions

Molecules and ions are held together by the attractions (bonds) arising from the protons and electrons *within* those particles. Energy always must be *added* to break chemical bonds, or to change a solid substance to a liquid and then to a gas. This added energy is needed to “unstick” the attracting particles. If the “unstuck” particles return to bonding condition which existed before they were separated, the same amount of energy that was added and stored during their separation must be *released*.

### Energy, Reactions, and Phase Changes

Changes in the potential energy of a chemical system can be the result of *chemical reactions* or *phase changes*.

In a chemical reaction, bonds between atoms break and new bonds form. As a result of chemical reactions, there is nearly always a characteristic *net* change in the energy stored in the substances. Energy must be added to break a bond, but more or less energy will be released when a different bond forms. This means that in a chemical reaction, energy is nearly always stored or released (to a major or minor extent).

In a phase change, the bonds between the *atoms* in a molecule do not change, and the formulas for substances therefore do not change. However, as a molecular substance changes phase from *solid* to *liquid* to *gas*, the weak attractions between the *molecules* must be

overcome during each phase change, so energy must be added. As the substance changes from *gas* to *liquid* to *solid*, that same amount of energy must be *removed* from the substance during each phase change.

- When a substance is melted, a characteristic amount of energy must be added per molecule to “unstick” the molecules so they can rotate and translate. The energy added to unstick the molecules is stored in the molecules that change from solid to liquid. If the liquid molecules change back to the solid state, the same amount of energy added to melt the solid must be *released* in order for the liquid molecules to solidify.
- When a substance boils, a characteristic amount of energy must be added per molecule. For that substance to condense from gas to liquid, that same amount of energy must be released.

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**Practice C:** Answer, and be able to answer from memory, these questions.

1. Define potential energy.
2. Name two types of chemical processes that can change the energy stored in molecules.
3. How does the heat of fusion of a substance (the heat/mole required to melt a certain mass) differ from the heat of freezing (the heat/mole released when the liquid changes to a solid)?

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### Energy and Phases

When energy is added to or removed from a pure substance, whether its *kinetic* or its *potential* energy changes depends on whether the substance is present in one phase or two.

Recall that by our definitions, a *substance* is composed of particles that all have the same chemical formula.

- When a substance is present in only *one* phase (all solid, all liquid, or all gas), adding or removing energy (such as by heating or cooling) changes the average *kinetic* energy of its particles (their temperature) but does *not* change the *potential* energy stored in the substance.
- During a phase *change* (such as melting or boiling), *two* phases must be present. If energy is added to or removed from a substance during a phase change, the *potential* energy stored in a substance *changes*, but the average *kinetic* energy of its particles does *not* change, and its temperature therefore stays constant.

During a phase change, if the two phases present are well mixed or in close contact, the temperature will be the same in both phases. If two phases are mixed and both phases are present after mixing, the temperature of the particles will have adjusted to become the same in both phases. A mixture of the solid and liquid phases of a substance will always be at the temperature that is its *melting point*.

## Potential Energy and Phases

The *solid* phase of a substance will always have *less* stored (potential) energy than its *liquid* phase, which will always have less potential energy than its *gas* phase.

$$\text{For a given substance: } PE_{\text{solid}} < PE_{\text{liquid}} < PE_{\text{gas}}$$

Changes in potential energy may not be as apparent as changes in kinetic energy, which are evident as temperature changes. Let us therefore examine some examples of energy changes during phase changes.

### Examples of Liquid-Gas Phase Changes

#### Boiling Water

In a kitchen at standard pressure, consider a tea kettle partially filled with cold water and placed on a lit gas stove. As long as the water in the kettle is *below* its *boiling* temperature, as it is heated by the flame its temperature rises. This increase in average kinetic energy is observable, and it means that the water molecules, on average, are moving faster. What is not observable, but is true, is that the *potential* energy stored in the water is *not* changing.

Boiling begins when the water temperature reaches 100°C. A thermometer will show that once the water begins a steady boil, *both* the liquid water *and* the steam above the boiling water have the same temperature (if precautions are taken to prevent “super-heating”). At standard pressure (101 kPa), for pure boiling water, that temperature will always be 100°Celsius, by definition.

During any phase *change* for any substance, *both* phases will have the *same temperature* as long as they are in close contact. This means that the particles in both phases have the same average *kinetic* energy.

After 5 minutes of boiling, quite a bit of heat has been added by the flame to the water in the tea kettle. However, a thermometer will show that both the water and steam remain at 100°C as long as any liquid water remains in the kettle.

Energy can neither be created nor destroyed. Where is all the energy being supplied by the flame going? The flame’s energy is being *stored* in the *gas* particles (steam) that form during the phase change.

A characteristic amount of energy must be stored in molecules as they change from being as close as possible in their liquid phase to being far apart in their gas phase.

If the flame remains lit beneath the kettle, the water will continue to boil until the last bit of liquid water is converted to steam. At that point, instead of two phases inside the tea kettle, there is only *one* phase (steam). Adding energy with *one* phase present will increase the *temperature* of the steam: its kinetic energy instead of its potential energy. If all of the water is allowed to boil to steam, there is no longer a phase change to absorb the energy supplied by the flame, and the temperature of the steam in the kettle (and of the kettle itself) will increase *very* quickly.

However, as long as *some liquid* water remains in the kettle, the highest temperature possible for the water *or* the steam is 100°C: much cooler than the flame below.

### Warming Leftovers

On a practical note, this is why a little water should be added when heating leftovers in a loosely covered pan. As long as there is some liquid water between the heat and the food, the maximum temperature of the water and the food will be 100° Celsius, enough to warm but not to burn most foods. If all of the water boils away, the food can burn quickly.

When water boils in the pan, it forms steam. When the steam reaches a cooler surface, it can condense to form water. When steam condenses on cool food in a pan, the same amount of potential energy which was stored in the steam as it formed from water must be lost from the steam. As the steam turns to water, energy is transferred to the food, and the “steamed food” heats quickly.

### Thunderclouds - Water Condensing

On a humid summer day, clear water vapor (a gas) in the atmosphere can condense to tiny drops of liquid water (clouds). As the water vapor condenses, the considerable amount of heat required to change liquid water to water vapor must be released, and the condensation of vapor to water heats the air around the water droplets. Since warmer air is less dense than colder air, it rises, creating an updraft that lifts both the moist air and the water droplets. Because the atmosphere generally cools with increasing altitude, more water vapor in the humid air forms more liquid water and more heat as it rises. As this cycle repeats, the cloud becomes a fast rising “thunderhead.”

As the liquid water droplets become larger with increased condensation, the drops become too heavy to be lifted by the updraft. The result is a thunderstorm. The falling raindrops create a powerful “downdraft” of air that strikes the ground and fans out ahead of and with the rain. The downdraft reverses the updraft feeding the thunderhead, eventually causing the thunderstorm to dissipate.

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**Practice D:** Answer these questions, then practice until you can answer the questions from memory before going on to the next section.

1. If substantial energy is added to a substance, and it remains the same substance but its temperature does not change, what does this tell you about the substance?
2. When does adding energy to a substance cause its temperature to rise?
3. For a given substance, which phase has the lowest amount of stored energy: solid, liquid, or gas?
4. In a kitchen where the atmospheric pressure is close to standard pressure, water is placed in a tea kettle and heated on a gas stove. At the point where the water first starts to boil,
  - a. what is the temperature of the liquid water in the kettle?
  - b. What is the temperature of the steam above the water in the kettle?
5. After 5 minutes of heating, about half of the water in the kettle has boiled away.
  - a. What is now the temperature of the liquid water in the kettle?
  - b. What is the temperature of the steam above the water in the kettle?

6. During the five minutes of boiling, the gas stove adds considerable energy to the water in the tea kettle.
- Has the kinetic energy of the water or steam changed?
  - Has the potential energy of the molecules that are still liquid water changed?
  - Has the potential energy of the molecules that were converted from water to steam changed?
  - Where has the energy gone that was supplied by the stove in those 5 minutes? What kind of energy has it become?

## Liquid-Solid Phase Changes

### Mixing the Solid and Liquid Phase

A stirred mixture of the solid and liquid phases of a substance will always adjust to the temperature that is the *melting point* of the substance.

For example:

- H<sub>2</sub>O melts and freezes at 0° Celsius at pressures at or near typical atmospheric pressure. It is a characteristic of water molecules that a stirred *mixture* containing water and ice will always adjust to a temperature of 0° C: the melting point of H<sub>2</sub>O. A mixture of ice and water is a good *constant temperature bath* or *cold pack*. It will stay at 0°C for as long as both ice and liquid water are present.
- When warm water is added to an ice-water mixture, two phases are present, and the temperature of the new mixture must adjust toward the melting (= freezing) point of water. As ice melts, the warm water molecules become colder. The kinetic energy lost by the warm water is *equal* to the potential energy *stored* in the molecules of ice that become liquid. The warm water continues to cool, and ice continues to melt, until either the new mixture reaches its melting point (0°C) or all of the ice melts.

### Melting Ice

When ice melts, a solid becomes a liquid. To change a solid substance to its liquid, energy must be added. The liquid particles have a *characteristic* higher amount of stored energy, per particle, than the solid particles.

While ice is melting, its temperature does not change, but heat must be added from the environment. This is why a mound of packed snow can take quite a while to melt even when air temperatures are well above freezing. Considerable heat from the environment must be absorbed by the solid ice molecules that become liquid water.

### Freezing Water In an Ice Tray

The liquid phase of a substance has inherently more stored energy than its solid phase. To convert liquid molecules to solid molecules, stored energy must be removed.

To change water into ice, the *same* amount of energy, per molecule, must be taken *out* of the water that is put into the ice to melt it.

- When warm water in an ice tray is placed in a freezer, the temperature of the water drops rapidly as its heat transfers to the freezer environment. When the water's temperature reaches  $0^{\circ}\text{C}$ , it begins to freeze.
- Unless potential energy leaves a liquid, the liquid cannot become solid. To freeze water, the air in a freezer must be colder than  $0^{\circ}\text{C}$  so that heat energy will flow out of the  $0^{\circ}\text{C}$  water. To provide an air temperature below  $0^{\circ}\text{C}$ , the freezer compressor pumps heat out until the air is about  $-20^{\circ}\text{C}$  inside most household freezers. You can feel the heat that is being pumped out if you place your hand in the space above the coils on the back or underside of a freezer while the compressor is running.
- After freezing begins, the water/ice mixture in an ice tray will stay at  $0^{\circ}\text{C}$  until *all* of the water freezes. During this time, the water and ice mixture will be the warmest spot in the freezer; warmer than the freezer contents that are already frozen and at  $-20^{\circ}\text{C}$ .
- Once the ice-tray water is completely frozen, one phase is present, and the temperature of the now solid ice cubes drops relatively quickly to the freezer's air temperature.

Ice cubes just removed from the freezer, at about  $-20^{\circ}\text{C}$ , are cold enough to both cool and then freeze the moisture on your skin, which can cause the ice cubes to stick to your fingers. However, at room temperature,  $-20^{\circ}\text{C}$  ice warms quickly. When it reaches  $0^{\circ}\text{C}$ , the ice begins to melt. Ice at  $0^{\circ}\text{C}$  is not cold enough to freeze skin moisture: melting ice will not stick to your skin.

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**Practice E:** Answer, and be able to answer from memory, these questions.

1. A mixture of crushed ice and water is added to an insulated container. After a minute of stirring, the temperature of the mixture no longer changes, and both ice and water remain.
    - a. What is the temperature of the ice? What is the temperature of the water?
    - b. Which phase has higher kinetic energy?
    - c. Which phase has higher potential energy?
  2. Warm water is added to an ice-water mixture in an insulated cup. After stirring for one minute, the temperature is stable, and ice and water remain.
    - a. What is the temperature of the water in the cup?
    - b. What is the temperature of the ice?
  3. During the one minute of stirring, the warm water lost some of its energy.
    - a. What kind of energy did it lose?
    - b. As the warm water lost its energy, what other change occurred?
    - c. Where is the energy that was lost by the warm water, and what kind of energy is it?
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## **Summary: Phases, Phase Changes, and Energy**

You may want to organize the following information into charts, numbered lists, and flashcards that will help with learning and retention in memory.

- For substances, the three phases and three phase changes are these:
  - Solids *melt* (or *fuse*) to become liquids; liquids *freeze* (or *solidify*) to become solids.
  - Liquids *boil* or *evaporate* to form gases; gases *condense* to become liquids.
  - Solids *sublimate* to become gases directly; gases that undergo *deposition* form solids.
- The *Law of Conservation of Energy* states that energy can neither be created nor destroyed (except in *nuclear* reactions). However, energy can be transferred between substances and to and from the environment. Energy can also change its form during chemical or physical processes.
- Two forms of energy are *potential* energy, defined as stored energy, and *kinetic* energy, defined as energy of motion.  $\text{Kinetic Energy} = \frac{1}{2} (\text{mass}) (\text{velocity})^2$
- Chemical substances can store energy in the attractions between atoms, molecules, and particles. During chemical reactions and phase changes, energy is stored or released.
- One way to store energy in a substance is to change its phase. The solid phase of a substance always has less stored (potential) energy than its liquid phase, which always has less potential energy than its gas phase.

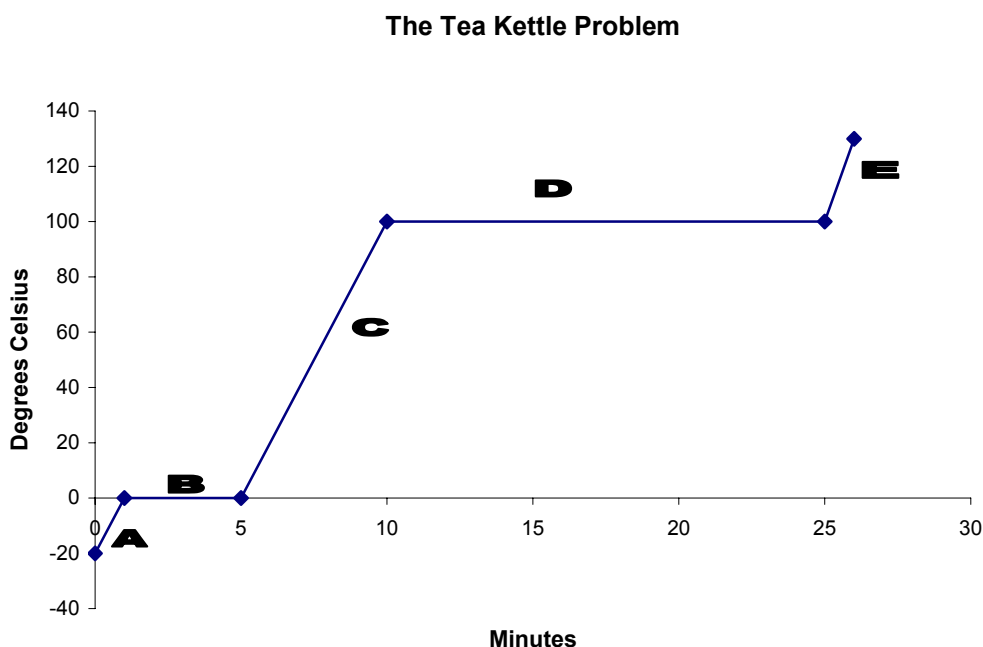
Potential energy of a substance: **solid < liquid < gas**

- When a substance is in *one* phase (all solid, liquid, or gas), adding or removing energy will change the average kinetic energy of its particles (its *temperature*), but *not* its potential energy.
- For a substance during a phase change,
  - adding or removing energy changes the potential energy, but not the average kinetic energy (temperature) of the particles.
  - Temperature remains constant and the temperature is the same in both phases as long as they are in close contact.
- The temperature at which a substance melts (its melting point) will equal the temperature at which it solidifies (melting point  $\equiv$  freezing point).
- In a stirred mixture of the solid and liquid phases of a substance, the temperature will be the melting point of the substance.
- The melting point is a characteristic of a substance. The melting point will be the same no matter how the substance is formed. The melting point can be used as evidence to identify a substance.
- A substance in its liquid phase will boil at any temperature at which its vapor pressure equals the atmospheric pressure above it. If the atmospheric pressure on the liquid is lowered, the liquid will boil at a lower temperature. If the atmospheric pressure is raised, the liquid will boil at a higher temperature.

- Boiling points are a characteristic which can be used to identify a substance, but only if the atmospheric pressure is known. Boiling points are far more sensitive to atmospheric pressure than melting points.
- Evaporation is a surface phenomenon; measurable evaporation will occur from all liquids (and some solids) at any temperature. However, a liquid *boils* only when gas bubbles form below the liquid surface and not just at its edges.

**Practice F:** At standard pressure, small cubes of ice are removed from a freezer and placed in a tea kettle. A thermometer is inserted into the ice cubes and the kettle is placed on a lit gas stove. The kettle is heated until one minute after all of the water has boiled away.

The graph below charts the changes in the temperature of the H<sub>2</sub>O molecules as they change from ice to water to steam.



### Questions

- How many phase changes occur during the above process?
- How many phases will have been present by the time the above process is completed?
- Which segment of the graph represents water boiling to steam?
- How can a change in the kinetic energy of the H<sub>2</sub>O be recognized during the process?
- How can a change in the potential energy of the system be recognized?
- In which lettered segments of the graph does potential energy remain constant?
- In which segments of the graph does average kinetic energy remain constant?

- In which portions of the graph do the H<sub>2</sub>O molecules have the largest amount of stored energy?
  - Which portions of the graph show energy from the flame being converted into potential energy?
- 

## **ANSWERS**

### **Practice A**

- Phases: solid, liquid, gas. Changes: melting, freezing, boiling, condensing, sublimation, deposition.
- Only the gas phase. There is substantial distance between particles only in the gas phase.
- Melting point = Freezing point, by definition.
  - A pure substance melts at a higher temperature than the same substance with impurities.
- When its vapor pressure equals the atmospheric pressure above it.
- Raise the liquid's vapor pressure by raising its temperature, or lower the atmospheric pressure above the liquid, such as by moving to higher altitude or into a partial vacuum.
- 101 kPa is standard pressure, so water boils at **100° C** by definition.
- Approximately 95 degree Celsius. At high altitude, atmospheric pressure is lower, and the water's vapor pressure will equal atmospheric pressure at a lower temperature.
- The water boils at a lower temperature, and at a lower temperature the changes needed to "cook" food take longer to occur.

### **Practice B**

- Kinetic energy is energy of motion.  $KE = \frac{1}{2}(\text{mass})(\text{velocity})^2$ .
- Batter #2 hits with twice as much energy.      3. Batter #3 hits with four times more energy.
- Temperature is a measure of the average kinetic energy of chemical particles.

### **Practice C**

- Stored energy                      2. Chemical reactions and phase changes.
- Heat of melting = heat of solidification. The heat added in melting must be released when a liquid solidifies.

### **Practice D**

- Two phases are present, and the substance is undergoing a change to a phase with more stored energy.
- When only one phase is present, which means the substance is not undergoing a phase change.
- Solid.      4a and 4b. Both the liquid water and the steam are at 100° C.
- 5a and 5b. Both the liquid water and the steam are still at 100° C.      6a. No.      6b. No.      6c. Yes
- 6d. The energy is now potential energy stored in those molecules that changed phase from liquid to gas.

### **Practice E**

- 1a. Both are at 0° C.      1b. Both have the same KE.      1c. The liquid water has higher PE.
- 2a and 2b. Water and ice are both at 0°. If both solid and liquid are present, both must be at the melting point.

- 3a. The warm water lost *kinetic* energy: its temperature fell.    3b. The warm water melted some ice.  
 3c. The kinetic energy lost by the water in cooling to 0° is now *potential* energy that is stored in the ice molecules that were previously ice, but the warm water melted.

### Practice F

- Two (melting and boiling)      2. Three (solid, liquid, and gas)      3. **D**
- The temperature *changes* (this occurs when the line is not in a “plateau” region.)
- Where the graph has a “plateau” region, heat is being added from the stove for several minutes but the temperature (average kinetic energy) remains constant, so potential energy must be increasing.
- A,C,E** – when the kinetic energy is changing.      7. **B and D** – the temperature stays constant.
- D and E** – the gas phase (the steam) which forms during D, and then heats during E, has the most potential energy.
- B and D** – during the two phase changes.

\* \* \* \* \*

## Lesson 21B: Specific Heat Capacity and Equations

**Timing:** If you have not already done so, before doing Lesson 21B, complete Lesson 17C on cancellation of complex units.

If your class assignments require calculations that include *PV work* before specific heat and calorimetry calculations, do Lesson 22A, then return here.

\* \* \* \* \*

### Units That Measure Energy

In chemistry, energy is usually measured in joules or calories.

- The **joule** (abbreviated **J**) is the SI unit measuring *energy*.

A joule is defined in physics in terms of **work**: as the amount of energy needed to accelerate 1 kg by 1 meter/sec<sup>2</sup> in 1 meter.

$$\text{work} = (\text{force})(\text{distance}) = (\text{mass})(\text{acceleration})(\text{distance}) .$$

Though joules are defined in terms of work, all forms of energy are equivalent and can be measured in any energy units. In chemistry, joules is unit that is used most often to measure the *heat energy* lost or gained in a chemical process.

- The **calorie** (abbreviated **cal**) is a metric unit that is also used to measure energy.

A chemical **calorie** is defined as the amount of heat needed to raise the temperature of one gram of liquid water by one degree (Celsius or kelvin).

- Because all forms of energy are equivalent, all energy units can be related by equalities.

The conversion between calories and joules is: **1 calorie = 4.184 joules**

4. In studies of nutrition, a **food Calorie** is the unit used to measure the heat released when food is burned completely and/or is metabolized in cells.

$$\boxed{1 \text{ food Calorie} = 1,000 \text{ chemical calories} = 1 \text{ kilocalorie (kcal)} = 4.184 \text{ kilojoules (kJ)}}$$

The calories listed on nutritional labels are food Calories (chemical kilocalories).

In chemistry texts, *food* Calories are written as Calories with a capital C, whereas *chemical* calories are written with a lower case c.

Nearly all chemistry courses assign problems using joules to measure energy. Some may also assign problems using chemical and/or food calories. You should learn the relationships needed for *your* course.

### Energy and Heat

An energy transfer between a system and its surroundings in a chemical or physical process may involve heat (symbol  $q$ ) and/or work ( $w$ ).

In science, the symbol  $\Delta$  (**delta**) means *change in*. When chemical reactions and processes take place, the change in the energy of the molecules involved (the chemical system) can be represented by

$$\Delta E_{\text{system}} = q + w$$

For example: Boiling water adds heat to the molecules. Burning gasoline releases heat. Work is required to compress a gas. When a compressed gas moves a piston against resistance, the molecules lose energy as the system does work.

In Lesson 22A, we will consider calculations that involve mechanical work. In this module, our focus will be on calculating **heat energy** (symbol  $q$ ).

### Specific Heat Capacity

In these lessons, we will define the amount of heat required to raise one *gram* of a substance by one *degree* Celsius or kelvin as the **specific heat capacity** (symbol small  $c$ ) of the substance. (Some textbooks use different terms and symbols for this quantity.)

In most calculations, specific heat capacity will be used to calculate the *total* energy change in a process. We will therefore learn the equation using specific heat capacity in this form:

For a substance in a single phase:  $\boxed{q = c \cdot m \cdot \Delta t}$

The symbol  $q$  represents heat energy. This equation means:

$$\begin{aligned} \text{The } \textit{heat energy} \text{ gained or lost by a substance} &= \\ &= (\textit{specific heat capacity of the substance}) \times (\textit{its mass}) \times (\textit{its change in temperature}) \end{aligned}$$

When heat is added to a system of chemical particles,  $q$  is defined as positive. When chemical particles lose heat,  $q$  is defined as negative.

The units of  $c$  are joules *per* (gram  $\cdot$  degree) *or* calories *per* (gram  $\cdot$  degree).

For example, the specific heat value for liquid water is written  $c_{\text{water}} = 4.184 \text{ J/g} \cdot \text{K}$

Recall that the *dot* between gram and K means that the two units are multiplied together in the numerator or denominator. These three notations are equivalent:

$$4.184 \text{ joule/gram} \cdot \mathbf{K} = 4.184 \frac{\text{J}}{\text{g} \cdot \mathbf{K}} = 4.184 \text{ J} \cdot \text{g}^{-1} \cdot \mathbf{K}^{-1}$$

(If your course or textbook uses the  $unit^{-1}$  or  $unit^{-\#}$  notation in calculations, you may want to complete Lesson 27F after this lesson.)

Specific heat capacity may also be measured in joules/*kilogram* • degree. You will learn below how to convert data to the consistent units needed to solve equations.

Note the difference indicated by the equation between *heat* and *temperature*.

- Temperature is an intensive property: when you measure a temperature, the value does not depend on the amount of matter being measured.
- Heat is an extensive property. When calculating the heat transferred in a process, what is being heated, the amount being heated, and how much heat is being transferred, all matter. On a gas stove, to bring water at room temperature to the point that it begins to boil, for a large amount of water you must supply more heat than for a small amount.

### Change in Temperature

In science, the symbol  $\Delta$  (**delta**) means *change in*. The symbol  $\Delta t$  (read “delta t”) means *change in temperature*. The definition of  $\Delta t$  is:

$$\Delta t \equiv t_{\text{final}} - t_{\text{initial}}$$

This definition means that a change in temperature must be labeled as positive when temperature increases and negative when it decreases.

A change in temperature will be the same *number* of degrees when measured in the Celsius or Kelvin scales. Why? The Kelvin and Celsius scales have the same *size* degree.

If, in Celsius,  $\Delta t = 25^{\circ}\text{C} - 0^{\circ}\text{C} = 25^{\circ}\text{C}$ , the same measurements recorded in kelvins will result in the *same number* for the *change*:  $\Delta T = 298 \text{ K} - 273 \text{ K} = 25 \text{ K}$

This means that if the temperature units in a problem are based on  $\Delta t$  measurements, the word **degree** and the symbols  $^{\circ}\text{C}$  and **K** are all *equivalent*.

Since specific heat capacity (*c*) is defined in the words and equation above as based on a *change* in temperature ( $\Delta t$ ), a value for *c* of “4.184 joules/ gram • **degree**” can also be written as “4.184 joules/ gram • **K**.”

When units are equivalent, they can cancel. In calculations using  $\Delta t$  values,

$$\frac{\text{joules} \cdot ^{\circ}\text{C}}{\text{K}} = \frac{\text{joules} \cdot \cancel{^{\circ}\text{C}}}{\cancel{\text{K}}} = \text{joules} \quad \text{and} \quad \frac{\text{calories} \cdot \text{K}}{\text{degree}} = \frac{\text{calories} \cdot \cancel{\text{K}}}{\cancel{\text{degree}}} = \text{calories}$$

**Practice A:** Assume that the temperature units below are all measurements of  $\Delta t$ . Do the unit cancellation, write the final unit.. If you need a review of the rules for unit cancellation, see Lesson 17C.

1.  $\frac{\text{joules}}{\text{gram} \cdot \text{K}} \cdot \text{g} \cdot ^\circ\text{C} =$

2.  $\frac{\text{joules}}{\frac{\text{joules}}{\text{gram} \cdot \text{K}} \cdot \text{g}} =$

3.  $\frac{\text{calories}}{\frac{\text{calorie}}{\text{gram} \cdot \text{degree}} \cdot ^\circ\text{C}} =$

4.  $\frac{\text{joules}}{\text{grams} \cdot ^\circ\text{C}} =$

5. Name two metric units that can be used to measure  $q$ .

### Values for Specific Heat Capacity ( $c$ )

Chemical substances have a *characteristic* specific heat capacity in each phase: a fixed amount of heat changes one gram of the substance by one degree. Some values for specific heat capacity are in the table on the right.

As in the case of  $\text{H}_2\text{O}$  in the table, for each substance, each *phase* has a different  $c$  value.

Heat capacity values apply only while a substance is in a single phase. A different measure for calculating heat changes will be needed when a substance is *changing* phase.

Substance	Specific Heat Capacity In J/g·K
$\text{H}_2\text{O}$ liquid	4.184
$\text{H}_2\text{O}$ solid	2.09
Cu solid	0.385
Fe solid	0.444

To solve calculations that include specific heat capacity, we will use the *equation* that includes specific heat capacity. Our rule will be:

**The  $c$  Prompt:** If you see the term *specific heat capacity* or its symbol  $c$  in a problem, write at the top of your DATA table this *equation* which uses  $c$ :

$$q = c \cdot m \cdot \Delta t$$

### Solving Problems Which Require Equations

In these lessons, we will refer to equalities that use symbols, such as  $q = c \cdot m \cdot \Delta t$ , as *equations* rather than *formulas* to distinguish them from chemical formulas, such as  $\text{H}_2\text{O}$ .

When solving problems using equations, we will add steps to our conversion method of problem solving.

If you have already completed the Ideal Gas module in these lessons, you have learned the following method for solving problems with equations. However, since many chemistry courses cover energy calculations *before* gas laws, we will describe the steps of the method in detail as it applies to energy problems as well.

## Solving With Equations

Problems in physical science can generally be put into three categories: those that can be solved with unit cancellation (conversions), those that require equations, and those requiring both.

We will use the specific heat equation to illustrate a consistent method for solving calculations that require equations. Starting with relatively easy examples, we will develop a method that also works for more difficult problems.

Easy problems can be solved in other ways, but to learn the *system* which is especially useful for the more difficult calculations that lie ahead, try the method used here.

Let us start with an example:

- Q.** When 832 joules of heat is added to a sample of solid copper (Cu), the temperature rises from 15.0°C to 33.0°C. Based on the specific heat capacity in the table above, how many grams of copper were in the sample?

To solve, complete the following steps in your notebook.

1. As always, begin by writing “WANTED: ?” and the unit you are looking for.
2. This problem mentions “specific heat capacity.” That’s the *c prompt*. In the DATA, write the memorized equation which includes specific heat capacity (*c*).
3. Below the equation, make a data table that lists *each symbol* in the equation.

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For this problem, your data section should include:

DATA:  $q = c \cdot m \cdot \Delta t$

$q =$

$c =$

$m =$

$\Delta t =$

4. After each symbol, based on *units*, write each number and unit supplied in the problem.
  - The symbol for heat energy is *q* and energy is measured in *joules*, so in this problem  $q = 832$  joules.
  - From the table value for copper:  $c = 0.385$  J/g·K
5. Put a ? after the symbol in the table that you are *looking for*. Add the unit and label of the quantity you are looking for.

Fill in the data table completely, and then check below.

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At this point, your paper should look like this:

WANTED: ? g Cu

DATA:  $q = c \cdot m \cdot \Delta t$

$$q = 832 \text{ joules}$$

$$c = 0.385 \text{ J/g}\cdot\text{K}$$

$$m = ? \text{ g Cu}$$

$$\Delta t = 33.0^\circ\text{C} - 15.0^\circ\text{C} = + 18.0^\circ\text{C}$$

6. SOLVE the fundamental memorized equation, using algebra, for the *symbol* WANTED. Do not plug in numbers until you have solved for the WANTED symbol. (Symbols move more quickly than numbers and their units.)

Try that step, then check below.

\* \* \* \* \*

SOLVE: Solving  $q = c \cdot m \cdot \Delta t$  for the symbol  $m$  WANTED,

$$? = m = \frac{q}{c \cdot \Delta t}$$

7. After solving in symbols, plug in the numbers and solve. Cancel units that cancel, but leave the units that do not cancel, and include them after the calculated number.

\* \* \* \* \*

On your paper should be

SOLVE:  $q = c \cdot m \cdot \Delta t$

$$? = m = \frac{q}{c \cdot \Delta t} = \frac{832 \text{ joules}}{0.385 \frac{\text{J}}{\text{g}\cdot\text{K}} \cdot 18.0^\circ\text{C}} = \frac{832 \text{ J}}{18.0^\circ\text{C}} \bullet \frac{1}{0.385 \frac{\text{J}}{\text{g}\cdot\text{K}}} = \frac{832 \text{ J}}{18.0^\circ\text{C}} \bullet \frac{\text{g}\cdot\text{K}}{0.385 \text{ J}} = 120. \text{ g Cu}$$

Note that in the step above, the term with a fraction in the denominator was separated and then simplified using the rules for reciprocals.

Double check the cancellation of the units for the last step above. Since *degrees* and  $^\circ\text{C}$  and  $\text{K}$  are all equivalent when they measure a  $\Delta t$ , as units they can cancel as units.

The above problem involved finding *grams* of Cu, but you did not need the molar mass to solve. This is because specific heat capacity is one of the rare quantities in chemistry that is defined based on grams rather than moles. Other heat problems *will* involve moles. Our rule will be

In *heat* problems, if you see *both* grams *and* moles of a substance as units in a problem, write the molar mass in your data, because you will likely need the molar mass to solve.

**Summary: Solving With Equations**

If you need a mathematical *equation* to solve a problem, follow these steps.

1. Write the fundamental, memorized equation.
2. Make a data table with each of the *symbols* in the equation.
3. Based on *units*, write each item of data after a *symbol* in the data table.
4. Memorize equations in *one* format, then use algebra to solve for the symbol WANTED. This will minimize the need to memorize.

For example, memorize:  $q = c \cdot m \cdot \Delta t$ .

Then if you WANT  $c$  or  $m$  or  $\Delta t$ , use algebra to solve the equation for that symbol.

Don't memorize:  $m = \frac{q}{c \cdot \Delta t}$  and  $c = \frac{q}{m \cdot \Delta t}$  and  $\Delta t = \frac{q}{c \cdot m}$

5. Solve the fundamental equation for the WANTED symbol *before* you plug in numbers.
6. Plug both numbers and units into equations. Rely on unit cancellation to check your work.

**Practice B:**

Make a set of flashcards covering the key definitions and equations in this lesson. Practice until you can answer each card automatically. Then, when doing the following problems, try to use your knowledge and your practice of the steps above to solve without looking back at the lesson.

1. Define what each of the symbols  $q$ ,  $c$ , and  $\Delta t$  represent.
2. When 681 joules of heat are added to 240. grams of a pure solid, the temperature of the solid rises by 22.0 degrees. What is the specific heat capacity of the solid?
3. If 361 joules are added to a 32.5 gram sample of iron (Fe) at 20.0°C, use the value for  $c$  from the table above and solve for the final temperature of the sample.

**ANSWERS**

**Practice A** You may use other methods of unit cancellation (see Lesson 17C) as long as you arrive at the same answers as these. Degrees and °C and K are all equivalent when they are used to measure a *change* in temperature ( $\Delta t$ ). If one is on top and one is on the bottom when you multiply terms, they can cancel.

1.  $\frac{\text{joules}}{\text{gram} \cdot \cancel{\text{K}}} \cdot \text{g} \cdot \cancel{\text{°C}} = \text{joules}$
2.  $\frac{\cancel{\text{joules}}}{\frac{\text{joules}}{\text{gram} \cdot \text{K}} \cdot \text{g}} = \frac{1}{\text{K}} = \text{K}$

3.  $\frac{\text{calories}}{\text{calorie} \cdot \text{gram} \cdot \text{degree}} = \frac{1}{1} = \text{grams}$       4.  $\frac{\text{joules}}{\text{grams} \cdot \text{°C}} = \frac{\text{joules}}{\text{grams} \cdot \text{°C}}$   
 (in Problem 4, nothing cancels.)
5. Joules and calories.

**Practice B**

1. The symbol  $q$  stands for heat energy,  $c$  is specific heat capacity and  $\Delta t$  means change in temperature.

2. WANTED:  $c = ?$

(Strategy: When “specific heat capacity” is mentioned, that calls the “c prompt.” Write:)

DATA:  $q = c \cdot m \cdot \Delta t$  (and make a data table to match all those symbols.)

$$q = 681 \text{ J}$$

$$c = ?$$

$$m = 240. \text{ g}$$

$$\Delta t = 22.0^\circ\text{C}$$

SOLVE: Since  $q = c \cdot m \cdot \Delta t$

$$? = c = \frac{q}{m \cdot \Delta t} = \frac{681 \text{ J}}{240. \text{ g} \cdot 22.0^\circ\text{C}} = 0.129 \frac{\text{J}}{\text{g} \cdot \text{degree}}$$

(Solve in symbols before plugging in numbers and units. Do the math for both numbers and units. Make sure the answer unit matches what the unit should be for the symbol WANTED.)

3. WANTED: Final temperature

Since  $\Delta t = \Delta t \equiv t_{\text{final}} - t_{\text{initial}}$  then  $t_{\text{final}} = t_{\text{initial}} + \Delta t$

Strategy: When  $c$  is mentioned, that's the prompt to write

DATA:  $q = c \cdot m \cdot \Delta t$  Make a data table to match those symbols.

$$q = 361 \text{ J}$$

$$c = 0.444 \text{ J/g}\cdot\text{K for Fe}$$

$$m = 32.5 \text{ g Fe}$$

$$\Delta t = ? \quad \text{WANTED Final } t = 20.0^\circ\text{C} + \Delta t$$

SOLVE: Since  $q = c \cdot m \cdot \Delta t$ , and we want  $\Delta t$ ,

$$? = \Delta t = \frac{q}{c \cdot m} = \frac{361 \text{ J}}{0.444 \frac{\text{J}}{\text{g} \cdot \text{K}} \cdot 32.5 \text{ g}} = 25.0 \text{ K} = \Delta t \quad \text{Done?}$$

$$\text{WANTED} = t_{\text{final}} = t_{\text{initial}} + \Delta t$$

$$\text{Final } t = 20.0^\circ\text{C} + \Delta t = 20.0^\circ\text{C} + 25.0^\circ\text{C or K} = 45.0^\circ\text{C final temperature}$$

A  $\Delta t$  is the same *number* of degrees in the Celsius and Kelvin temperature scales.

\* \* \* \* \*

## Lesson 21C: Energy, Water, and Consistent Units

The substance most often used to supply or absorb heat in a chemical process is *liquid water*. Most courses require that the value for the specific heat capacity of water be memorized. In heat calculations that involve liquid water, we will use this rule:

***c* Water Prompt:** If a problem mentions *energy* or *heat* or *joules* or *calories* -- **and liquid water**, write in your data table the equation using specific heat capacity,

$$q = c \cdot m \cdot \Delta t$$

In the DATA table with those 4 symbols, write

$$c = c_{\text{water}} = 4.184 \text{ J/g} \cdot \text{K} \quad (\text{or } c_{\text{water}} = 1 \text{ calorie/g} \cdot \text{K})$$

Choose the *c* value with an energy unit that matches the energy unit in the problem.

Using this prompt, problems involving heat and water can be solved in the same way as the specific heat problems in the previous lesson.

In calculations involving liquid water, assume that 1 mL liquid H<sub>2</sub>O = 1.00 gram liquid H<sub>2</sub>O unless a more precise density is noted.

Note that though the common name for H<sub>2</sub>O is water, in problems dealing with energy it is important to distinguish between *ice*, *water*, and *steam*. These three phases for H<sub>2</sub>O have different values for *c*. However, unless ice or steam is specified, in heat problems you should assume that *water* means *liquid water*.

### Consistent Units

For an equation to work, the units must match the requirements of the equation.

For example, the equation for specific heat capacity requires *mass* (usually grams, occasionally kg). If the data is given in *moles*, you must convert moles to grams or kg before you solve.

In addition, when solving equations, units must be **consistent**.

For example, in an equation involving *mass*, grams or kilograms may be used, but not both. You must choose a mass unit, and then convert the other masses to that unit. Which unit should you choose?

Which unit should you choose? In most cases, you may solve equations in any consistent units, but some ways of choosing consistent units will solve more quickly than others. To solve heat problems, we will use this rule:

Convert DATA to the units in the most *complex* unit.

For example: If a heat calculation includes a unit of "joules/kg·K," convert the units in the DATA to joules and kilograms.

The best time to convert to consistent units is *early* in a problem. The best place to convert to consistent units is in the DATA table.

Keeping those points in mind, try this example in your notebook. If you get stuck, peek at a bit of the answer on the next page, then try again.

**Q.** 16.0 moles of water at 25.0°C is supplied with 28.0 kJ from a bunsen burner. If all of the heat is absorbed by the water, what will be the water's final temperature?

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**Answer**

When you see *joules* and liquid water, that's the *c water prompt*. Write the equation that includes specific heat capacity, a data table to match its symbols, and fill in *c* for liquid water. Because the data in the problem includes kJ as a unit, pick the *c* value that includes joules.

DATA:  $q = c \cdot m \cdot \Delta t$

$q =$

$c = 4.184 \text{ joules/gram} \cdot \text{K}$

$m =$

$\Delta t =$

Since the units supplied in the problem do *not* match the units of the complex unit, write a ? and a unit beside each symbol that *is* consistent with the *complex* unit.

DATA:  $q = ? \text{ joules} =$

$c = 4.184 \text{ joules/gram} \cdot \text{K}$

$m = ? \text{ grams} =$

$\Delta t = ? \text{ K or } ^\circ\text{C}$     **WANTED final temp = 25.0°C + Δt**

Note that a  $\Delta t$  value in degrees Celsius and kelvins is the same.

Add the remaining data from the problem to the table, converting to the consistent units as you go.

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DATA:  $q = ? \text{ joules} = 28.0 \text{ kJ} = 28.0 \times 10^3 \text{ J}$     (done by inspection)

$c = 4.184 \text{ J/g} \cdot \text{K}$

$m = ? \text{ g} = 16.0 \text{ mol H}_2\text{O} \cdot \frac{18.0 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} = 288 \text{ g H}_2\text{O}$

$\Delta t = ? \text{ K or } ^\circ\text{C}$     **WANTED final temp. = 25.0°C + Δt**

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SOLVE:  $? = \Delta t = \frac{q}{c \cdot m} = \frac{28.0 \times 10^3 \text{ J}}{4.184 \frac{\text{J}}{\text{g} \cdot \text{K}} \cdot 288 \text{ g}} =$

$= 28,000 \text{ J} \cdot \frac{\text{g} \cdot \text{K}}{4.184 \text{ J}} \cdot \frac{1}{288 \text{ g}} = 23.2 \text{ K increase} = \Delta t$

Since heat is being added to water, the temperature will increase. You may keep track of the direction of the temperature change using signs on  $\Delta t$  or with labels noting an increase or decrease temperature.



**ANSWERS**

1. a. ? J = 0.25 kJ =  $0.25 \times 10^3 \text{ J} = 2.5 \times 10^2 \text{ J} = 250 \text{ J}$   
 b. ? g H<sub>2</sub>O(l) = 75 mL H<sub>2</sub>O(l) =  $75 \text{ g H}_2\text{O}(l)$  (1.00 g liquid water = 1 mL)  
 c. ? g H<sub>2</sub>O(l) = 8.9 L H<sub>2</sub>O(l) = 8,900 mL H<sub>2</sub>O(l) =  $8,900 \text{ g H}_2\text{O}(l)$  or  $8.9 \times 10^3 \text{ g H}_2\text{O}(l)$

2. WANTED: ? J

(Strategy: When you see joules and liquid water, write: )

$q = c \cdot m \cdot \Delta t$ , make a data table with those symbols, and put **c** for water in the table.

DATA:  $q = ? \text{ J}$  WANTED

$c = 4.184 \text{ J/g}\cdot\text{K}$  for liquid water (so find mass in grams)

$m = ? \text{ g} = 36.0 \text{ mL} = 36.0 \text{ g}$  for liquid water (1 mL water = 1.00 g water)

$\Delta t = ? \text{ K}$  or  $^\circ\text{C} = 15.0^\circ\text{C}$

(The mL of water are converted above to the mass units that match the **c** unit.)

SOLVE:  $? = q = c \cdot m \cdot \Delta t = 4.184 \frac{\text{J}}{\text{g}\cdot\text{K}} \cdot 36.0 \text{ g} \cdot 15.0^\circ\text{C} = 2,260 \text{ J}$

3. WANTED: *Initial temp.* Since  $\Delta t \equiv t_{\text{final}} - t_{\text{initial}}$  then  $t_{\text{initial}} = t_{\text{final}} - \Delta t = \text{WANTED}$

(Strategy: When you see joules and liquid water, write)

$q = c \cdot m \cdot \Delta t$  and  $c_{\text{water}}$  (**c** water prompt)

DATA:  $q = ? \text{ J} = -6.70 \text{ kJ} = -6.70 \times 10^3 \text{ J} = -6,700 \text{ J}$  (convert to units of **c**)

$c = 4.184 \text{ J/g}\cdot\text{K}$  (**c** water prompt)

$m = ? \text{ g} = 15.0 \text{ mol H}_2\text{O} \cdot \frac{18.0 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} = 270. \text{ g H}_2\text{O}$

When grams are needed, but moles are given, do the conversion in the data table.)

$\Delta t = \Delta t \equiv t_{\text{final}} - t_{\text{initial}}$  so  $t_{\text{initial}} = t_{\text{final}} - \Delta t = \text{WANTED}$

SOLVE:  $? = \Delta t = \frac{q}{c \cdot m} = \frac{-6,700 \text{ J}}{4.184 \frac{\text{J}}{\text{g}\cdot\text{K}} \cdot 270. \text{ g}} = -5.93 \text{ K} = \Delta t$

WANTED =  $t_{\text{initial}} = t_{\text{final}} - \Delta t = 21.4^\circ\text{C} - (-5.93^\circ\text{C or K}) = 27.3^\circ\text{C}$

(Since the water is losing heat, its initial must be warmer than the final temperature, and it is.)

4. WANTED: ? = **mass of water**

(Strategy: When you see joules and liquid water, write: )

$q = c \cdot m \cdot \Delta t$  (the “c water” prompt)

DATA:  $q = ?$  calories = 54 kilocalories = 54,000 calories (convert to units of  $c$ )  
 $c = 1$  calorie/g • K for liquid water (the “ $c$  water” prompt)  
 (choosing a value for  $c$  in calories will simplify solving, since  $q$  is in calories and units must be consistent. However, the calories in  $q$  could also be converted to joules, and the value for  $c$  using joules used. Both methods give the same answer.)

(SF: because the  $c$  for water is also the definition of a calorie, the 1 is exact.)

$m = ?$  g WANTED

$$\Delta t = \boxed{\Delta t \equiv t_{\text{final}} - t_{\text{initial}}} = 5^{\circ}\text{C} - 75^{\circ}\text{C} = -70.^{\circ}\text{C}$$

(Subtracting, the *place* determines doubt)

SOLVE:  $\boxed{q = c \cdot m \cdot \Delta t}$ , (solve in symbols before numbers)

$$? = m = ? \text{ g} = \frac{q}{c \cdot \Delta t} = \frac{54,000 \text{ calories}}{1 \text{ calorie} \cdot 70.^{\circ}\text{C}} = 770 \text{ g water}$$

5. WANTED:  $q$  in joules

(Strategy: Note that although both are  $\text{H}_2\text{O}$ , the  $c$  value for ice is not the same as for liquid water.

Since the problem mentions  $c$ , that’s our “ $c$  prompt.” Write the equation that uses  $c$ .)

DATA:  $\boxed{q = c \cdot m \cdot \Delta t}$

$q = ?$  J = WANTED

$c = 2.09$  J/g•K for ice

(The equation *requires* mass ( $m$ ) and the  $c$  unit uses grams, but the ice data is in moles. Convert the ice moles to the mass unit required. The relationship between grams and moles is the molar mass.)

$$m = ? \text{ g} = 4.50 \text{ mol H}_2\text{O} \cdot \frac{18.0 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} = 81.0 \text{ g H}_2\text{O(s)}$$

Ice begins to melt when it reaches  $0.0^{\circ}\text{C}$ .

$$\Delta t = ? \text{ K or } ^{\circ}\text{C} = -20.0^{\circ}\text{C} \text{ to } 0.0^{\circ}\text{C} = 20.0^{\circ}\text{C}$$

(The data has now been converted to the 3 units used by  $c$ . The equation can work because the units cancel properly.)

SOLVE:  $? = q = c \cdot m \cdot \Delta t = 2.09 \frac{\text{J}}{\text{g} \cdot \text{K}} \cdot 81.0 \text{ g} \cdot 20.0^{\circ}\text{C} = 3,390 \text{ J}$

\* \* \* \* \*

## Lesson 21D: Calculating Joules Using Unit Cancellation

In solving heat problems, a key step is often to calculate the energy lost or gained in a chemical process. However, there are a number of equations that solve for energy. How do we know which to use when?

Rather than memorizing a large number of equations, **unit cancellation** can be used to calculate energy. Unit cancellation is simply the conversion-factor method with the rules loosened a bit to accommodate complex units. The principle is the same: if you arrange the *units* to cancel to result the WANTED unit, the numbers attached to the units will be in the right place to produce the correct answer.

Unit cancellation can also be used to “design formulas,” or as hints to help to remember complex formulas. However, unit cancellation must be used carefully.

Using heat calculations, let us compare solving with equations to unit cancellation.

### Equations To Calculate Energy

1. The equation for calculating heat or energy using *specific heat capacity* (*c*) is

$$\boxed{\text{Heat energy lost or gained} = q = c \cdot m \cdot \Delta t}$$
 In words, this equation means

The heat energy gained or lost = (*specific heat capacity*) x (mass) x (change in °C or K)

Other equations can be used to calculate energy. Three of those equations are:

2. The **molar heat capacity** (symbol capital C) of a substance is defined as the amount of heat required to raise one *mole* of the substance by one degree.

The equation is: change in heat energy =  $\boxed{q = C \cdot \text{moles} \cdot \Delta t}$

3. For heats of *combustion* or *phase changes*, the equation for heat lost or gained is

$$\boxed{q = (\text{heat of process/mass or moles}) \cdot (\text{mass or moles})}$$

4. For *bomb calorimeter* calculations, the equation for heat energy lost or gained is

$$\boxed{q = (\text{heat capacity of calorimeter/degree}) \cdot (\Delta t)}$$

Problems involving items 2, 3, and 4 are frequently encountered, but we would prefer *not* to memorize those formulas. Calculations using those quantities can instead be solved using the *units* supplied in the problems.

Note that

- All four equations above solve for energy (*q*), which may be in joules or calories.
- Not all of the equations involve temperature, but those that do always a *change* in temperature, so *degrees* and °C and K will all be equivalent.
- None of the equations include proportionality constants; *q* is calculated by a straightforward multiplication of numbers and their units.

Under these special circumstances, the *units* in a problem can be used, without needing a memorized equation, to calculate energy. Let's learn the method by example.

**Q1.** If a problem's data includes the unit  $\frac{\text{joules}}{\text{K}}$

and the energy in joules is WANTED, what must you do to solve?

\* \* \* \* \*

$$? \text{ joules} = \frac{\text{joules}}{\text{K}} \text{ times (kelvins)}.$$

To get joules from joules/K, multiply by the data whose units are kelvins.

The fundamental rule is: Let the units tell you what to do.

The **K** in the unit above does not indicate whether K is a temperature, such as 273 K, or a change in temperature, such as  $\Delta t = 20 \text{ K}$  or  $^{\circ}\text{C}$ . However, in all of the *energy* equations above, **degrees**,  $^{\circ}\text{C}$ , and **K** all represent a  $\Delta t$ , and not a *T*. In similar energy calculations, you can assume that **degrees**,  $^{\circ}\text{C}$  or **K** measure a *change* in temperature.

Try another example.

**Q2.** If a problem's data has a unit of  $\frac{\text{joules}}{\text{mol} \cdot \text{K}}$ ,

and the joules of energy is WANTED, what equation would you design?

\* \* \* \* \*

$$? \text{ joules} = \frac{\text{joules}}{\text{mol} \cdot \text{K}} \text{ times (moles) times (kelvins)}$$

Unit-cancellation rules are similar to conversion rules, but expanded.

- *Complex* ratio units, like  $\text{J/g}\cdot\text{K}$ , can be used right-side up *or* upside down.
- *Single* units can be used on top, or *inverted*, as in "1/(X grams)"
- Units may be multiplied in any order. If you want a single unit, you can even start with a ratio unit as long as the units cancel to give the WANTED unit at the end.

Unit cancellation is a kind of jigsaw puzzle. Arrange the data as pieces, right-side up or upside down, so that the units on the right *cancel* to give the unit that you WANT on the left. This will result in the right answer for the numbers and the units.

Using the two examples above as a guide, try this problem.

**Q3.** Solve for joules using these "numbers" and units: **X** joules/g·K, **Y**  $^{\circ}\text{C}$ , and **Z** g.

\* \* \* \* \*

**Answer:** ? joules =  $\frac{\text{X joules}}{\text{g} \cdot \text{K}} \cdot \text{Y } ^\circ\text{C} \cdot \text{Z grams} = \text{X} \cdot \text{Y} \cdot \text{Z} \text{ joules} .$

The terms to multiply may be listed in any order. Try one more.

**Q4.** Solve for ? grams using: X joules/g·K, Y °C, and Z joules.

\* \* \* \* \*

When *complex* units are involved, though no particular order is required, it will often help in arranging the units if you *start* in your *given* with a unit that puts the *answer unit* (grams in the above case) where you WANT it in the answer.

$$? \text{ grams} = \frac{1 \text{ grams} \cdot \text{K}}{\text{X joule}} \cdot \frac{1}{\text{Y } ^\circ\text{C}} \cdot \text{Z joules} = \frac{\text{Z}}{\text{XY}} \text{ grams}$$

## Practice A

Using the method above, try every other problem, and more if you need more practice. Not sure how to proceed? Peek at the answer at the end of the lesson, then try again.

1. Solve for **K** using X joules, Y joules/g·K, and Z grams.
2. Solve for **moles** of liquid H<sub>2</sub>O using X degrees, 4.184 joules/g·K, and Z joules.
3. Solve for **joules** using X degrees, Y calories/g·K, and Z grams. (4.184 joules = 1 cal.)
4. Solve for **calories** using X degrees, Y joules/g·K, and Z kilograms.

## Cases When Unit Cancellation Does Not Work

Unit cancellation by itself does *not* work for equations such as  $\text{KE} = 1/2 mv^2$  or **Volume of a sphere** =  $4/3 \pi r^3$ . Those relationships have constants that must be included in the calculations to get correct answers.

Unit cancellation does work for relationships based on equations *without* constants, such as

$$q = c \cdot m \cdot \Delta t \text{ or distance} = (\text{rate})(\text{time}) \text{ or area of a rectangle} = \text{base} \cdot \text{height},$$

$$\text{or even } E = mc^2 .$$

It is important, therefore, to use unit cancellation in place of memorized equations only for equations that do *not* have proportionality constants.

However, though the units alone do not always predict proper equations, if you are unsure about recalling a correct equation, unit cancellation will often supply good *hints* about what the symbols must be, and where they must be, in an equation that solves for the unit.

## Using Unit Cancellation to Calculate Energy

Use the unit cancellation method above to solve this problem.

**Q.** A sample of aluminum weighs 16.5 grams. How many joules are required to raise the temperature of the aluminum from 20.0°C to 50.0°C? The molar heat capacity of aluminum is 24.3 J/mol·K.

\* \* \* \* \*

Answer

WANTED : ? J

Strategy: This problem uses *molar* not *specific* heat capacity, so  $q = c \cdot m \cdot \Delta t$  cannot be used directly. Instead, try unit cancellation. The symbols used for an equation data table are not needed. Simply list as DATA the numbers and units, in the manner done for conversion factors. To solve, arrange the units to cancel correctly.

\* \* \* \* \*

DATA: 16.5 g Al  
 $\Delta t = 50.0^\circ\text{C} - 20.0^\circ\text{C} = 30.0^\circ\text{C}$   
 24.3 J/mol•K  
 27.0 g Al = 1 mol Al (See both grams and moles? Need molar mass)

Adjust your work if needed, and then check the answer below.

\* \* \* \* \*

SOLVE: ? J =  $24.3 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot \frac{1 \text{ mol Al}}{27.0 \text{ g Al}} \cdot 16.5 \text{ g Al} \cdot 30.0^\circ\text{C} = 446 \text{ joules}$

The terms that are multiplied can be in any order, so long as they are right-side up compared to those above.

You could solve this problem using the equation for *molar* heat capacity, in the same way you used the equation for *specific* heat capacity. However, to do so, you need to memorize the equation for molar heat capacity. With unit cancellation, you can solve without memorizing the many equations that calculate  $q$ . Instead, let the units tell you what to do.

\* \* \* \* \*

When should you use the original conversion rule “if you want a ratio, start with a ratio?”  
 When should you use the looser unit cancellation rules? A good rule of thumb is

- In a problem where all of the DATA can be listed as *single* units or *equalities*, the rule “if you want a single unit, start with a single unit” will automatically arrange your factors right-side up.
- In a problem that includes a complex unit, in a form such as  $x/y \cdot z$ , the rule “in the *given*, put the answer unit where you WANT it” will help to arrange factors.

The looser unit-cancellation rules work in *both* cases, but they can take a bit longer to arrange. In both cases, the unit-cancellation concept is the same.

**Summary: Solving With Unit Cancellation**

For energy calculations that do not use *specific* heat capacity ( $c$ ), try unit cancellation.

1. List WANTED and DATA as done for conversion factor problems, without symbols.
2. If you see grams and moles for a substance, write the molar mass in the DATA table.
3. Arrange the numbers and units so that the units cancel to give the WANTED units.

---

**Practice B:** Using the method above, try these. If you are not sure how to proceed, peek at the answers, then try again.

- The heat of vaporization of water is 9.7 kcal/mole. How much heat would it take to vaporize 0.75 grams of water? (Solve in joules.)
  - A “bomb calorimeter” is used to absorb and measure the heat released when a substance is burned. If the heat capacity of a bomb calorimeter is 6.00 kJ/K, and a reaction releases 42,600 calories of heat, what will be the increase in the calorimeter temperature?
  - Calculate the heat needed to raise 2.5 moles of ice from  $-40.0^{\circ}\text{C}$  to  $0.0^{\circ}\text{C}$ . (The  $c$  for ice is  $2.09 \text{ J/g}\cdot\text{K}$ ) (Though this problem mentions  $c$ , try solving with unit cancellation.)
- 

## **ANSWERS**

**Practice A:** Your factors may be in any order but must be right-side up compared to these.

- Solve for **K** using **X** joules, **Y** joules/g·K, and **Z** grams.

$$? \text{ K} = \frac{1 \text{ g}\cdot\text{K}}{\text{Y joules}} \cdot \frac{1}{\text{Z g}} \cdot \text{X joules} = \frac{\text{X}}{\text{YZ}} \text{ K}$$

- Solve for moles of liquid  $\text{H}_2\text{O}$  using **X** degrees, **4.184** joules/g·K, and **Z** joules.

$$? \text{ mol H}_2\text{O} = \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \cdot \frac{1 \text{ g}\cdot\text{K}}{4.184 \text{ joule}} \cdot \frac{1}{\text{X degrees}} \cdot \text{Z joules} = \frac{\text{Z}}{4.184 \cdot 18.0 \cdot \text{X}} \text{ mol H}_2\text{O}$$

When a heat problem includes g *and* mol of a substance formula, you will likely need molar mass.

Since moles was WANTED, and one of the units was complex, a *given* was picked with moles on top. BUT – if the units cancel, ANY order may be used for the conversions.

- Solve for joules using **X** degrees, **Y** calories/g·K, and **Z** grams.

$$? \text{ joules} = \frac{\text{Y calories}}{\text{g}\cdot\text{K}} \cdot \frac{4.184 \text{ joules}}{1 \text{ calorie}} \cdot \text{Z grams} \cdot \text{X degrees} = (4.184)\text{YZX} \text{ joules}$$

Since a joules term was not supplied in the data, the energy term calories was placed on top to start, where the energy term needs to be in the answer, and then converted to joules, but any order is OK.

- Solve for calories using **X** degrees, **Y** joules/g·K, and **Z** kilograms.

$$? \text{ calories} = \frac{\text{Y joules}}{\text{g}\cdot\text{K}} \cdot \frac{1 \text{ calorie}}{4.184 \text{ joule}} \cdot \text{Z kg} \cdot \frac{10^3 \text{ g}}{1 \text{ kg}} \cdot \text{X degrees} = \frac{(1,000)\text{YZX}}{4.184} \text{ calories}$$

**Practice B**

1. WANTED: ? J

Strategy: Since specific heat capacity is not mentioned, the equation using  $c$  cannot be used. Instead, use unit cancellation or conversion-factor rules. List the data, then arrange the units to give the units WANTED.

DATA: 9.7 kcal/mol H<sub>2</sub>O ( or 9.7 kcal = 1 mol H<sub>2</sub>O)

0.75 g H<sub>2</sub>O

18.0 g H<sub>2</sub>O = 1 mol H<sub>2</sub>O (grams and moles of H<sub>2</sub>O are both in the data)

SOLVE: Since a heat unit is wanted, you can start with a heat unit on top:

$$? \text{ joules} = 9.7 \frac{\text{kcal}}{\text{mol H}_2\text{O}} \cdot \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \cdot \frac{10^3 \text{ cal}}{1 \text{ kcal}} \cdot \frac{4.184 \text{ J}}{1 \text{ cal}} \cdot 0.75 \text{ g H}_2\text{O} = 1,690 \text{ joules}$$

Since these units are all “simple”  $y/x$  ratios, you could also start with the single unit 0.75 g H<sub>2</sub>O using the conversion factor rules to solve for ratios. The answer will be the same no matter what rules you choose to help to arrange your conversions.

2. WANTED: ?  $\Delta t$ 

(Strategy: This problem mentions heat capacity, but not *specific* heat capacity, so we cannot use the  $c$  prompt equation. Since the equation is not available, try unit cancellation. )

DATA: 6.00 kJ/K

4,260 calories

$$\text{SOLVE: } ? \text{ }^\circ\text{C} = \frac{1 \text{ K}}{6.00 \text{ kJ}} \cdot \frac{1 \text{ kJ}}{10^3 \text{ J}} \cdot \frac{4.184 \text{ J}}{1 \text{ cal}} \cdot 42,600 \text{ cal.} = 29.7 \text{ K} = \Delta t$$

(The order of the conversions can be different, as long as the conversions are all same-side up and you get the same answer. Note that capital **K** is the abbreviation for **kelvins**, and a lower case **k** is the abbreviation for **kilo-**.)

3. WANTED: ? **joules** (joules is the SI energy unit, and heat is a form of energy)

(Strategy: Though the  $c$ -prompt can be used, in this problem try unit-cancellation rules.)

DATA: 2.5 moles H<sub>2</sub>O (the chemical formula for ice is H<sub>2</sub>O)

18.0 g H<sub>2</sub>O = 1 mol H<sub>2</sub>O (the problem includes moles *and* grams of H<sub>2</sub>O )

$\Delta t = 40.0^\circ\text{C} - 0.0^\circ\text{C} = 40.0^\circ\text{C}$

2.09 J/g•K

$$\text{SOLVE: } ? \text{ J} = 2.09 \frac{\text{J}}{\text{g}\cdot\text{K}} \cdot \frac{18.0 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \cdot 2.5 \text{ mol H}_2\text{O} \cdot 40.0^\circ\text{C} = 3,800 \text{ J}$$

This problem can be solved with the equation  $q = cm\Delta t$ . Equations are usually safer to use if you know the equation, since unit cancellation does not work for relationships that include proportionality constants. However, **both** the  $c$ -prompt equation *and* unit cancellation can be used to solve specific heat capacity problems.

\* \* \* \* \*

## Lesson 21E: Calorimetry

The heat involved in a reaction or a phase change is often measured by having that heat absorbed by another substance, such as by water in a **calorimeter** (an insulated container), or by the material in the body of a **bomb calorimeter**.

In **calorimetry** problems, there are *two* entities: one that *loses* energy, and the other that *gains* the lost energy. The key relationship is the fundamental law of conservation of energy: in a chemical process, energy can neither be created nor destroyed.

To simplify calorimetry, we will use these rules.

1. When you see that a problem has two components: one losing and one gaining heat, write at the top of your DATA:

**In calorimetry: Energy lost by one = Energy gained by the other.**

2. Divide the rest of your DATA table into two columns or parts: E gainer and E loser.

The two parts will have the *same value* for the *energy* (joules or calories) lost and gained. The strategy to solve will be to calculate the energy for the part that does not contain the WANTED unit, then to write that energy in the part that includes the WANTED unit, and then to solve for the WANTED unit.

The first task in a calorimetry problem is to identify and label which component is the heat *loser* and which is the heat *gainer*. Some rules for identifying heat losers and gainers:

- If a substance *burns* (combustion) or *explodes*, it is *losing* its stored heat energy.
- If a substance gets colder, it is *losing* its kinetic energy.
- If a substance gets hotter without participating in a chemical reaction, it is *gaining* heat.

Let's try the method on a problem.

**Q.** A 18.0 gram food sample is placed in a bomb calorimeter with excess oxygen and burned. The calorimeter temperature rises by 9.3°C. The heat capacity of the calorimeter is 3.50 kJ/K. What is the energy content of the food, in J/g?

Do these steps in your notebook.

1. This is a *calorimetry* problem because it has two energy parts. The food loses stored energy. The calorimeter gains that same amount of energy as kinetic energy: its temperature increases. Write the fundamental calorimetry relationship in your DATA.
2. Below the fundamental relationship, set up your data table in two columns: E loser and E gainer. Include the key relationship:  $E \text{ lost} = E \text{ gained}$

E loser = food

E lost =

(=)

E gainer = calorimeter

E gained =

3. Enter every number and unit in the problem into the data table. Carefully separate the *E loser* from the *E gainer* data.

Do those steps, and then check your answer below.

★ ★ ★ ★ ★

4. Your paper should look like this.

In calorimetry: Energy lost by one = Energy gained by other.

E Loser = food

E Gainer = calorimeter

E lost = ?

(=)

E gained = ?

18.0 grams food burned

9.3°C =  $\Delta t$  for calorimeter

WANTED = ? = joules/gram food

3.50 kJ/K for calorimeter

Two rules are important in a two-column DATA table.

- As with any problem with two entities, take care not to use DATA that applies to one part to solve for the other part.

The exception is the linked variable, which has the same value in both columns and/or parts.

- Almost always, the column with the WANTED unit will have two unknown quantities, and the other column will have one: the linked variable ( $q$ ). You will need to solve for the column with one ? first.

In this problem, you do not know enough data to find joules lost by the food. You do know enough to find the joules gained by the calorimeter. Do that calculation first, and then check your answer below.

\* \* \* \* \*

6. With conversions in any order,

$$? \text{ joules gained by calorimeter} = 9.3^\circ\text{C} \cdot 3.50 \frac{\text{kJ}}{\text{K}} \cdot \frac{10^3 \text{ J}}{1 \text{ kJ}} = 32,500 \text{ joules}$$

Enter this answer in *both* columns of your DATA table. The energy gained by the calorimeter must equal the energy lost from the 18.0 grams of food as it burned.

7. Solve for the WANTED unit, then check below.

\* \* \* \* \*

$$8. \text{ SOLVE: WANTED} = ? \frac{\text{J}}{\text{g food}} = \frac{32,500 \text{ J}}{18.0 \text{ g food}} = \mathbf{1,800} \frac{\text{J}}{\text{g food}} \quad (2 \text{ sf in } \Delta t)$$

\* \* \* \* \*

### **Summary: Calorimetry**

When a problem has a heat or energy *loser* and a *gainer*, the steps are

1. Identify which substance is the energy loser and which is the energy gainer.
2. Make two separate data columns or parts: one for the loser, one for the gainer.
3. Identify which part (loser or gainer) has the unit you WANT.
4. Use equations *or* units to calculate the *energy* ( $E$  or  $q$ ) for the *other* part. Use the data in the column for that part.
5. Write that energy for the other part as data for the WANTED part, and solve.

\* \* \* \* \*

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## Practice

Add the new rules in this lesson to your previous flashcards for this chapter. Run the cards until you can answer each automatically. Then complete as many of the following problems as you need to feel confident. More difficult problems are toward the end.

Use the method above. If you get stuck, peek at the answer and try again.

- Water in an insulated container is used to trap the heat released when a flask of liquid sodium thiosulfate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ ) solidifies.
  - If there are 25.0 grams of  $\text{H}_2\text{O}$  in the container, and the  $\text{H}_2\text{O}$  temperature rises from  $10.0^\circ\text{C}$  to  $37.6^\circ\text{C}$  as the phase change occurs, how much energy is released by the phase change?
  - If 2.0 moles of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$  is used in the experiment, what is the heat released by the solidification, in joules per mole?
- A 40.0 gram metal sample is heated to  $100.0^\circ\text{C}$  in boiling water and then immersed in an insulated calorimeter containing 25.0 grams of water at  $26.6^\circ\text{C}$ . After stirring, the metal and water are both at  $30.0^\circ\text{C}$ . What is the specific heat capacity of the metal?
- Large cubes of ice are dropped into an insulated calorimeter with 100. mL of warm water at  $49.6^\circ\text{C}$ . The mixture is stirred until the temperature is  $0.0^\circ\text{C}$ , and the ice remaining is then removed. The volume of the water is found to be 162 mL.
  - How many grams of ice melted?
  - What is the heat of melting of the ice, in J/g?
- The burning of methanol ( $\text{CH}_3\text{OH}$ ) releases 638 kJ/mol. How much heat in kJ is released when 12.8 grams of methanol are burned?
- Methane ( $\text{CH}_4$ ) is the primary constituent of natural gas. Its heat of combustion is 890 kJ/mol. How many grams of methane would need to be burned to raise the temperature of 55 gallons of water from  $10.^\circ\text{C}$  to  $37^\circ\text{C}$ ? (1 gallon = 3.78 liters)

---



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## ANSWERS

- This problem involves **two** substances and heat. Use the calorimetry rules.

- Write the fundamental calorimetry relationship.
- Identify the heat loser and gainer; keep two separate data tables.
- Energy lost = energy gained; find the energy from the other, use that to find the WANTED unit.

The liquid  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$  *loses* potential energy as it becomes solid, and the water *gains* that energy.

This problem has already been divided: part (a) for the energy gainer, and (b) for the energy loser.

COMMON DATA: In calorimetry: Energy lost by one = Energy gained by the other.

Part a. WANT: ? Energy **gained** by **water**. (Solve in joules unless other units are requested.)

Grams of  $\text{H}_2\text{O}$  in a heat problem calls the “water c” prompt:

When you see energy and liquid water in a problem, write):

$$\boxed{q = c \cdot m \cdot \Delta t} \quad (\text{and set up a data table to match this equation})$$

DATA:  $q = ? \text{ J}$   
 $c = 4.184 \text{ J/g}\cdot\text{K}$   
 $m = 25.0 \text{ g H}_2\text{O}$   
 $\Delta t = 37.6^\circ\text{C} - 10.0^\circ\text{C} = 27.6^\circ\text{C up}$

SOLVE:  $? = q = c \cdot m \cdot \Delta t = 4.184 \frac{\text{J}}{\text{g}\cdot\text{K}} \cdot 25.0 \text{ g} \cdot 27.6^\circ\text{C} = \mathbf{2,887 \text{ J}}$  gained by water

Carry an extra *sf* until the final part. If needed, adjust your work, then complete part b.

★ ★ ★ ★ ★

Part b. WANT:  $? \frac{\text{J}}{\text{mol Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{ H}_2\text{O}}$

Strategy: Use energy from first part.  $E \text{ lost} = E \text{ gained}$ .

DATA:  $2,887 \text{ J}$  lost in becoming solid  
 $2.0 \text{ mol}$  of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{ H}_2\text{O}$

SOLVE:  $? \frac{\text{J}}{\text{mol Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{ H}_2\text{O}} = \frac{2,887 \text{ J}}{2.0 \text{ mol Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{ H}_2\text{O}} = \mathbf{1,400} \frac{\text{J}}{\text{mol Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{ H}_2\text{O}}$

2. The problem involves **two** substances and heat, so use the calorimetry rules:

- Write the fundamental calorimetry relationship.
- Identify the heat loser and gainer, keep two separate data tables;
- $E \text{ lost} = E \text{ gained}$ . Find the *energy* from the not WANTED part. Use that to find the WANTED unit.

In this problem, the metal loses energy as it cools, and the water gains that energy.

COMMON DATA:  $\boxed{\text{In calorimetry: Energy lost by one} = \text{Energy gained by the other.}}$

WANTED: specific heat capacity (**c**) of the *metal*

Strategy: Solve for energy gained by the other part, the *water*, first.

**For energy gainer – water**

WANTED: ? Energy gained by water.

Strategy: When you see **water** in a heat problem, use the “c water” prompt. Write:

$$\boxed{q = c \cdot m \cdot \Delta t} \quad \text{Do a data table with those symbols, add the water } c \text{ value.}$$

DATA:  $q = ? = \text{J}$   
 $c = \mathbf{4.184 \text{ J/g}\cdot\text{K}}$  for liquid **water**  
 $m = 25.0 \text{ g H}_2\text{O}$

$$\Delta t = 30.0^\circ\text{C} - 26.6^\circ\text{C} = 3.4^\circ\text{C up} \quad (2 \text{ sf})$$

SOLVE:  $? = q = c \cdot m \cdot \Delta t = 4.184 \frac{\text{J}}{\text{g}\cdot\text{K}} \cdot 25.0 \text{ g} \cdot 3.4^\circ\text{C} = \mathbf{356 \text{ J}}$  gained by water

**For energy loser – metal**

Strategy: Since you want specific heat capacity (**c**), you can use unit cancellation **or** use the equation using **c**:

$$\boxed{q = c \cdot m \cdot \Delta t}$$
 and set up a data table to match the equation

DATA:  $q = 356 \text{ J}$  lost by metal (from *other* part. That's the *key* relationship.)

$$c_{\text{metal}} = ? = \text{WANTED}$$

$$m = 40.0 \text{ g metal}$$

$$\Delta t = 100.0^\circ\text{C} - 30.0^\circ\text{C} = 70.0^\circ\text{C lower}$$

SOLVE: Since  $\boxed{q = c \cdot m \cdot \Delta t}$

$$? = c = \frac{q}{m \cdot \Delta t} = \frac{356 \text{ J}}{40.0 \text{ g} \cdot 70.0^\circ\text{C}} = 0.13 \frac{\text{J}}{\text{g} \cdot \text{degree}}$$

Note that the answer units are the units expected for a **c** value.

3a. WANT: ? g ice melted.

DATA: The amount of ice that melted is  $162 \text{ mL} - 100 \text{ mL} = 62 \text{ mL}$  ice melted

For liquid water,  $1.00 \text{ g} = 1 \text{ mL}$ , so  $62 \text{ g}$  of the water was made by the ice melting  
=  $62 \text{ g}$  ice melted.

3b. In this part, you have a heat loser (the warm water) and a heat gainer (the ice that melted). That makes this a calorimetry calculation. A key is to label and separate the data for the *warm water* and the *ice*

In calorimetry: Energy lost by one = Energy gained by other.

WANTED: specific heat capacity (**c**) of the *ice*

Strategy: Solve for energy lost by the not WANTED part, the *water*, first.

**For energy gainer – water**

WANTED: ? Energy lost by water.

Strategy: When you see **water** in a heat problem, use the “c water” prompt. Write:

$$\boxed{q = c \cdot m \cdot \Delta t}$$
 Do a data table with those symbols, add the water **c** value.

DATA:  $q = ? = \text{J}$

$$c = 4.184 \text{ J/g}\cdot\text{K} \quad \text{for liquid water}$$

$$m = 100. \text{ mL H}_2\text{O} = 100. \text{ g H}_2\text{O}$$

$$\Delta t = 49.6^\circ\text{C} - 0.0^\circ\text{C} = 49.6^\circ\text{C} \quad (\text{subtraction} = \text{doubtful place} = 3 \text{ sf})$$

SOLVE:  $? = q = c \cdot m \cdot \Delta t = 4.184 \frac{\text{J}}{\text{g}\cdot\text{K}} \cdot 100. \text{ g} \cdot 49.6^\circ\text{C} = 20,760 \text{ J}$  lost by water

**For energy gainer – ice**

WANTED:  $\frac{\text{J}}{\text{g ice melted}}$  (A complete label is especially helpful in this problem)

DATA: **20,760 J** lost by water = **20,760 J** gained by ice (from *other* part: the *key* relationship.)  
g ice melted = 62 g ice melted (from Part a)

WANTED:  $\frac{\text{J}}{\text{g ice melted}} = \frac{\mathbf{20,760 J \text{ gained by ice}}}{62 \text{ g ice melted}} = \mathbf{330} \frac{\text{J}}{\text{g ice melted}}$

4. WANT: heat ( $q$ ) in kJ

DATA: 638 kJ released = 1 mol CH<sub>3</sub>OH burned

12.8 g CH<sub>3</sub>OH

32.0 g CH<sub>3</sub>OH = 1 mol CH<sub>3</sub>OH (grams prompt)

When the data is mostly equalities, with one single-unit WANTED and *given*, how might you solve?

\* \* \* \* \*

SOLVE: Try conversions.

? =  $q$  in kJ = 12.8 g CH<sub>3</sub>OH  $\cdot$   $\frac{1 \text{ mol CH}_3\text{OH}}{32.0 \text{ g CH}_3\text{OH}}$   $\cdot$   $\frac{638 \text{ kJ released}}{1 \text{ mol CH}_3\text{OH burned}}$  = 255 kJ heat released

5. The problem involves *two* substances and heat, so use the calorimetry rules.

- Write the fundamental calorimetry relationship.
- Identify the heat loser and gainer; keep two separate data tables.
- $E$  lost =  $E$  gained, find the *energy* from the other, use that to find the WANTED unit.

In this problem, the methane loses stored energy as it burns, the water gains that energy.

COMMON DATA: In calorimetry: Energy lost by one = Energy gained by the other.

a. Final WANTED: grams methane.

Strategy: Solve for energy gained by water first.

**Energy gainer – water:**

WANT: ? joules gained by water.

Grams of water in a heat problem calls the *c-water* prompt.: Write:

$q = c \cdot m \cdot \Delta t$  and set up a data table to match the equation

DATA:  $q = ? = \text{joules}$

$c = 4.184 \text{ J/g}\cdot\text{K}$  for liquid water

$m = ? \text{ g H}_2\text{O} = 55 \text{ gal H}_2\text{O} \cdot \frac{3.78 \text{ L}}{1 \text{ gal}} \cdot \frac{1 \text{ mL}}{10^{-3} \text{ L}} \cdot \frac{1.00 \text{ g water}}{1 \text{ mL water}} = 2.08 \times 10^5 \text{ g H}_2\text{O}$

$\Delta t = 37^\circ\text{C} - 10^\circ\text{C} = 27^\circ\text{C}$

SOLVE: ? =  $q = c \cdot m \cdot \Delta t = 4.184 \frac{\text{J}}{\text{g}\cdot\text{K}} \cdot 2.08 \times 10^5 \text{ g} \cdot 27^\circ\text{C} = 2.35 \times 10^7 \text{ J}$

If needed, adjust your work to this point, and then finish the problem.

\* \* \* \* \*

**Energy loser – methane:**

WANTED: ? g CH<sub>4</sub> burned

DATA: 890 kJ = 1 mol CH<sub>4</sub> burned. ( you may write x/y units as ratios or equalities)  
 2.35 x 10<sup>7</sup> joules (use *E* for *other* part to solve for WANTED)  
 16.0 g CH<sub>4</sub> = 1 mol CH<sub>4</sub> (since units for CH<sub>4</sub> use g and moles, need molar mass)

Strategy: If you don't see specific heat capacity, which solves with an equation, try using units.  
 Since all of these units are x/y simple ratios, as opposed to x/y•z complex ratios, you might use the rule "If you want a single unit, start with a single unit." The squiggles above work backwards --from the answer unit through the conversions to the *given* single unit. But any order of multiplying is OK.

$$\text{SOLVE: } ? \text{ g CH}_4 = 2.35 \times 10^7 \text{ J} \cdot \frac{1 \text{ kJ}}{10^3 \text{ J}} \cdot \frac{1 \text{ mol CH}_4}{890 \text{ kJ}} \cdot \frac{16.0 \text{ g CH}_4}{1 \text{ mol CH}_4} = 420 \text{ g CH}_4$$

The factor which limits the *sf* in the answer is the  $\Delta t$  value, which only had 2 *sf*.

\* \* \* \* \*

## Summary: Energy Calculations

A summary for phases and phase changes is listed at the end of Lesson 21A.

1. The Law of Conservation of Energy: energy can neither be created nor destroyed by chemical processes.
2. In chemistry, energy is usually measured in joules or calories.
  - a. The joule (J) is the SI unit measuring energy. Joules are defined in terms of "work."
  - b. The calorie (cal) is another metric unit used to measure energy.

A chemical calorie is defined as the amount of heat needed to raise the temperature of one gram of liquid water by one degree (Celsius or Kelvin).

3. Because all forms of energy are equivalent, all energy units can be related by equalities.

$$\boxed{1 \text{ calorie} = 4.184 \text{ joules}}$$

4.  $\boxed{1 \text{ food Calorie} = 1,000 \text{ chemical calories} = 1 \text{ kilocalorie (kcal)} = 4.184 \text{ kilojoules (kJ)}}$

Food Calories are abbreviated with a capital *Cal.*, chemical calories as *cal*.

5. The *specific heat capacity* (symbol small *c*) of a substance is defined as the amount of heat required to raise one gram of the substance by one degree (Celsius or Kelvin).

The units of *c* are joules *per* (gram · degree) or calories *per* (gram · degree).

6. The symbol  $\Delta$  means *change in*. The symbol  $\Delta t$  means change in temperature.

$$\boxed{\Delta t \equiv t_{\text{final}} - t_{\text{initial}}}$$

A  $\Delta t$  value should be labeled as positive or negative, or as increasing or decreasing.

A change in temperature is the same number of degrees whether measured in °C or K.

For  $\Delta t$  measurements, the terms *degree* and °C and K are all equivalent. When terms are equivalent, they can cancel as units.

7. **The c Prompt:** If you see the term *specific heat capacity* or its symbol  $c$  in a problem, write at the top of your data this equation that includes  $c$  :

$$q = c \cdot m \cdot \Delta t$$

Heat energy ( $q$ ) is defined as positive when energy is added to a chemical system and negative when energy leaves.

8. IF you need an *equation* to solve a problem,
- write the fundamental, memorized equation in your data.
  - Write a data table with each of the symbols in the equation.
  - Use units to match the data with the symbols in the data table.
  - Memorize equations in one format; use algebra to solve for symbols WANTED.
  - Solve the equation for the WANTED symbol *before* you plug in numbers.
  - Put both numbers and units into equations. Do the math for numbers *and* units.
9. **The c water prompt:** If a problem mentions energy *or* heat *or* joules *or* calories -- and liquid water -- write the  $c$  prompt equation:  $q = c \cdot m \cdot \Delta t$ , a data table listing those symbols, and enter  $c = c_{\text{water}} = 4.184 \text{ J/g}\cdot\text{K}$  (or  $c = 1 \text{ calorie/g}\cdot\text{K}$ ).
10. Units must be *consistent* when substituted into equations. When units are not consistent, or do not match what is needed in an equation,
- pick appropriate units to convert DATA to (preferably those used in a complex unit in the problem),
  - Write the chosen unit after each symbol in the DATA.
  - Convert the supplied units to the chosen units in the DATA table, then solve.
11. Unit cancellation can be used in place of memorized equations when equation relationships do not include constants. Most equations that calculate heat energy ( $q$ ) in chemistry can be solved with unit cancellation.
- List WANTED and DATA as done for conversion problems, without labeling measurements with symbols.
  - Arrange numbers and units so that the units cancel to give the WANTED units.
12. Calorimetry: When a problem has a heat or energy loser and a gainer, the steps are:
- Identify which substance is the energy loser, and which is the energy gainer.
  - Make two separate data columns or parts: one for the loser, one for the gainer.
  - Identify which part (loser or gainer) has the unit WANTED.
  - Use equations *or* units to calculate the heat energy ( $q$ ) in the column or part that does *not* have the final WANTED unit.
  - Write that heat energy value as data in the column or part that includes the final WANTED unit, then solve for the WANTED unit.

# # # # #

## Module 22 — Heats of Reaction ( $\Delta H$ )

**Prerequisites:** You should be able to do most of the calculations in this module if you have completed Lesson 10B (Balancing Equations).

\* \* \* \* \*

### Lesson 22A: Energy, Heat, and PV Work

**Timing:** Some courses address *PV work* at this point, before  $\Delta H$  calculations; others include *PV work* as part of a thermodynamics unit later in the course. Do this lesson at this time when you are assigned calculations that involve *PV work* in *your* course. This topic is not essential for the  $\Delta H$  calculations in the remainder of this module.

\* \* \* \* \*

#### Thermodynamics

Thermodynamics studies relationships involving heat and work. The rules for thermodynamics help us to predict why reactions go in the direction they do, as well as the changes in energy and in the arrangements of particles that occur during reactions and processes. In Modules 21 and 22, our interest is primarily measuring the changes in *heat energy* that occur during chemical processes. Other aspects of thermodynamics are addressed in Module 36.

#### System Versus Surroundings

To study thermodynamics, it is helpful to divide the universe into two parts. In chemistry,

- The **system** is the *particles* of interest, which may be atoms, molecules, or ions.
- The **surroundings** is the environment outside of the system.

Universe = system + surroundings
----------------------------------

To explain chemical changes, the system and the surroundings are accounted for separately.

For example, in a chemical reaction, if a collection of molecules lose energy, the same amount of energy must be gained by the surrounding environment (as heat or work).

#### The First Law: Conservation of Energy

**Energy** can be described as the capacity to do work. The **first law of thermodynamics** is the law of **conservation of energy**:

In physical and chemical processes, energy can neither be created nor destroyed.
--

The exception to this law is *nuclear* reactions, in which energy can be created from, or converted to, mass. Nuclear processes are the major reactions in stars, but some nuclear reactions occur on earth, such as in nuclear reactors and radioactive decay. However, unless nuclear processes are specified, you should assume for problems in chemistry that the first law is obeyed.

The first law means that in chemical or physical processes, there is no change in the total energy of the system and its surroundings. In equation form, for a chemical change,

$$\Delta E_{\text{universe}} = E_{\text{universe final}} - E_{\text{universe initial}} = 0 \quad (\text{Equation 1})$$

### Internal Energy, Heat, and Work

During physical and chemical changes, though the *total* energy before, during, and after the process cannot change, energy can change its form, such as from potential to kinetic. In addition, energy can flow into and out of a system.

- The **internal energy** of a system ( $E_{\text{internal}}$  or  $E_{\text{system}}$ ) is the total of the potential and kinetic energy of its particles.

$$E_{\text{system}} = \text{PE} + \text{KE}$$

- Energy can flow into and out of a system as **heat** ( $q$ ) or **work** ( $w$ ).

**Heat** is defined as a transfer of thermal energy between two systems that are at different temperatures. As defined in physics, there are many types of **work**. One type of work is the energy that is transferred as a force acts over a distance ( $w = F \cdot d$ ).

The change in the internal energy of a system during a process can be calculated by

$$\Delta E_{\text{internal}} \text{ or } \Delta E_{\text{system}} = q + w \quad (\text{Equation 2})$$

When heat ( $q$ ) is added to a system, or work ( $w$ ) is done on a system (such as by compressing a gas), the internal energy of the system increases. If a process or reaction releases heat from the system to its surroundings, or if the expansion of gas particles under pressure does work (such as creating a force that moves a resistant object), energy must leave the system.

The change in energy ( $\Delta E$ ) is termed a **state function**. In state functions, only the initial and final states matter. The steps between the initial and final states do not matter. In equation form,

$$\Delta E = E_{\text{final}} - E_{\text{initial}} \quad (\text{Equation 3})$$

The values for  $q$  and  $w$  during a process do vary depending on *how* the change occurs (though the *total* of  $q + w$  does not), so  $q$  and  $w$  are not state functions. By convention in thermodynamics, symbols for state functions, such as  $\Delta E$ , are written in upper case, and non-state functions such as heat ( $q$ ) and work ( $w$ ) are assigned lower-case symbols.

### Units and Signs

By the law of dimensional homogeneity (Lesson 11G), terms that are added or subtracted on one side of an equation must have the same units, and the units must be the same on both sides of an equation. When using SI units, energy is measured in joules. For the units of  $\Delta E$ ,  $q$ , and  $w$ ,

- in equation 3, since a change in energy is the difference between two values in joules, the SI unit for  $\Delta E$  must be *joules*.

- In equation 2, the SI units for *heat* and *work* must be the same as  $\Delta E$ : *joules*. Heat and work measure transfers of *energy*.

The variables  $\Delta E$ ,  $q$ , and  $w$  must be assigned *signs*: their values can be positive or negative. In chemistry (but not necessarily in other sciences), we define the signs from the perspective of the *system*: the chemical particles in a process. In chemistry calculations,

- if energy flows out of a system into its surroundings,  $\Delta E$  is given a negative sign, because the system loses internal energy.
  - If the energy flowing *out* of a system of particles produces heat, such as when a substance burns, the  $q$  value is given a negative sign because the *system* has lost heat energy. Such a process is termed **exothermic**.
  - If a chemical process does work, such as when burning produces gases that expand and move a piston that is under pressure, the  $w$  value for that process is given a negative sign because the system is losing internal energy as it converts that energy to work.
- If energy flows into the system,  $\Delta E$  must be assigned a positive sign, because the system gains energy.
  - If heat is added to a system, such as by boiling water molecules, the  $q$  value for the process is given a positive sign because the system gains internal energy, and the process is termed **endothermic**.
  - If work is done on a chemical system, such as when you compress the air in a bicycle tire with a hand pump, the  $w$  value for the process is given a positive sign. As the air in the tire is compressed, the molecules gain internal energy (the capacity to do work) from the work put into the system.

**Practice A:** Chart and learn the rules above, *then* answer these questions from memory.

1. From the perspective of the particles in a chemical system,
  - a. if heat is added to the particles, is the sign of  $q$  positive *or* negative ?
  - b. If a gas expands by pushing a piston that is under pressure, is the sign of  $w$  positive *or* negative ?
2. If a substance burns, but no work is done,
  - a. is the sign of  $q$  positive *or* negative ?
  - b. Is the sign of  $\Delta E$  positive *or* negative ?
  - c. Is the reaction exothermic *or* endothermic?
3. If a gas is compressed by a piston, but no heat is added to the gas,
  - a. is the sign of  $w$  positive *or* negative ?
  - b. is the sign of  $q$  positive *or* negative ?
  - c. Is the sign of  $\Delta E$  is positive *or* negative ?
4. If 30.0 joules of heat is released by burning, and the gases produced do 25.0 joules of work in moving an automotive piston, what is the  $\Delta E$  for the process?

## PV Work

In physics, we investigate many types of work. One type is the **mechanical** work done in accelerating a mass over a distance:

$$\text{Work} = \text{force times distance} = f \cdot d = m \cdot a \cdot d = \text{mass times acceleration times distance.}$$

In chemistry, we are most interested in the work done during a chemical reaction or process. This type of work include **electrical** work (work done by moving charges) and **PV** work (the work involved in the expansion or compression of a gas).

For the special case of the expansion or compression of a gas, the *PV* work involved can be calculated by

$$\text{Work content of system} = - (\text{external pressure}) \text{ times } (\text{change in the volume of the gas})$$

$$\text{or, in symbols, } \boxed{w_{\text{system}} = - P_{\text{external}} \Delta V_{\text{system}}} \quad (\text{Equation 4})$$

When a gas *expands* against external pressure,  $\Delta V$  is positive. Since pressure is always positive, based on equation 2, the value for the work must be *negative*. This makes sense: when a gas expands against pressure, it does work on its surroundings, and for energy to be conserved, the *system* must lose internal energy.

In calculations, to converting between the SI units of work (joules) and the units for *PV* work, you will need this equality:

$$\boxed{1 \text{ liter} \cdot \text{atmosphere} = 101 \text{ joules}} \quad (\text{Equation 5})$$

## Enthalpy

$$\text{Enthalpy (H) is a property defined as } \boxed{H_{\text{system}} = E_{\text{system}} + P_{\text{system}} V_{\text{system}}}$$

where  $E_{\text{system}}$  is the internal energy of the system, and  $P_{\text{system}}$  is the pressure exerted by the system.

By convention, when thermodynamic equations are written in chemistry (by not in all other sciences), if a symbol is not assigned a subscript, the subscript is assumed to be *system* (as opposed to *surroundings*). The equation above is then written as

$$\boxed{H = E + PV} \quad (\text{Equation 6})$$

In chemical processes, we are most interested in the *change* in enthalpy ( $\Delta H$ ):

$$H_{\text{final}} - H_{\text{initial}} = \boxed{\Delta H = \Delta E + \Delta(PV)} \quad (\text{Equation 7})$$

Let's explore what  $\Delta H$  means. For the special case in which the external pressure on a system is held constant, equation 7 becomes

$$\boxed{\Delta H = \Delta E + P\Delta V} \quad \text{at constant pressure} \quad (\text{Equation 8})$$

When we substitute our definition for "PV work,"  $\boxed{w = - P\Delta V}$  into equation 2:

$$\boxed{\Delta E = q + w}, \text{ equation 2 becomes}$$

$$\boxed{\Delta E = q - P\Delta V}. \text{ Substituting this result into equation 8, } \Delta H \text{ becomes}$$

$$\Delta H = \Delta E + P\Delta V = (q - P\Delta V) + P\Delta V = q \quad \text{or}$$

$$\boxed{\Delta H = q \quad \text{at constant pressure}} . \quad \text{(Equation 9)}$$

This last equation means:

If pressure on a system is held constant, and any work is limited to "PV work," change in enthalpy ( $\Delta H$ ) represents the *heat flow* to or from a system:  $q$  .

The  $\Delta H$  of a reaction is termed the *heat of reaction*. The  $\Delta H$  for a phase change may be described with terms such as *heat of melting*, *heat of fusion* or *heat of vaporization*.

### $\Delta H$ , $\Delta E$ , and $\Delta PE$

For the special case of a chemical process in which pressure is constant and the change in volume is small:

$$\Delta H = \Delta E + P\Delta V \approx \Delta E + P(\sim 0) \approx \Delta E + \sim 0 \approx q \quad \text{or}$$

$$\boxed{\Delta H \approx \Delta E \approx q} \quad \text{if pressure is constant and the volume change is small}$$

Reactions in which the change in volume is very small include

- Reactions that do not involve gases, and
- Gas reactions in which the moles of gas do not change.

Using the calorimetry calculations in Module 21, by calculating the heat transfer ( $q$ ) during a process at constant volume or pressure, we can calculate the  $\Delta H$  value for the process.

Even for reactions in which the volume does change substantially, in *most* cases the size of the PV-work term is *small* compared to the heat term ( $q$ ), so that

$$\Delta E = q + \text{small } w = \Delta H - P\Delta V \approx \Delta H - \text{small} \approx q \quad \text{or}$$

$$\boxed{\Delta H \approx \Delta E \approx q} \quad \text{for most reactions} \quad \text{(Equation 10)}$$

This equation means that in most (though not all) processes,  $\Delta H$  measures the approximate change in internal energy of a system.

Finally, the internal energy of a system ( $E$ ) is the combination of its kinetic and potential energy. The temperature of a system is a measure of its average kinetic energy: if temperature does not change,  $\Delta E_{\text{kinetic}} = 0$  . For reactions run at constant temperature and pressure with a small work term,

$$\Delta H = \Delta E + P\Delta V = (\Delta E_{\text{potential}} + \Delta E_{\text{kinetic}}) + P\Delta V = (\Delta E_{\text{potential}} + \sim 0) + \sim 0 \approx q \quad \text{or}$$

$$\boxed{\Delta H \approx \Delta E_{\text{potential}} \approx q} \quad \text{for most reactions at constant } P \text{ and } T \quad \text{(Equation 11)}$$

For example, during a solid-liquid phase change for a substance under constant pressure, the volume change is very small, and the temperature is constant. The change in enthalpy, which is equal to the flow of heat into or out of the system, is approximately equal to the change in the potential energy of the system.

**Summary: Energy and Enthalpy**

1. In studying the energy changes during physical or chemical processes, it is helpful to divide the universe into the system (the chemical particles) and its surroundings.

$$\text{Universe} = \text{system} + \text{surroundings}$$

2. Energy can be described as the capacity to do work.
3. The first law of thermodynamics is the law of conservation of energy: in chemical (non-nuclear) processes, energy can neither be created nor destroyed.

In equation form: 
$$\Delta E_{\text{universe}} = E_{\text{total final}} - E_{\text{total initial}} = 0$$

4. The **internal energy** of a system ( $E_{\text{internal}}$  or  $E_{\text{system}}$ ) is the total of the potential and kinetic energy of its particles.

$$E_{\text{system}} = \text{PE} + \text{KE}$$

5. In chemical processes, energy can change form, such as from kinetic to potential energy, and energy can flow into and out of a system as heat ( $q$ ) or work ( $w$ ).

In chemical processes: 
$$\Delta E_{\text{system}} = q + w$$

6. Energy ( $E$ ), heat ( $q$ ), and work ( $w$ ) in the SI system are measured in joules (J).
7. Measurements of heat, work, and changes in energy and enthalpy are assigned signs from the perspective of the *system*.
- If heat is added to the system,  $q$  is given a positive sign. If a reaction or process releases heat from the system to the surroundings,  $q$  is given a negative sign.
  - If work is done on a system, such as in compressing a gas,  $w$  is positive. If a system does work, such as an expanding gas moving a piston that is under pressure, the system loses energy and  $w$  is negative.

8. In the case of PV work by a gas, 
$$w_{\text{system}} = - P_{\text{external}} \Delta V_{\text{system}}$$

9. In chemistry, if no subscript is given after a symbol in a thermodynamic equation, assume the subscript is *system*.

10. In converting from PV work units to energy units: 
$$1 \text{ liter} \cdot \text{atm} = 101 \text{ joules}$$

11. The definition of enthalpy ( $H$ ) is 
$$H = E + PV$$

and  $H_{\text{final}} - H_{\text{initial}} = \Delta H = \Delta E + \Delta(PV)$  if work is limited to PV work.

12. For reactions in which the external pressure on a system is held constant and work is limited to "PV work,"  $\Delta H$  will measure the flow of *heat energy* into or out of the system.

$$\Delta H = q$$

13. If pressure is constant and the change in volume is small, and/or if the work term is much smaller than  $q$  (true for most reactions): 
$$\Delta H \approx \Delta E \approx q$$

**Practice B:** Learn the Summary points 5 through 12 above, then do these problems.

- If a sample of gas is compressed from 4.5 to 2.5 liters by 606 joules of work done on the system, what is constant external pressure on the gas, in atmospheres?
- When hydrogen gas ( $\text{H}_2$ ) is burned under constant pressure,  $\Delta H = -284 \text{ kJ/mol}$ . How much heat in kJ is released when 0.12 g of  $\text{H}_2$  burns?

## ANSWERS

### Practice A

- If heat is added to the particles, the sign of  $q$  is **positive**. The particles gained energy.
  - If a gas expands by pushing a piston that is under pressure, the sign of  $w$  is **negative**. The system has done work on its environment, and in the process the system loses internal energy. In the equation  $w = -P_{\text{external}} \Delta V_{\text{system}}$ ,  $\Delta V$  is positive, and  $P$  must be positive, so  $w$  is negative.
- $q$  is **negative**. In burning, the surroundings gain heat. The system must lose heat.
  - $\Delta E = q + w$ . If  $q$  is negative and  $w$  is 0,  $\Delta E$  must be **negative**. If the system loses heat with no work involved, the system loses energy, and  $\Delta E$  for the system must be negative.
  - If the surroundings gain heat, the reaction is **exothermic**.
- $w$  is **positive**. Work is done on the system. Energy is added to the system.
  - $q$  is **zero**: neither positive nor negative.
  - $\Delta E = q + w$ . If  $w$  is positive and  $q$  is 0,  $\Delta E$  must be **positive**.
- WANTED:  $\Delta E$   
 DATA:  $-30.0 \text{ J} = q$       When heat is released to the surroundings,  $q$  is negative.  
 $-25.0 \text{ J} = w$       When work is done on the surroundings,  $w$  is negative.  
 SOLVE:  $\Delta E = q + w = -30.0 \text{ J} + (-25.0 \text{ J}) = -55.0 \text{ J}$   
 In both releasing heat and doing work, the system of particles loses internal energy.

### Practice B

- WANTED: external  $P$  in atm.

The equation that relates external pressure, work, and volume change is  $w = -P_{\text{external}} \Delta V$

In problems that use the  $PV$ -work formula, you will likely need the conversion  $1 \text{ liter} \cdot \text{atm} = 101 \text{ joules}$

\* \* \* \* \*

DATA:  $w = +606 \text{ J}$       When work is done on the system,  $w$  is positive.  
 $\Delta V = \text{final} - \text{initial} = 2.5 \text{ L} - 4.5 \text{ L} = -2.0 \text{ L}$       The system loses volume.

SOLVE:  $w = -P_{\text{external}} \Delta V$ .

$$P_{\text{external}} \text{ in atm.} = \frac{-w}{\Delta V} = \frac{-606 \text{ J}}{-2.0 \text{ L}} = \frac{303 \text{ J}}{\text{L}} \cdot \frac{1 \text{ liter} \cdot \text{atm}}{101 \text{ joules}} = 3.0 \text{ atm}$$

2. Tip: You will need an equation plus conversions.

\* \* \* \* \*

WANTED:  $q$  in **kJ**

The equation that relates  $q$  and  $\Delta H$  is  $\Delta H = q$  at constant pressure.

For conversions, list the DATA as equalities and single units.

DATA:  $-284 \text{ kJ} = 1 \text{ mol H}_2$  (2 equivalent amounts)

$2.016 \text{ g H}_2 = 1 \text{ mol H}_2$  (grams prompt)

$0.12 \text{ g H}_2$  (the single-unit given).

SOLVE:  $? \text{ kJ} = 0.12 \text{ g H}_2 \cdot \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} \cdot \frac{-284 \text{ kJ}}{1 \text{ mol H}_2} = -17 \text{ kJ} = q$

\* \* \* \* \*

## Lesson 22B: Exo- and Endothermic Reactions

**Timing:** Begin this lesson when you are assigned  $\Delta H$  calculations.

\* \* \* \* \*

### The Energy Stored in Substances

Energy is stored in a substance during its formation. The amount of energy stored in a substance is dependent on (1) its atoms and bonds, and how they are arranged, and (2) the physical state of the substance: whether it is a gas, liquid, solid, or in solution.

Energy can be stored in the bonds of a substance. Some types of bonds have relatively large amounts of stored energy compared to others. For example, the C—H bond stores more energy than an O—H or a C—O bond.

Petroleum products have considerable commercial value in large part because they contain high-energy C—H bonds that release their energy when burned to form O—H and C—O bonds. That energy can be used to supply heat or to do work.

### Enthalpy and $\Delta H$ Terminology

1. In general terms, the property **enthalpy** ( $H$ ) is often described as the “heat content” of a substance: a measure of the energy that can be extracted from a substance.

The absolute enthalpy ( $H$ ) of a system is not possible to measure, but the absolute enthalpy ( $H$ ) of a particle can be assigned a value relative to an arbitrary zero enthalpy. In enthalpy measurements, an arbitrary zero enthalpy is assigned to elements in their standard state, and the absolute enthalpy of other particles compared to those zero values by measuring the  $\Delta H$  for chemical reactions and processes.

2.  $\Delta H$  is the symbol for *change* in enthalpy during a reaction or process.  $\Delta H$  is defined as:

$$\Delta H = (\text{enthalpy stored in products}) \text{ minus } (\text{enthalpy stored in reactants})$$

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

During most chemical processes, the change in enthalpy ( $\Delta H$ ) of a system is a measure of the heat flow ( $q$ ) into or out of the system.

3. The SI *units* of  $\Delta H$  are *joules*. In equations that include energy terms, the coefficients are understood to be moles.

If a chemical equation has *one* mole of *one* substance as a product, the units of  $\Delta H$  can be written either as joules (J) or as joules/mol (J/mol). In energy equations, the energy term will often be expressed in kilojoules (kJ).

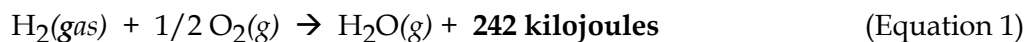
4. Energy and enthalpy changes in chemical processes can be classified as either **exothermic** or **endothermic**.
- Exothermic reactions are those in which heat is released to the environment (*exo-* is a prefix from ancient Greek meaning “out of”). Heat flows *out* of the chemical *particles* in exothermic reactions.
  - Endothermic reactions are those in which heat is required. Heat must flow *endo*, “to the inside,” into the chemical particles.

### $\Delta H$ Notation

The energy change in a reaction can be expressed in two ways: *either* as a reactant or product *inside* the reaction equation, *or* written in  **$\Delta H$  notation** *after* the equation.

### Exothermic Reactions

The explosive burning of hydrogen gas is exothermic. The reaction can be written as



This equation indicates that heat is a *product* of the reaction: energy is released to the environment. When energy is a term in a reaction equation, the coefficients are understood to be in *moles*. An omitted coefficient is assumed to represent one mole.

Though the energy term can be written inside the equation as in equation (1), more often the energy factor is represented using  $\Delta H$  notation. The above reaction is written as



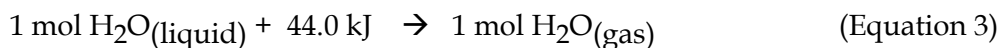
When equations include  $\Delta H$  notation, the units of  $\Delta H$  are always *energy* units (such as joules or calories), and the coefficients of the reaction equation are read in *moles*.

In the above reaction,  $\Delta H$  has a negative sign. For *exothermic* reactions,  $\Delta H$  is *defined* as *negative*. The minus sign indicates the chemical *particles* have *lost* stored energy in the reaction. Some of the energy stored in the reactant particles is released into the environment as the products are formed.

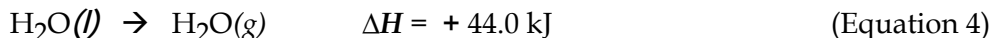
### Endothermic Reactions

When the products of a reaction have a higher stored energy than the reactants, energy must be added to the chemical particles for the reaction to take place. Cooking food, melting ice, and boiling water are examples of chemical process that require energy to be added. For these reactions,  $\Delta H$  will have a *positive* sign, because the chemical *particles gain* stored energy.

For example, the process of boiling water can be represented as either



OR as

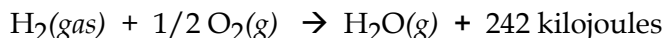


For *endothermic* reactions, the  $\Delta H$  value is always *positive*.

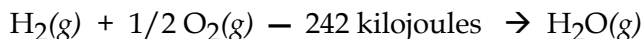
This reaction is an example of why, when representing the energy involved in a chemical process, the *phase* of each particle must be shown: (s), (l), (g), or (aq). The solid, liquid, gas, and aqueous phases of a substance have different amounts of stored energy.

### Writing Energy Terms Inside Reactions

The explosion of hydrogen gas in reaction (1) above was written as



By the rules of algebra, we could also write the above reaction as



However, by the conventions of chemistry, we do *not* write negative signs in front of energy terms that are written *inside* reaction equations. An energy term written *inside* a reaction equation is always assigned a *positive* sign: written on the right side (as a product) for exothermic reactions, and on the left (as something which needs to be added) for endothermic reactions.

Energy terms are always positive *inside* equations, but may be positive or negative as  $\Delta H$ .

### Summary

To solve problems involving energy equations, first commit the following rules to memory.

#### Rules for Representing Energy Changes in Chemical Processes

When an energy term is included in a chemical equation:

1. The coefficients are in *moles*.
2. The *phase* of each particle must be shown: (s), (l), (g), or (aq).
3. In *exothermic* reactions, energy is released into the environment. The energy term is shown
  - EITHER with a *positive* sign on the *products* side;
  - OR (preferred) with a *negative*  $\Delta H$  value written after the reaction.

4. In *endothermic* reactions, energy must be added as the reaction proceeds. The energy term is shown
  - EITHER with a *positive* sign on the *reactants* side of the equation,
  - OR with a *positive*  $\Delta H$  value written *after* the reaction.
5. The SI *units* of  $\Delta H$  are *joules*. In equations that include energy terms, the coefficients are understood to be moles. If a chemical equation has *one* mole of *one* substance as a product, the units of  $\Delta H$  can be written either as joules (J) or as joules/mol (J/mol).

After you learn the rules, complete the problems below to cement your knowledge.

**Practice A:** Answers are at the end of this lesson. Check your answer after each part.

1. Re-write these equations so that the heat term appears as a product or a reactant inside the equation.
  - a.  $C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ}$
  - b.  $1/2 N_2(g) + 1/2 O_2(g) \rightarrow NO(g) \quad \Delta H = +90.3 \text{ kJ}$
2. Label each reaction in (1) above as either exothermic or endothermic.
3. Re-write these equations using  $\Delta H$  notation.
  - a.  $H_2O_2(l) + 187.6 \text{ kJ} \rightarrow H_2(g) + O_2(g)$
  - b.  $C(s) + 1/2 O_2(g) \rightarrow CO(g) + 110.5 \text{ kJ}$
4. After each reaction in problem (3) above, add a label identifying the side that has more energy stored in its particles: the *reactants* or the *products*.

### Reversing Equations That Include Heat Terms

In theory, any chemical reaction can go backwards. In practice, many do.

Any reaction with a heat term inside will be true if written in the reverse direction.

Example: Since, from equation (3) above,  $H_2O(\text{liquid}) + 44.0 \text{ kJ} \rightarrow H_2O(\text{gas})$

This will also be true:  $H_2O(\text{gas}) \rightarrow H_2O(\text{liquid}) + 44.0 \text{ kJ}$

Given a reaction in which a  $\Delta H$  value represents an energy change, the reaction can be written in the *reverse* direction if you change the sign of  $\Delta H$ .

Example: Since, from equation 4 above,  $H_2O(l) \rightarrow H_2O(g) \quad \Delta H = +44.0 \text{ kJ}$

This equation is also true:  $H_2O(g) \rightarrow H_2O(l) \quad \Delta H = -44.0 \text{ kJ}$

If an amount of energy must be added to change reactants to products, this same amount will be released when products are changed back to reactants. In chemical and physical processes, energy must be *conserved*.

**Multiplying Equations That Include Heat Terms**

Given a known balanced equation that includes an energy term, the *coefficients* representing the moles of the reactants and products may *all* be multiplied or divided by the same factor, provided you do the same to the *energy* term.

**Examples**

- a. Since  $\text{H}_2(\text{gas}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) + 242 \text{ kJ}$  is true,  
Then  $2 \text{H}_2(\text{gas}) + 1 \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) + 484 \text{ kJ}$  (all doubled) is also true.
- b. Since  $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H = -242 \text{ kJ}$  is true,  
Then  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) \quad \Delta H = -484 \text{ kJ}$  (all doubled) is also true.

**Summary**

Memorize these additional rules for energy terms in equations.

6. Reactions that include energy terms can be *reversed* (written backwards). If  $\Delta H$  notation is used, *change the sign* of  $\Delta H$ .
7. All coefficients and energy terms in a balanced equation can be multiplied or divided by a factor. If  $\Delta H$  notation is used, do the *same* to the  $\Delta H$ .

Once you have the above seven rules firmly in memory, try the problems below.

**Practice B:** Do every other problem. Save the rest for your next practice session.

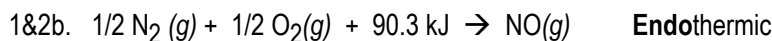
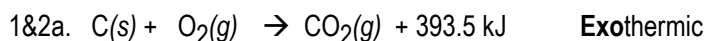
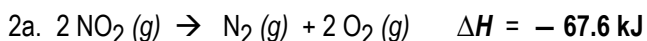
1. Write these reactions in the reverse direction. Express the energy term as a  $\Delta H$  value.

- a.  $\text{UF}_6(\text{l}) \rightarrow \text{UF}_6(\text{g}) \quad \Delta H = +30.1 \text{ kJ}$
- b.  $\text{C}(\text{s}) + 2 \text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) \quad \Delta H = -74.9 \text{ kJ}$

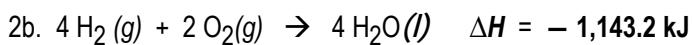
2 Use these 4 “known” reactions to fill in the blanks below.



- a.  $2 \text{NO}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{O}_2(\text{g}) \quad \Delta H = \underline{\hspace{2cm}}$
- b.  $4 \text{H}_2(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow 4 \text{H}_2\text{O}(\text{l}) \quad \Delta H = \underline{\hspace{2cm}}$
- c.  $8 \text{H}_2\text{SO}_4(\text{l}) \rightarrow 8 \text{H}_2(\text{g}) + \text{S}_8(\text{s}) + 16 \text{O}_2(\text{g}) \quad \Delta H = \underline{\hspace{2cm}}$

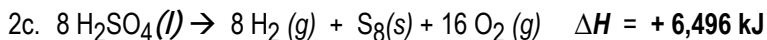
**ANSWERS****Practice A****Practice B**

This reaction is table reaction # 3 doubled and written backwards: double and change sign of  $\Delta H$ .



This reaction is table reaction #2 quadrupled – be careful to distinguish the gas/liquid/solid *states*.

Significant figures: Multiplying by an exact number does not change the *place* with doubt.



This is table reaction #4 multiplied by 8: multiply  $\Delta H$  by 8. Since this reaction is also written backwards from reaction #4; change the sign of  $\Delta H$ .

\* \* \* \* \*

## Lesson 22C: Adding $\Delta H$ Equations (Hess's Law)

**Timing:** Do this lesson when you are assigned problems that require finding a  $\Delta H$  by adding equations with  $\Delta H$  values attached.

\* \* \* \* \*

### Hess's Law

**Hess's law of heat summation** states that the enthalpy change in an overall chemical process can be calculated by adding its individual steps.

This means that for reactions where the heat of reaction ( $\Delta H$ ) is *not* known,  $\Delta H$  can be calculated by adding reactions for which  $\Delta H$  is known.

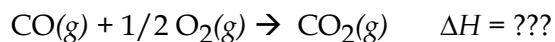
#### Rules For Adding Equations With $\Delta H$ Terms

All reaction equations with energy terms can be *added*.

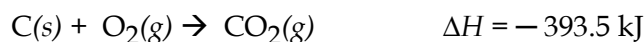
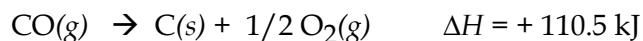
- Multiple equations can be added to produce one net equation.
- Like particles on *opposite sides* of the *arrows* in the added reactions can *cancel*.
- *Like particles* on the same side of the *arrows* of added equations can *add*.
- All particles to the left of the arrows add to become the reactants in the final equation.
- All particles to the right of the arrows add to become the products of the final reaction.
- The final  $\Delta H$  will be the added  $\Delta H$  values of the reactions being added.

The meaning of these rules is best explained with an example. Apply the above rules to the following problem, and then check the answer below.

**Q.** Find the heat of reaction for the burning of carbon monoxide



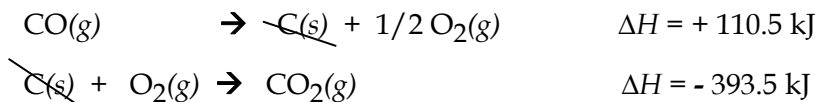
by *adding* these two reactions.



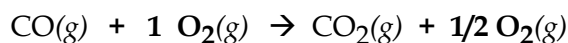
\* \* \* \* \*

**Answer**

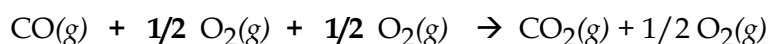
When adding, first cancel *like* terms on *opposite* sides of the arrows in the equations being added. Writing your equations with the arrows lined up one above the other will help keep the two *sides* separated.



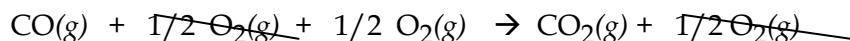
If we add the reactions at this point, the result is:



However, another cancellation can be made. The **1** O<sub>2</sub> on the left can be *split* into

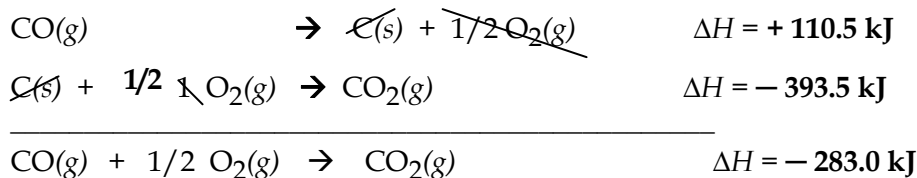


The 1/2 O<sub>2</sub> on the right now cancels a 1/2 O<sub>2</sub> on the left, leaving 1/2 O<sub>2</sub> on the left.



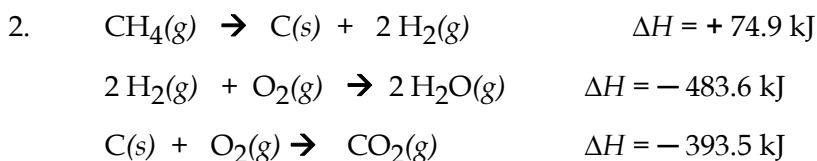
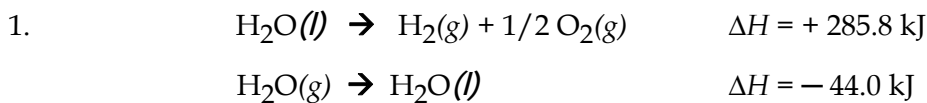
After cancellation, the result is the *reaction* that was WANTED.

When reactions add to give the reaction wanted, add the  $\Delta H$ 's to find the  $\Delta H$  wanted.



This process of adding equations will become easier with practice.

**Practice A:** Add these equations and their  $\Delta H$  values. Check answers as you go.

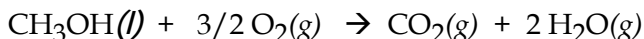


**Finding An Unknown  $\Delta H$  By Adding Equations**

When  $\Delta H$  for an equation is not known, it can be found by adding equations for which  $\Delta H$  is known. The key is to arrange the known equations so that they *add* to result in the equation with the unknown  $\Delta H$ .

The following problem will illustrate a *system* for deciding *which* known equations to add, as well as when to multiply and reverse them.

**Q.** Find the  $\Delta H$  for the burning of methyl alcohol,



using these three equations for which  $\Delta H$  values are supplied.



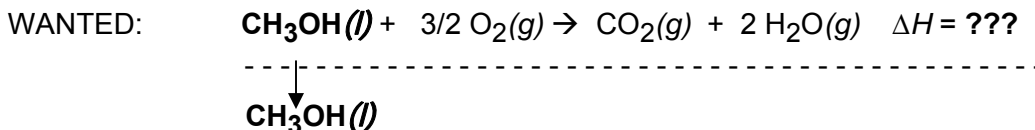
Complete the following steps in your notebook.

1. Write the WANTED equation, and then draw a dotted line beneath it.
2. Re-write the *first* term in the WANTED equation, *with* its coefficient, *below* the dotted line.

(Putting a WANTED reactant on the side where it must be in the final added equation will help to arrange the rest of the added equations).

\* \* \* \* \*

At this point, your paper should look like this:



3. Find an equation that both *includes* the *dropped* particle *and* has a known  $\Delta H$ .

\* \* \* \* \*

$\text{CH}_3\text{OH}$  is part of equation (1) in the problem, which includes a  $\Delta H$ .

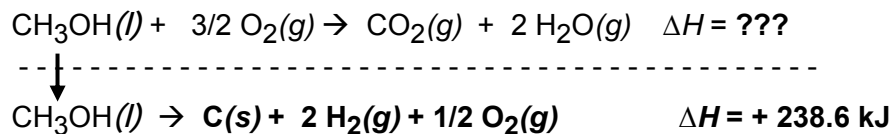
Your goal is to write a known equation, *reversed* and/or *multiplied* if needed, so that the *dropped* particle is on the side it is dropped on and has the same coefficient as the particle dropped.

If needed, reverse the direction of the *known* equation so that the term dropped below the line is on the *side* of the arrow, left or right, where it was dropped. If needed, multiply the coefficients of the *known* equation so that the coefficient of the dropped particle is the coefficient WANTED. *Modify* and write the  $\Delta H$  value after the equation.

Try that step, then check your answer below.

\* \* \* \* \*

In this problem, 1  $\text{CH}_3\text{OH}$  is needed on the *left* side of the arrow, so write known equation (1) *backwards*.



Because the known equation must be reversed, reverse the *sign* of its  $\Delta H$ .

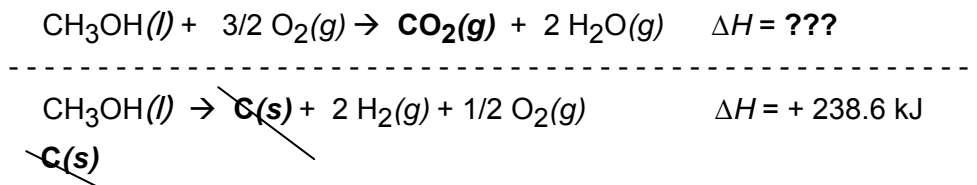
- A TIP that works often in problems involving *burning* or *combustion* (both mean reacting with  $\text{O}_2$  gas) is “don’t worry about  $\text{O}_2$  until the end.” If the equations have been chosen properly, when you add the terms at the end,  $\text{O}_2$  should have the coefficient WANTED. This will be a check that you have selected the reactions properly.
- Now compare the first particle on the *right* side of the arrow *below* the dotted line to the particles WANTED on the right *above* the dotted line.

If what you **have** *below* the dotted line does not exactly match what is WANTED *above* the dotted line, get rid of the UNwanted particle. Start a new equation on the line *below* by writing the unwanted particle, with its coefficient, on the side where it will *cancel* the same term in the first equation.

Try that step, then check your answer below.

\* \* \* \* \*

In this problem, after the arrow and below the dotted line, is  $\text{C}(s)$ . What is WANTED on the right that contains carbon is  $\text{CO}_2$ , so we need to get rid of  $\text{C}(s)$ . Write  $\text{C}(s)$  at the start of a **new** equation below, on the **side** where it will cancel when the equations are added:

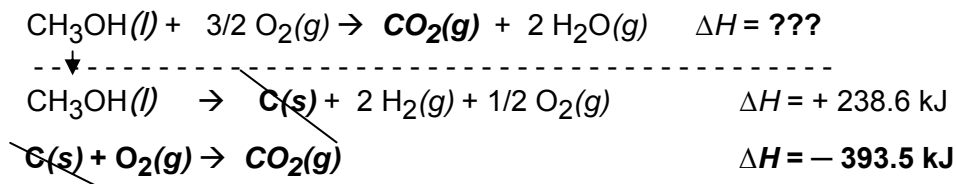


Then find an equation with a known  $\Delta H$  that both *includes* the particle in the bottom equation that you set up to cancel, and places its atoms in a compound WANTED *above* the dotted line.

Try that step, then check your answer below.

\* \* \* \* \*

The equation that converts the  $\text{C}(s)$  you need to get rid of on the left to the  $\text{CO}_2$  you WANT on the right is equation (3) supplied in the problem.



5. Ignoring  $O_2$ , compare the particles *below* the dotted line to what is WANTED above the dotted line. If there is *any* particle and coefficient below the dotted line that does not match exactly what is WANTED above the line, put the coefficient and particle that is *not* WANTED where it will *cancel*. Then find an equation that will convert the unwanted particle to a WANTED particle.

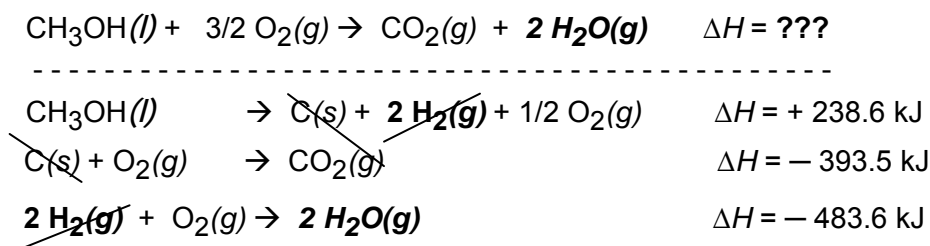
Take a look: what coefficient and particle below the dotted line do you *not* want?

\* \* \* \* \*

Ignoring  $O_2$ , it is  $2 H_2(g)$ . Try step 5, and then check the answer below.

\* \* \* \* \*

After the arrow and below the dotted line, is  $2 H_2$ . What is WANTED that contains hydrogen is  $2 H_2O$ . So, write  $2 H_2$  below in a new equation where it will cancel, and find an equation that converts  $H_2$  to the  $H_2O$  WANTED.

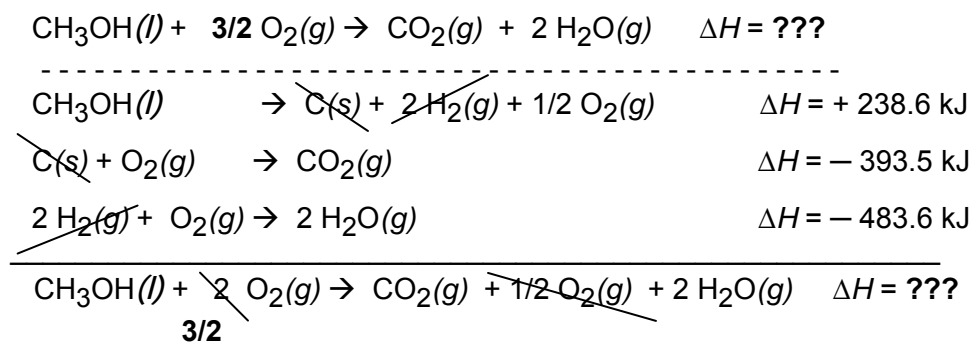


Equation (2) supplied in the problem, *and* its  $\Delta H$ , is doubled.

6. Compare what is WANTED above the dotted line to what is written below the line. If what is below adds to give what is above, *add* the equations *below* the dotted line. Then add the  $\Delta H$  values to get the WANTED  $\Delta H$ .

\* \* \* \* \*

Your paper should look like this:



Note that the  $O_2$  coefficient, after cancellation, matches what is WANTED. That's an indication that you have probably added the proper equations.

Once the *equations* below the dotted line add to give the equation WANTED, add the modified  $\Delta H$  values.

\* \* \* \* \*

$$\Delta H = +238.6 - 393.5 - 483.6 = -638.5 \text{ kJ} \quad \text{Done!}$$

**Summary:** To find an unknown  $\Delta H$  for a reaction equation,

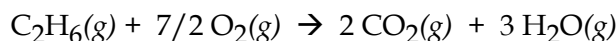
- write the equation WANTED; write a dotted line below it.
- Drop the first coefficient and particle below the dotted line.
- Including that first coefficient and particle, write an equation with a known  $\Delta H$ .
- Add other equations with known  $\Delta H$  values that cancel particles you don't want, form particles you want, and add to give the equation WANTED.
- Add the  $\Delta H$  values.

**Practice B:** Use the method above on these. If you get stuck, check a part of the answer and try again. More practice can be found in the next lesson.

1. Use the first two equations to find  $\Delta H$  for the third: the heat required to melt ice.



2. The gas ethane ( $\text{C}_2\text{H}_6$ ) is one of the constituents of natural gas, a major component of the world energy economy. The equation for the burning of ethane is

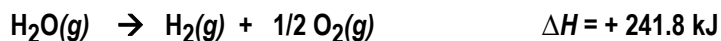
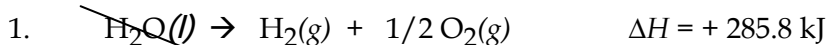


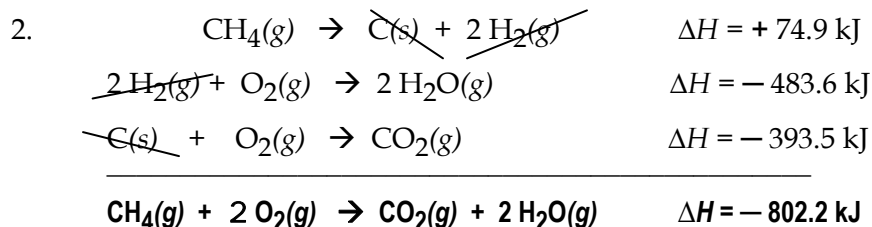
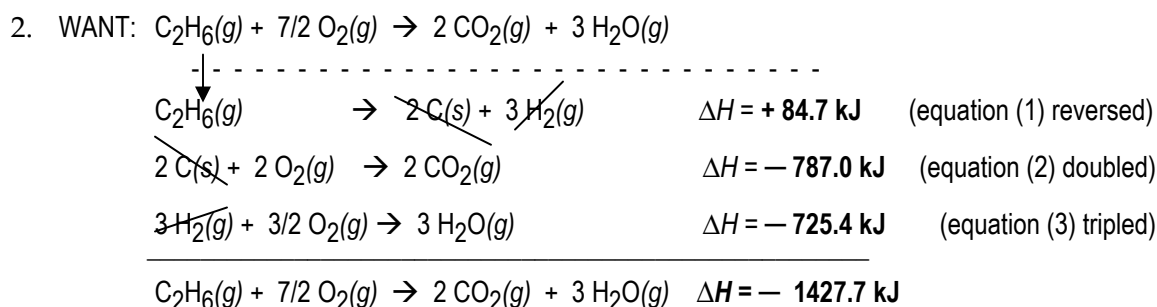
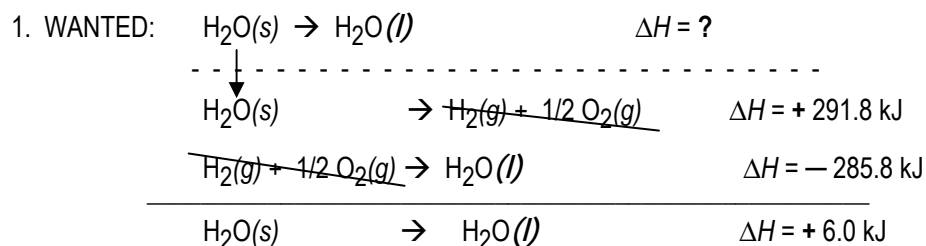
Use the formation equations below to find  $\Delta H$  for the burning of ethane.



## ANSWERS

### Practice A



**Practice B**

\* \* \* \* \*

**Lesson 22D: Heats of Formation and Element Formulas**

**Timing:** Complete this lesson when you are asked to solve problems using heats of formation.

\* \* \* \* \*

**Gas Versus Thermodynamic Standard Conditions**

The history of chemistry has given us multiple definitions for *standard* conditions.

- For *gas law* calculations, standard temperature and pressure (STP) is defined as  $0^\circ\text{C}$  and 1 atmosphere pressure.
- For *thermodynamic* measurements, for substances to be in their **standard state**,
  - *elements* must be at  $25^\circ\text{C}$  and 1 atm pressure and (in most cases) in the phase and/or solid structure that is most stable.
  - *Compounds* that are *gases* must be at *one atmosphere* pressure.
  - *Substances in solutions* must have a concentration of 1 mol/L.
  - *Solid and liquid compounds* are in their standard state under nearly all conditions if they are in the form that is most stable at  $25^\circ\text{C}$  and 1 atm pressure.

You should be aware of the difference between *gas* and *thermodynamic* standard conditions, but in most problems it will be clear from the context which definition of “standard conditions” applies.

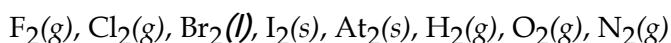
### Writing the Standard State For Elements

To work with formation equations, you will need to be able to write the *standard state* of elements: both the molecular *formula* of the element and the *state* (gas, liquid, or solid) in which it is most stable at room temperature (25°C) and one atmosphere pressure. The following are rules for writing formulas and standard states for most of the elements you will encounter in first-year chemistry.

1. Only *two* elements are *liquids* at room temperature: mercury (Hg) and bromine (Br<sub>2</sub>).
2. Over 75% of the elements are *metals*, and the formulas for all metals (except mercury) are written as *monatomic solids*.

Examples of element formulas for metals: Na(s), Al(s), Ag(s), Hg(liquid)

3. Eight elements are **diatomic**: The 5 halogens, plus the *gases* hydrogen, oxygen, and nitrogen:



4. Except for hydrogen, all of the 11 elements that are *gases* at room temperature are toward the top and right of the periodic table. The gaseous elements are 5 of the diatomics: H<sub>2</sub>(g), O<sub>2</sub>(g), N<sub>2</sub>(g), F<sub>2</sub>(g), Cl<sub>2</sub>(g); plus all 6 of the monatomic noble gases.
5. Some periodic tables indicate the *state* of each element at 25°C by the color of the element symbol: often solids are black, the two liquids blue, and gases red.
6. If a table of heats of formation shows a particle with a value for its heat of formation ( $\Delta H^\circ_f$ ) of *zero*, the formula shown will be that of the *element* in its *standard state*.

Example: In the table at the right, for the elements chlorine and hydrogen, the formulas in their standard state are the formulas with the **zero  $\Delta H$** : Cl<sub>2</sub>(g) and H<sub>2</sub>(g).

The single-atom forms of each element can be formed at room temperature, but, as their higher enthalpy indicates, they are less stable than the molecules formed from *two* neutral atoms. They therefore tend to react readily with other particles.

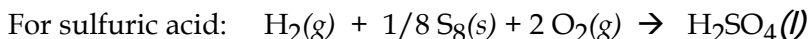
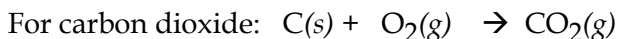
Formula	$\Delta H^\circ_f$ in kJ/mole
Cl(g)	+ 121.0
Cl <sub>2</sub> (g)	0
H <sub>2</sub> (g)	0
H(g)	+ 218.0

7. Other frequently encountered non-metal elements are S<sub>8</sub>(s) and P<sub>4</sub>(s).

**Writing Formation Equations**

A **formation equation** is a balanced equation in which the reactants are *all elements*, the product is *one mole of one compound*, and the elements and the compound are all in their standard states.

Examples of formation equations are

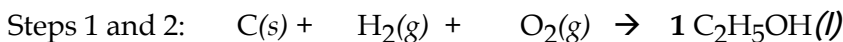


To write a formation equation for a compound,

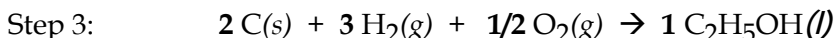
1. To the right of an arrow, write the compound formula with a coefficient of 1.
2. On the left, for each of the *elements* that make up the compound, write the formula of the element in its *standard state* at 25°C and 1 atmosphere pressure.
3. Add element coefficients (that often include fractions) to *balance* the equation.

Try **Q**. Write the formation reaction for ethanol:  $\text{C}_2\text{H}_5\text{OH}(l)$

\* \* \* \* \*



\* \* \* \* \*



**Practice A:** Learn the rules above. Then, for each numbered problem, do every other letter. Check answers as you go. Save a few for your next practice session.

1. Which of these are not elements in their standard state?
  - a.  $\text{H}_2(g)$
  - b.  $\text{CO}(g)$
  - c.  $\text{Co}(s)$
  - d.  $\text{Hg}(g)$
  - e.  $\text{N}(g)$
  - f.  $\text{Cl}_2(l)$
2. Write the formulas for these elements in their standard state at room temperature.
  - a. Fluorine
  - b. Iron
  - c. Oxygen
  - d. Carbon
  - e. Nitrogen
3. Write balanced formation equations for these compounds.
  - a.  $\text{NaCl}(s)$
  - b.  $\text{HCl}(g)$
  - c.  $\text{Al}_2\text{O}_3(s)$
  - d.  $\text{C}_2\text{H}_6(g)$
  - e.  $\text{NO}_2(g)$

**Defining Zero For  $\Delta H$** 

Every particle has a characteristic enthalpy that depends on its structural formula and its state. The absolute enthalpy of a substance cannot be measured, but we can work around this because in chemical processes, we are concerned with *changes* in enthalpy that occur ( $\Delta H$ ). To measure enthalpy changes, we can assign an *arbitrary* zero point to the enthalpy scale, and then measuring change relative to that zero value. For enthalpy, the zero point that has been chosen is: all *elements* in their standard state are *assigned* a heat of formation ( $H^\circ_f$ ) of zero kJ/mol.

For all elements in their standard state,  $\Delta H^{\circ}_f \equiv 0$  kJ/mol.

### Heat of Formation

A particle in a given state has a *characteristic heat of formation* ( $\Delta H^{\circ}_f$ ) and this can be considered to be the value for its enthalpy. For elements in their standard state, this value is always 0 kJ/mol. For all other particles,  $\Delta H^{\circ}_f$  is the change in enthalpy that occurs in its formation reaction.

In the symbol for a heat of formation,  $\Delta H^{\circ}_f$ , the subscript **f** means “formed from elements in their standard state.” The superscript degree symbol  $^{\circ}$  means that the particle formed is also in its standard state.

Values for heats of formation are often provided in reference tables. The table at the right tells us that

1. *Graphite* (used in “pencil lead”) and *diamond* are composed of solid carbon.
2. Graphite and diamond are often represented by the same molecular formula: C(s).

Name	Formula	$\Delta H^{\circ}_f$ in kJ/mol
Graphite	C(s)	0
Diamond	C(s)	+ 1.9
Carbon Dioxide	CO <sub>2</sub> (g)	− 393.5
Methane	CH <sub>4</sub> (g)	− 74.9
Steam	H <sub>2</sub> O(g)	− 241.8

However, they have different structural formulas, and graphite has slightly lower enthalpy. Graphite is therefore the *more stable* of the two forms of pure carbon. The system with *lower* enthalpy is termed “more stable” because more energy must be added to change it.

The most stable form at at 25°C is designated as the *standard state* of an element.

Heats of formation are the  $\Delta H$  values for *formation equations*. Formation equations may be written with  $\Delta H$  values labeled as either  $\Delta H$ ,  $\Delta H^{\circ}$  or  $\Delta H^{\circ}_f$ .

#### Examples

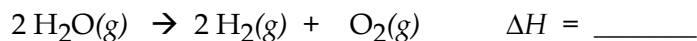
For carbon dioxide:  $C(s) + O_2(g) \rightarrow CO_2(g)$        $\Delta H^{\circ}_f = -393.5$  kJ/mol

For sulfuric acid:  $H_2(g) + 1/8 S_8(s) + 2 O_2(g) \rightarrow H_2SO_4(l)$        $\Delta H^{\circ}_f = -812$  kJ/mol

A formation equation can be treated as any other equation with a  $\Delta H$  attached: it can be multiplied, reversed, and added.

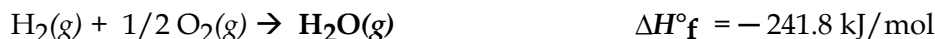
If you are given a  $\Delta H^{\circ}_f$  value for a compound in a problem or in a table, you can write a formation equation for the compound, attach the  $\Delta H^{\circ}_f$ , and then reverse, multiply, or add that equation to find  $\Delta H$  values for other reactions. Try this example.

**Q.** Using a  $\Delta H^{\circ}_f$  in the table above, write the  $\Delta H$  for

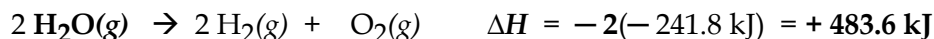


\* \* \* \* \*

Starting from a  $\Delta H^\circ_f$  table value, to find  $\Delta H$  for a related equation, first write the balanced formation *equation* and attach its  $\Delta H^\circ_f$ .



Then reverse and/or multiply the formation reaction to get the WANTED reaction.



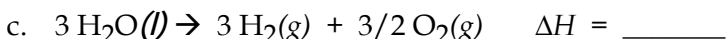
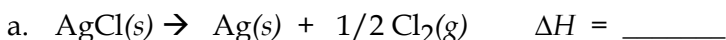
Note that the unit converts from kJ/mol to kJ when the product is no longer one mole of one substance. Note also that if a formation equation is multiplied or reversed, the  $\Delta H^\circ_f$  becomes a  $\Delta H$  because the equation is no longer a *formation equation*.

**Practice B:** Learn the rules above. Then, for each numbered problem, do every other letter. Check answers as you go. Save a few for your next practice session.

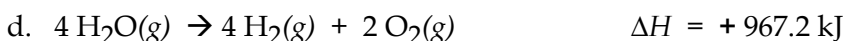
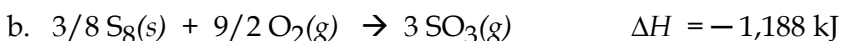
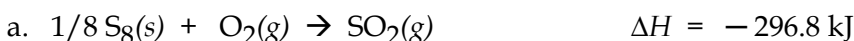
1. In your notebook, based on the table data at the right, write the formation equation for each compound and attach a  $\Delta H$  value to each equation.

Formula	$\Delta H^\circ_f$ in kJ/mol
$\text{NH}_3(\text{g})$	-45.9
$\text{AgCl}(\text{s})$	-127.0
$\text{NO}(\text{g})$	+90.3
$\text{H}_2\text{O}(\text{l})$	-285.8

2. Using the table values from Problem 1, write  $\Delta H$  values for these reactions.



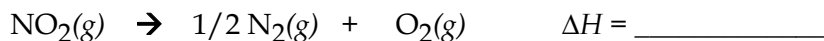
3. Which of the reactions in Problem 2 are endothermic?
4. Circle the *compounds* involved in each of these reactions, then write the value for the heat of formation ( $\Delta H^\circ_f$ ) for each compound.



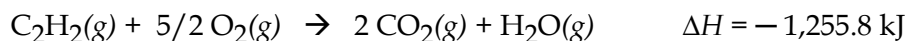
5. Which equation(s) in Problem 4 are formation equations?

6. Use this table data to find  $\Delta H$  values for the two reactions below, then add the two reactions and their  $\Delta H$  values.

Formula	$\Delta H^\circ_f$
$\text{NO}_2(\text{g})$	+ 33.8 kJ/mol
$\text{NO}(\text{g})$	+ 90.3 kJ/mol



7. Acetylene gas can be burned to produce the extremely hot flame used in a “cutting torch.” The equation is



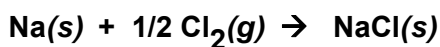
Use the above equation plus the table values to find the heat of formation for acetylene.

Formula	$\Delta H^\circ_f$ in kJ/mole
$\text{H}_2\text{O}(\text{g})$	- 241.8
$\text{CO}_2(\text{g})$	- 393.5

## **ANSWERS**

### **Practice A**

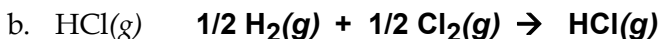
- b, d, e, and f.** b.  $\text{CO}(\text{g})$  is a compound. d.  $\text{Hg}(\text{g})$ . Mercury is a liquid at room temperature.  
 e.  $\text{N}(\text{g})$ . Nitrogen as an element is  $\text{N}_2$ . f.  $\text{Cl}_2(\text{l})$ . Chlorine is a gas at room temperature.
- a. Fluorine  **$\text{F}_2(\text{g})$**  Fluorine is a halogen. All halogen elements are diatomic. Fluorine is at the top right of the periodic table, where several elements are gases at room temperature.  
 b. Iron  **$\text{Fe}(\text{s})$**  Iron is a metal. All metal elements are monatomic solids (except mercury).  
 c. Oxygen  **$\text{O}_2(\text{g})$**  Oxygen is a gas at room temperature. The fact that the formula for the element oxygen is  $\text{O}_2$  must be memorized.  
 d. Carbon  **$\text{C}(\text{s})$**  The elemental form of carbon is graphite (“pencil lead”).  
 e. Nitrogen  **$\text{N}_2(\text{g})$**  The air we breathe is about 80% nitrogen gas. The diatomic formula for elemental nitrogen gas is used frequently and must be memorized.
- a.  $\text{NaCl}(\text{s})$  In formation equations, **elements** in their standard state are the reactants, **one** mole of the **compound** is the product, and coefficients must be **added** that **balance** the equation:



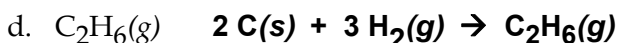
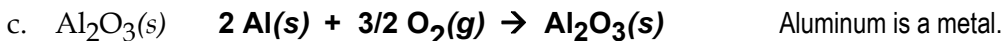
Sodium is a metal. For metals, the formula is written as one atom; all are solids except Hg.

Chlorine is a halogen: all halogen elements are diatomic. In the halogen column, the elements above bromine are gases, and below bromine are solids, at room temperature.

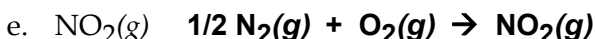
NaCl is a compound: it has more than one kind of atom. You must add coefficients that keep the same particle formulas, but make one mole of the compound in a balanced equation.



Hydrogen atoms are stable at room temperature as  $\text{H}_2$  gas; this element formula should be memorized.



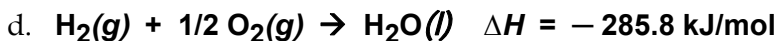
Some texts write **C(graphite)** to distinguish graphite, diamonds, buckyballs, and other forms of pure carbon. Graphite is the "standard state" form of carbon.



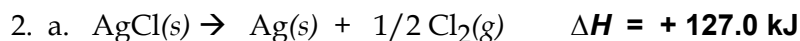
### Practice B



When translating heats of formation into formation equations, elements are added as reactants, one mole of the compound is the product, and the heat of formation is the  $\Delta H$  for the reaction.



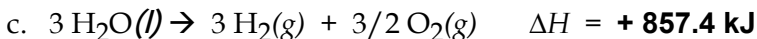
When a reaction has one product and its coefficient is one, the units of  $\Delta H$  may be written as either kJ/mol or as kJ. In equations with energy terms, coefficients are in moles.



When starting from the table, first write out the formation reaction, as in answer 3b. Then, since this problem asks for the *reverse* of the formation reaction, change the *sign* of  $\Delta H$ .

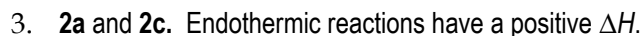


Starting from the table, first write the formation reaction, as in answer 3a. Then, since this problem doubles the formation reaction, double the  $\Delta H$ .



This problem is table equation 3d, tripled and reversed.

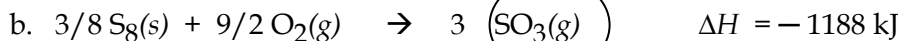
When a reaction does not have one particle as a product, the units of  $\Delta H$  are kJ.



4. Compounds have more than one kind of atom.

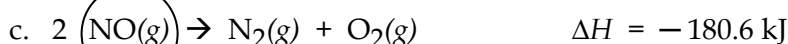


Assuming that all of the formulas in the reactants are elements in their “standard state” (and they are), this is a formation reaction for one mole of  $\text{SO}_2(\text{g})$ . The heat of this reaction ( $\Delta H$ ) is therefore the heat of formation of the compound:  $\Delta H^\circ_f$  for  $\text{SO}_2(\text{g}) = -296.8 \text{ kJ/mol}$



In this reaction, the elements are on the left, the compound is on the right, and **3** moles of compound is formed. For a *formation reaction* involving heat, we must make **one** mole of the compound. To get the formation reaction, multiply all terms of the given reaction by  $1/3$ .

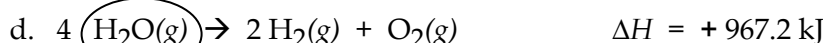
$$\Delta H^\circ_f = 1/3 \times (-1188 \text{ kJ}) = -396.0 \text{ kJ}.$$



In a formation reaction, elements must be on the left, so this reaction must be reversed.

Reversing this reaction, the sign of  $\Delta H$  is reversed. This is double a formation reaction, so the  $\Delta H$  would be cut in half for the heat of formation. Heats for formation must be for *one* mole of compound.

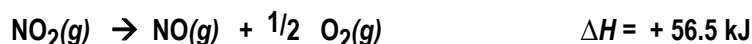
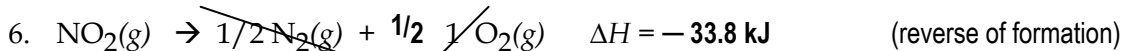
$$\Delta H^\circ_f \text{ for NO}(\text{g}) = 1/2 \times (-180.6 \text{ kJ}), \text{ reversed} = +90.3 \text{ kJ}.$$



This is the formation reaction for water vapor, quadrupled and reversed. To find to the formation reaction, write the reaction backwards, changing the sign of  $\Delta H$ . Then multiply the coefficients and  $\Delta H$  by  $1/4$ , to make **one** mole of water vapor.

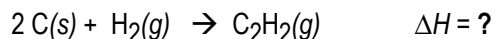
$$\Delta H^\circ_f \text{ for water vapor} = 1/4 \times (+967.2 \text{ kJ}) \text{ reversed} = -241.8 \text{ kJ}$$

5. Only **4a**. Formation equations must have elements in their standard state on the left and *one* mole of a *non*-element on the right.



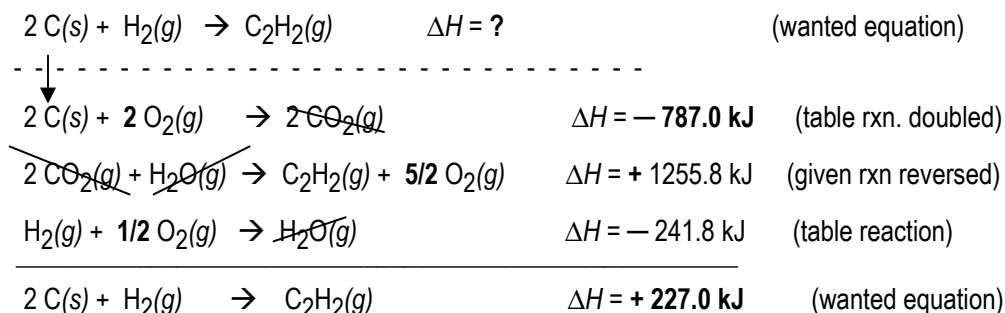
When you add the equations,  $1/2 \text{O}_2$  cancels on both sides. When the equations are written so that the arrows do not line up in a column, be careful to cancel substances on *opposite* sides of the arrows.

7. The heat of *formation* of acetylene is WANTED. That equation would be:



\* \* \* \* \*

Arrange the given equations to add and cancel to result in the equation wanted. The equations may be added in any order. In burning (combustion) reactions, the  $\text{O}_2$  coefficients should add correctly if the equations to be added are correct. Here, the  $5/2 \text{O}_2$  on both sides will cancel.



\* \* \* \* \*

## Lesson 22E: Using Summation To Find $\Delta H$

Enthalpy is a state function: the change in enthalpy in a process ( $\Delta H$ ) is simply the *difference* between the total enthalpy of the particles at the end (the products) and at the beginning (the reactants). This means that one way to measure the enthalpy change of a reaction is to add up the enthalpy values of all of the products, then subtract the enthalpy values of all of the reactants.

$$\Delta H_{\text{reaction}} = \text{sum of } \Delta H^\circ_{\text{f}} \text{ for final particles} - \text{sum of } \Delta H^\circ_{\text{f}} \text{ for initial particles}$$

$\Delta H^\circ_{\text{f}}$  values measure the enthalpy in one mole of a particle. Two moles of the particles will have double that value for their total enthalpy.

Apply the logic of the above to this

Q. If we needed to find  $\Delta H$  for the reaction in problem 7 above



and we know the  $\Delta H^\circ_{\text{f}}$  for each of the particles in the equation, as given in the table at the right,

- a. calculate the total  $\Delta H^\circ_{\text{f}}$  of the *products* of the above reaction, based on the table and reaction coefficients.

Formula	$\Delta H^\circ_{\text{f}}$
H <sub>2</sub> O(g)	-241.8 kJ/mol
CO <sub>2</sub> (g)	-393.5 kJ/mol
C <sub>2</sub> H <sub>2</sub> (g)	+227.0 kJ/mol

\* \* \* \* \*

$$\begin{aligned}
 \text{Total } \Delta H^\circ_{\text{f}} \text{ of the products} &= 2 (\Delta H^\circ_{\text{f}} \text{ of CO}_2\text{(g)}) + 1 (\Delta H^\circ_{\text{f}} \text{ of H}_2\text{O(g)}) = \\
 &= 2 (-393.5 \text{ kJ}) + 1 (-241.8 \text{ kJ}) = -1,028.8 \text{ kJ}
 \end{aligned}$$

- b. Find the total  $\Delta H^\circ_{\text{f}}$  of the *reactants*.

\* \* \* \* \*

$$\begin{aligned}
 \text{Sum of } \Delta H^\circ_{\text{f}} \text{ of the reactants} &= 1 (\Delta H^\circ_{\text{f}} \text{ of C}_2\text{H}_2\text{(g)}) + 5/2 (\Delta H^\circ_{\text{f}} \text{ of O}_2\text{(g)}) = \\
 &= 1 (+227.0 \text{ kJ}) + 5/2 (0 \text{ kJ}) = +227.0 \text{ kJ}
 \end{aligned}$$

O<sub>2</sub>(g) is an element, and the  $\Delta H^\circ_{\text{f}}$  of all elements is 0 kJ.

c. Using the equation above with sums, find  $\Delta H$  for the reaction.

★ ★ ★ ★ ★

$$\begin{aligned}\Delta H_{\text{reaction}} &= \text{sum of } \Delta H^{\circ}_{\text{f}} \text{ of products} - \text{sum of } \Delta H^{\circ}_{\text{f}} \text{ of reactants} \\ &= -1,028.8 \text{ kJ} - (+227.0 \text{ kJ}) = -1,255.8 \text{ kJ}\end{aligned}$$

Compare this answer to the  $\Delta H$  supplied after the reaction in problem 7 above.

What is the difference between the above Question Part c and problem 7?

- In this question, we knew all of the heats of **formation** for the particles in the reaction.
- In problem 7, we WANTED one of the heats of formation, and had data for a reaction that was not a formation reaction, but could be used to find the  $\Delta H^{\circ}_{\text{f}}$ .

To find a reaction  $\Delta H$ , if the  $\Delta H^{\circ}_{\text{f}}$  values for all of the compounds in an equation are known, this summation method is likely to be quicker than writing out formation equations and adding using Hess's law. However, in problems with data that *mix* formation and non-formation reactions, such as problem 7, the summation method does not work, but writing out the formation reactions then adding both types of reactions using Hess's law does work.

Hess's law is slower, but it will solve using heats of formation equations, non-formation equations, or a mixture of the two.

To find  $\Delta H_{\text{reaction}}$ , a suggested strategy that may speed your work is

- use the summation method *if* you know *all* of the needed  $\Delta H^{\circ}_{\text{f}}$  values.
- If not, write out the formation equations and add equations using Hess's Law.

Let's summarize:

To find  $\Delta H_{\text{reaction}}$ :

1. *If* standard enthalpy of formation ( $\Delta H^{\circ}_{\text{f}}$ ) values are known for *all* of the particles in a chemical reaction, the  $\Delta H$  of the reaction can be calculated by substituting those values into the state function equation that defines  $\Delta H$ :

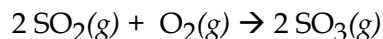
$$\begin{aligned}\Delta H_{\text{reaction}} &= \Delta H_{\text{final}} - \Delta H_{\text{initial}} \\ &= \text{sum of } \Delta H^{\circ}_{\text{f}} \text{ of products} - \text{sum of } \Delta H^{\circ}_{\text{f}} \text{ of reactants} \\ &= [\text{sum of (coefficient} \times \Delta H^{\circ}_{\text{f}} \text{) of products}] - [\text{sum of (coefficient} \times \Delta H^{\circ}_{\text{f}} \text{) of reactants}]\end{aligned}$$

Abbreviated in symbols, we will call this the heat of formation **summation equation**.

$$\Delta H_{\text{reaction}} = \sum c \Delta H^{\circ}_{\text{f}} \text{ of products} - \sum c \Delta H^{\circ}_{\text{f}} \text{ of reactants}$$

2. If *not all* of the needed  $\Delta H^{\circ}_{\text{f}}$  values are known, write out the formation equations and other supplied equations, adding the equations using Hess's Law.

Try **Q.** Use the table and the summation equation to find  $\Delta H$  for this reaction.



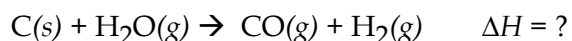
Formula	$\Delta H^\circ_f$ in kJ/mole
$\text{SO}_2(g)$	- 296.8
$\text{SO}_3(g)$	- 396.0

\* \* \* \* \*

$$\begin{aligned} \Delta H &= [\text{sum of (coefficient} \times \Delta H^\circ_f \text{) of products}] - [\text{sum of (coefficient} \times \Delta H^\circ_f \text{) of reactants}] \\ &= [2(-396.0 \text{ kJ})] - [2(-296.8 \text{ kJ}) + 0 \text{ kJ}] = \mathbf{-198.4 \text{ kJ}} \end{aligned}$$

**Practice.** On these, use the summation equation and table values to find  $\Delta H$ .

1. Steam can be added to hot coal (which is primarily carbon) to produce a burnable mixture:

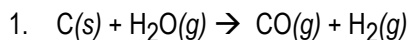


Formula	$\Delta H^\circ_f$ in kJ/mol
$\text{CO}(g)$	- 110.5
$\text{H}_2\text{O}(g)$	- 241.8

2. For the burning of ethane, a component of natural gas, balance the equation, then find  $\Delta H$ .

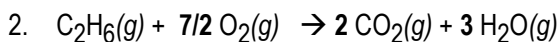


Formula	$\Delta H^\circ_f$ in kJ/mol
$\text{C}_2\text{H}_6(g)$	- 84.7
$\text{CO}_2(g)$	- 393.5
$\text{H}_2\text{O}(g)$	- 241.8

**ANSWERS****Practice**

$$\Delta H_{\text{reaction}} = (\text{sum of } \Delta H^\circ_f \text{ values of products}) - (\text{sum of } \Delta H^\circ_f \text{ values of reactants})$$

$$= (-110.5 + 0) - (0 + -241.8) = 241.8 - 110.5 = +131.3 \text{ kJ}$$



$$\Delta H_{\text{reaction}} = \sum c \Delta H^\circ_f \text{ of products} - \sum c \Delta H^\circ_f \text{ of reactants}$$

$$= [2(-393.5 \text{ kJ}) + 3(-241.8)] - [1(-84.7 + 7/2(0))] = -1427.7 \text{ kJ}$$

\* \* \* \* \*

**SUMMARY: Heats of Reaction ( $\Delta H$ )**

A summary for initial thermodynamic and PV work equations is given at the end of Lesson 22A. The summary below covers calculations that involve  $\Delta H$ .

If you have not already done so, you may want to organize this summary into charts, numbered lists, and flashcards that help with long-term memory.

1. Energy ( $E$ ), heat ( $q$ ), and work ( $w$ ) in the SI system are measured in joules (J).
2. If the external pressure on a system is held constant and work is limited to "PV work", then the heat flow in or out of a system of particles equals its change in enthalpy.

$$\Delta H = q \quad \text{at constant P and PV work.}$$

3. In equations that include energy terms, the coefficients are in *moles*.
4. In energy equations, the *phase* of each particle must be shown: (s), (l), (g), or (aq).
5. In **exothermic** reactions, energy is *released* into the environment, and the energy term is shown
  - EITHER with a *positive* sign on the *products* side;
  - OR (preferred) with a *negative*  $\Delta H$  value written *after* the equation.
6. In **endothermic** reactions, energy must be *added*, and the energy term is shown
  - EITHER with a *positive* sign on the *reactants* side of the equation,
  - OR with a *positive*  $\Delta H$  written *after* the reaction.
7. Reactions involving energy or heat can be *reversed* (the equation can be written backwards). If a  $\Delta H$  is attached to the equation, *change the sign* of  $\Delta H$ .
8. All reaction coefficients and energy terms can be multiplied or divided by a number. If  $\Delta H$  notation is used, do the same to the value of  $\Delta H$ .

9. Equations with energy terms can be added to produce a new equation.
- Like particles on the same side in different equations can add, and on opposite sides can cancel.
  - When equations are added,  $\Delta H$  values add according to their signs.
10. **Hess's Law.** When  $\Delta H$  for an equation is not known, it can be found by adding together equations for which  $\Delta H$  is known.
- Write the reaction equation WANTED, then a dotted line below it.
  - Write the first coefficient and substance formula below the dotted line.
  - Find an equation with a known  $\Delta H$  that includes that first formula. Adjust the direction and coefficients of the known equation to put the dropped particle and its coefficient on the side where it is WANTED. Modify and include a  $\Delta H$ .
  - Arrange other equations and their known  $\Delta H$  to cancel particles not wanted, and add to result in the equation WANTED.
11. In a *formation* equation, the reactants are all *elements* in their *standard state* at 25°C and 1 atm pressure, and the product is *one mole* of a compound or other particle that is not an element.
12. The *heat* of formation ( $\Delta H^\circ_f$ ) of a compound is the amount of heat required or released when one mole of the compound is formed from its elements in their standard state.
13. All elements in their standard state are assigned a heat of formation of *zero* kJ/mole.
14. The standard enthalpy value for a compound ( $\Delta H^\circ$ ) is its  $\Delta H^\circ_f$ .
15. If heats of formation are known for all of the substances in a reaction, the  $\Delta H$  of the reaction can be found by substituting  $\Delta H^\circ_f$  values into:

$$\Delta H = \Delta H_{\text{final}} - \Delta H_{\text{initial}}$$

$$\Delta H = [\text{sum of (coefficient} \times \Delta H^\circ) \text{ of products}] - [\text{sum of (coefficient} \times \Delta H^\circ) \text{ of reactants}]$$

$$\text{or } \boxed{\Delta H_{\text{reaction}} = \sum c \Delta H^\circ_f \text{ of products} - \sum c \Delta H^\circ_f \text{ of reactants}}$$

16. To find a  $\Delta H_{\text{reaction}}$ , Hess's law is slower, but it will solve using heats of formation equations, non-formation equations, or a mixture of both.

# # # # #