Unit 7
Thermodynamics I
# - The First Law of Thermodynamics

Learning Objectives

After mastering this unit you will be able to:

– Define work and heat using standard sign conventions.

– Define state functions and explain their importance.

– State the first law of thermodynamics in words and as an equation.

– Use calorimetric data to obtain values for ΔU and ΔH for chemical reactions.

– Define ΔH_f^0 and write formation reactions for compounds.

– Explain Hess's law in your own words.

– Calculate $\Delta H°$ for chemical reactions from tabulated data.
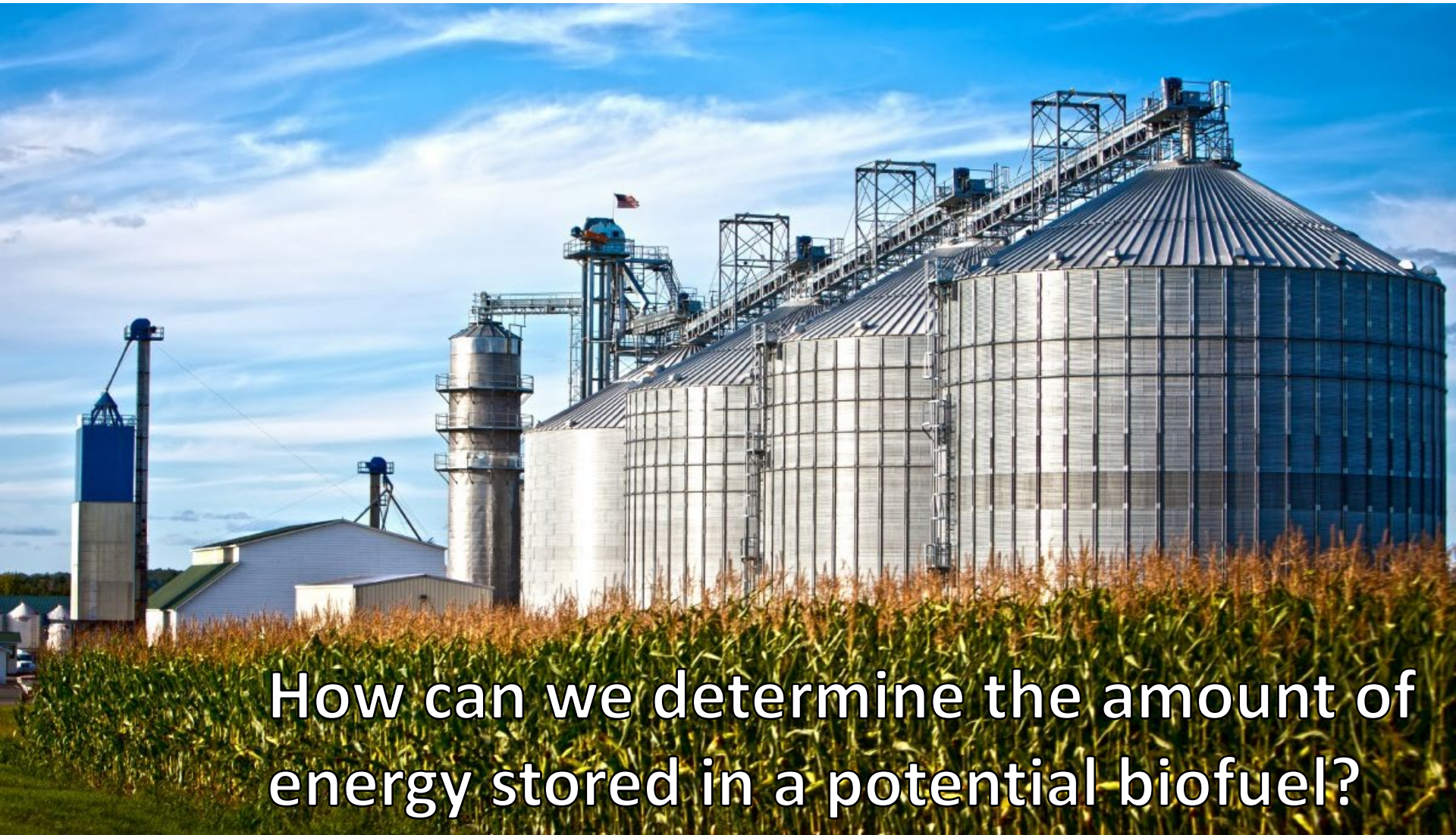
How can we determine the amount of energy stored in a potential biofuel?

Profound Quote for Today

"Classical thermodynamics... is the only physical theory of universal content concerning which I am convinced that, within the framework of applicability of its basic contents, will never be overthrown."

- Albert Einstein

Context: Thermodynamics vs. Kinetics
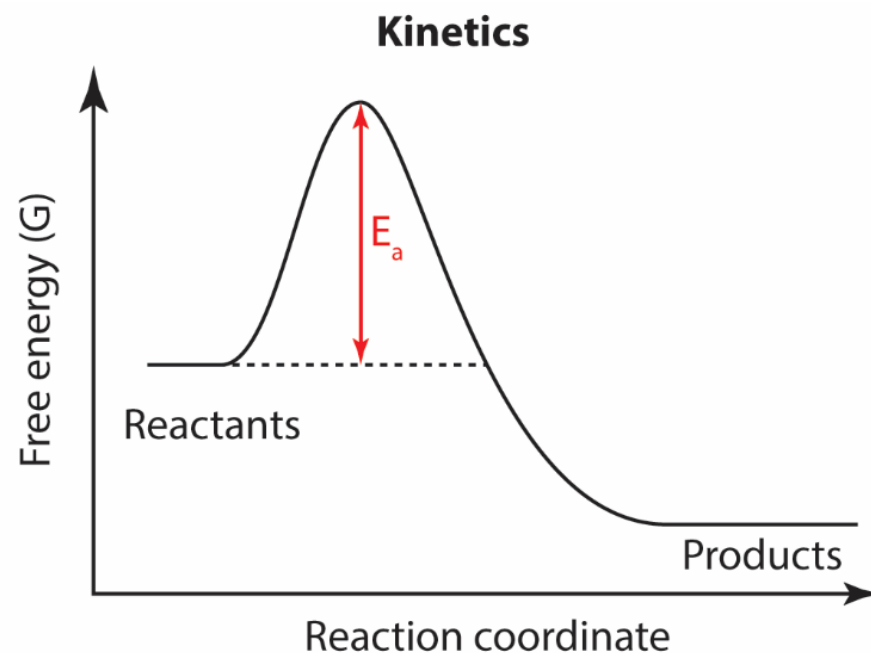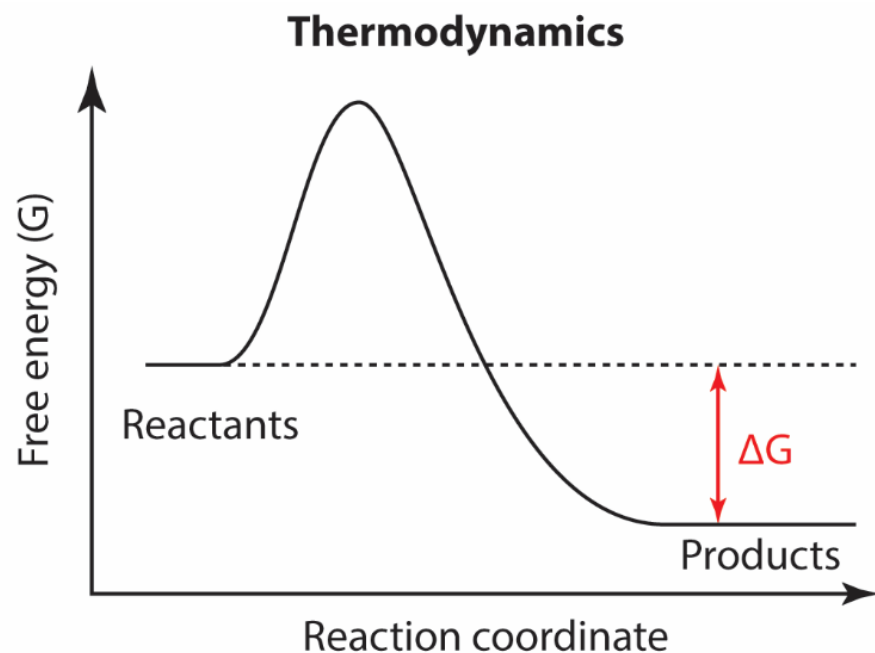
- Is it spontaneous? Are the products more stable than the reactants? (Thermodynamics)
- Is it fast? Is it so slow that the reaction isn't really happening? (Kinetics)
- A reaction that may be thermodynamically favored may still not occur due to kinetic factors.

Definitions

System: Part of the universe that interests us.

Surroundings: The rest

Universe $\equiv$ System + Surroundings

Boundary: Interface between the system and the surroundings

Properties of a system:
State functions such as mass, number, volume, temperature, pressure, *etc*.

Equation of state:
Set of state functions describing a system related by an algebraic expression, *e.g.*, $PV = nRT$
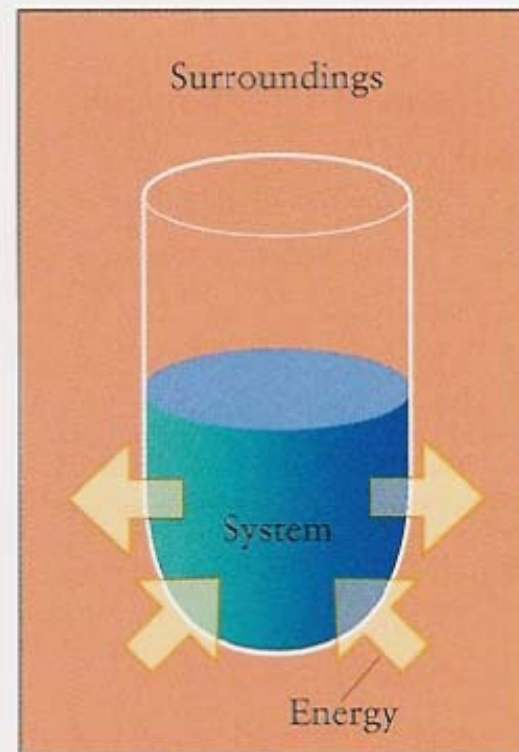

FIGURE 6.3 The system is the sample or reaction mixture in which we are interested. Outside the system are the surroundings. The system plus its surroundings is sometimes called the universe.

Open, closed, isolated system

- **Open** system: Can exchange both energy and matter with its surroundings
- **Closed** system: Can exchange energy but not matter with its surroundings
- **Isolated** system: Can exchange neither energy nor matter with its surroundings
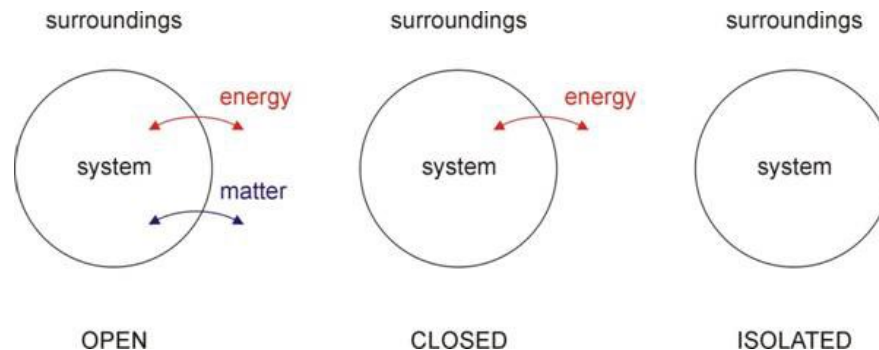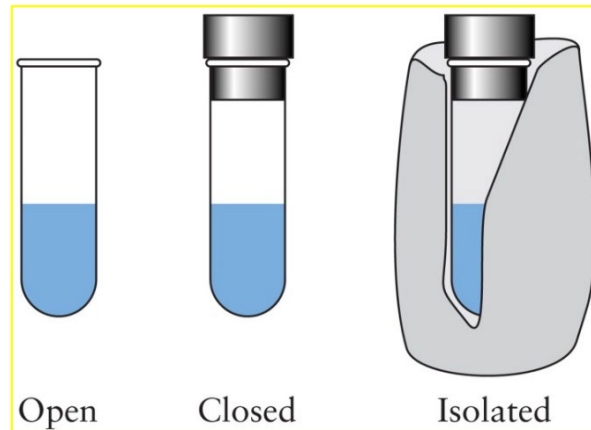
Processes under various conditions

- **Isothermal** Process: A <u>constant temperature</u> process. (Note that it may be necessary for the surroundings to act as a heat reservoir or sink in order to keep the system temperature fixed, and that in general the system boundary must permit heat flow.)
- **Isobaric** Process: A <u>constant pressure</u> process.
- **Isochoric** Process: A <u>constant volume</u> process.
- **Adiabatic** Process: A process in which <u>no heat transfer</u> (q=0).

Extensive vs. Intensive Properties

- **Extensive** properties scale with the size (quantity) of the system.
  Ex: volume, mass, number of moles, heat capacity, internal energy.

- **Intensive** properties do NOT scale with the size (quantity) of the system.
  Ex: temperature, pressure, concentration, viscosity coefficient, diffusion coefficient

- The **ratio of two extensive** thermodynamic properties is an **intensive** property.
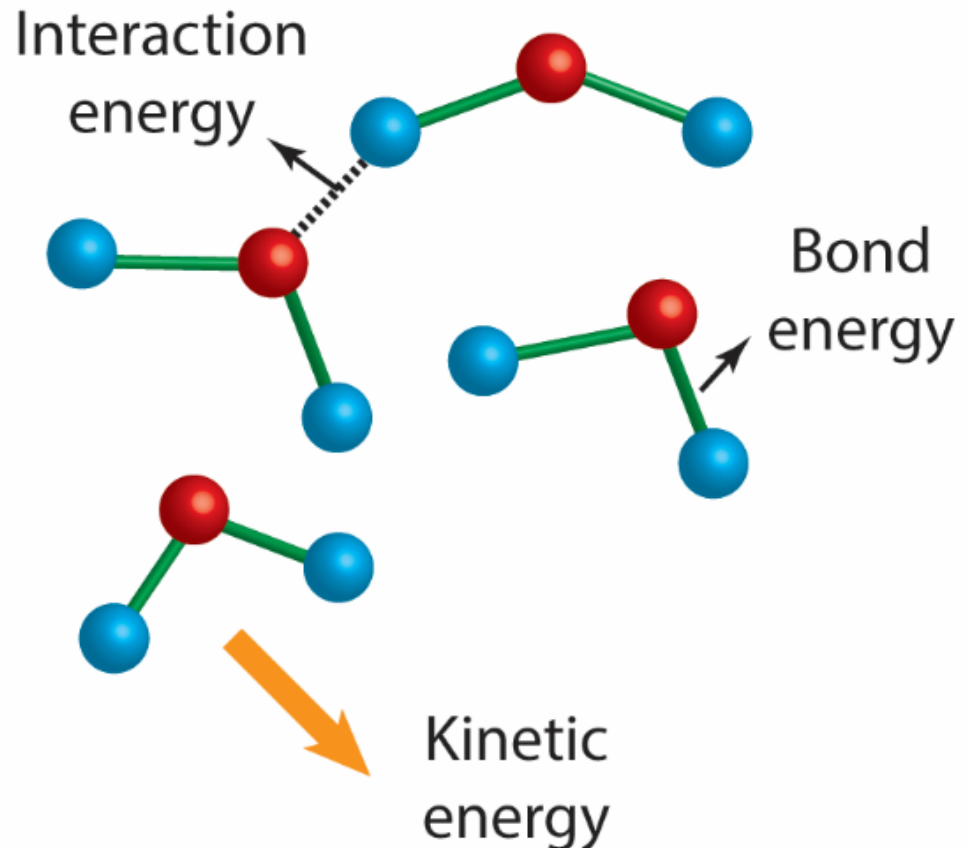 Ex: molar mass, molar volume, density, specific heat.

Internal Energy (*U*)

U is the total energy (sum of kinetic and potential energies) of all the particles in the system.

Kinetic (thermal) energy

- o Translational
- o Rotational
- o Vibrational

Chemical energy

- o Bond energies
- o Intermolecular interact

- The 1st Law is a mathematical expression for the conservation of energy.

$$\Delta U = q + w$$

ΔU = Change in Internal Energy
q = heat transfer
w = work

- Infinitesimal form: $dU = dq + dw$

- When heat and work account for all energy exchange between the system and surroundings, this energy change must equal the change in total energy of the system.

Sign convention

$$\Delta U = U_{\text{final}} - U_{\text{initial}} = q + w$$

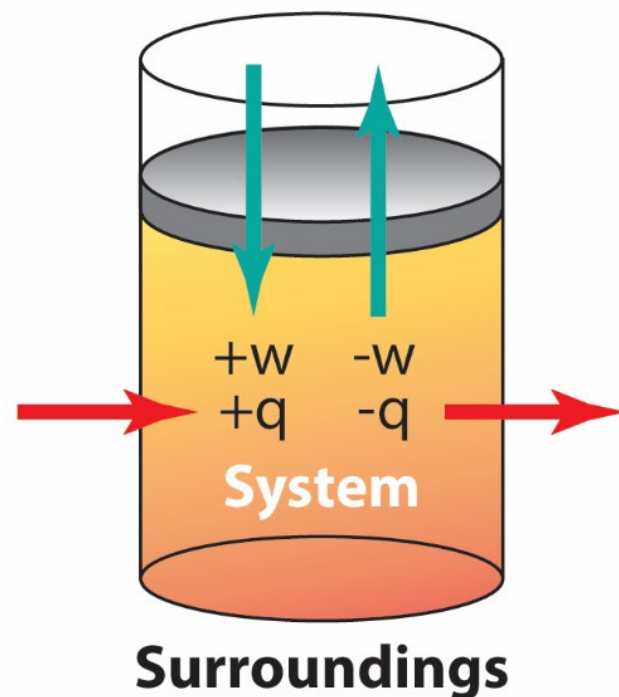ΔU = Change in Internal Energy
q = heat
w = work

|	
Energy flow in (+ signs)	Heat flow <u>into</u> system
	Work done <u>on</u> system (compression)
Energy flow out (- signs)	Heat flow <u>out</u> of system
	Work done <u>by</u> system (expansion)

Heat Transfer (q)

- **Heat transfer** is the energy transferred between the system <u>due to a temperature difference</u>.

- Example: energy transfer from a hot object to a cold object.

- **Sign convention:**
  - ❑ <u>Positive</u> (q > 0) for heat flow from surroundings to system (endothermic)
  - ❑ <u>Negative</u> (q < 0) for heat flow from system to surroundings (exothermic)

hot

cold
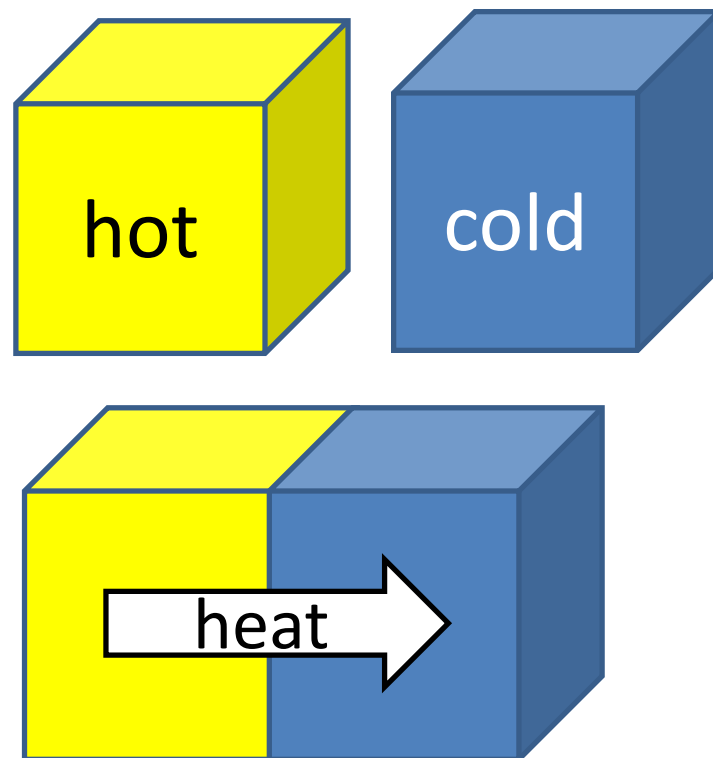
heat

Heat Capacity

- **Heat capacity (C):** the amount of heat transfer needed to raise the temperature of a given system by one degree (without phase changes occurring).

$$C \equiv \frac{dq}{dT} \approx \frac{q}{\Delta T}$$

  – Heat capacity depends on material <u>property</u> and <u>the amount</u> of the material.

- $C_P \equiv$ heat capacity under <u>constant pressure</u>.

- $C_V \equiv$ heat capacity under <u>constant volume</u>.

- **molar heat capacity** $C_{P,m} \equiv \dfrac{C_P}{n}$ (J mol^{-1} K^{-1})

- **specific heat capacity** $c_{P,s} \equiv \dfrac{C_P}{W}$ (J g^{-1} K^{-1})

Heat and Temperature Changes

Heat transfer depends on:

1. Amount of temperature change ($\Delta T \equiv T_{final} - T_{initial}$)

2. Quantity of the substance (n or m)

3. Identity of the substance ($C_{p,m}$ or c_p)

$$q = nC_{p,m}\Delta T = mc_p\Delta T$$

Specific and Molar Heat Capacities

Substance	Specific Heat, c_p (J g^{-1} K^{-1})	Molar Heat Capacity, $C_{p,m}$ (J mol^{-1} K^{-1})
Al (s)	0.900	24.3
Cu (s)	0.385	24.5
H_2O (s)	2.09	37.7
H_2O (l)	4.18	75.3
H_2O (g)	2.03	36.4

Values for H_2O are unusually high!

Example: Molar heat capacity to specific heat

Substance	Specific Heat, c_p (J g^{-1} K^{-1})	Molar Heat Capacity, $C_{p,m}$ (J mol^{-1} K^{-1})
H_2O (s)	2.09	37.7

Iron has a lower constant pressure molar heat capacity ($C_{p,m}$) than mercury. Pure blocks of each element, containing 1 mole of atoms, are heated to 300 K and allowed to transfer 50 J of energy to the surroundings, with pressure kept constant. How will the temperature change of the two blocks differ? The molecular weights of Iron and Mercury are 55.8 g mol^{-1} and 200.6 g mol^{-1}, respectively.

A) The temperature change of the iron block will be greater than that for mercury.

B) The temperature change of mercury block will be greater than that for iron.

C) Cannot be determined from the information given.

D) Both blocks will be at the same final temperature.

Clicker Question

	Iron	Mercury
$C_{p,m}$	small	large
n	1	1
T_i	300K	300K
q	-50 J	-50 J
ΔT	ΔT_{Fe}	ΔT_{Hg}

$$q = n_{Fe} \cdot C_{p,m,Fe} \cdot \Delta T_{Fe} = n_{Hg} \cdot C_{p,m,Hg} \cdot \Delta T_{Hg}$$

$$\Rightarrow C_{p,m,Fe} \cdot \Delta T_{Fe} = C_{p,m,Hg} \cdot \Delta T_{Hg}$$

small   large   large   small

Iron has a lower constant pressure molar heat capacity than mercury. Pure blocks of each element, containing 1 mole of atoms, are heated to 300 K and allowed to transfer 50 J of energy to the surroundings, with pressure kept constant. How will the temperature change of the two blocks differ? The molecular weights of Iron and Mercury are 55.8 g mol^{-1} and 200.6 g mol^{-1}, respectively.

A) The <u>temperature change</u> of the <u>iron block</u> will be <u>greater</u> than that for mercury. ✓

B) The temperature change of mercury block will be greater than that for iron.

C) Cannot be determined from the information given.

D) Both blocks will be at the same final temperature.

Work (*w*)

- Work is the energy transferred between system and surroundings when a force causes displacement.

- For example:

  ❑ Pressure-volume work (changing system volume against an external pressure)

  ❑ Gravitational work (moving mass in a gravitational field)

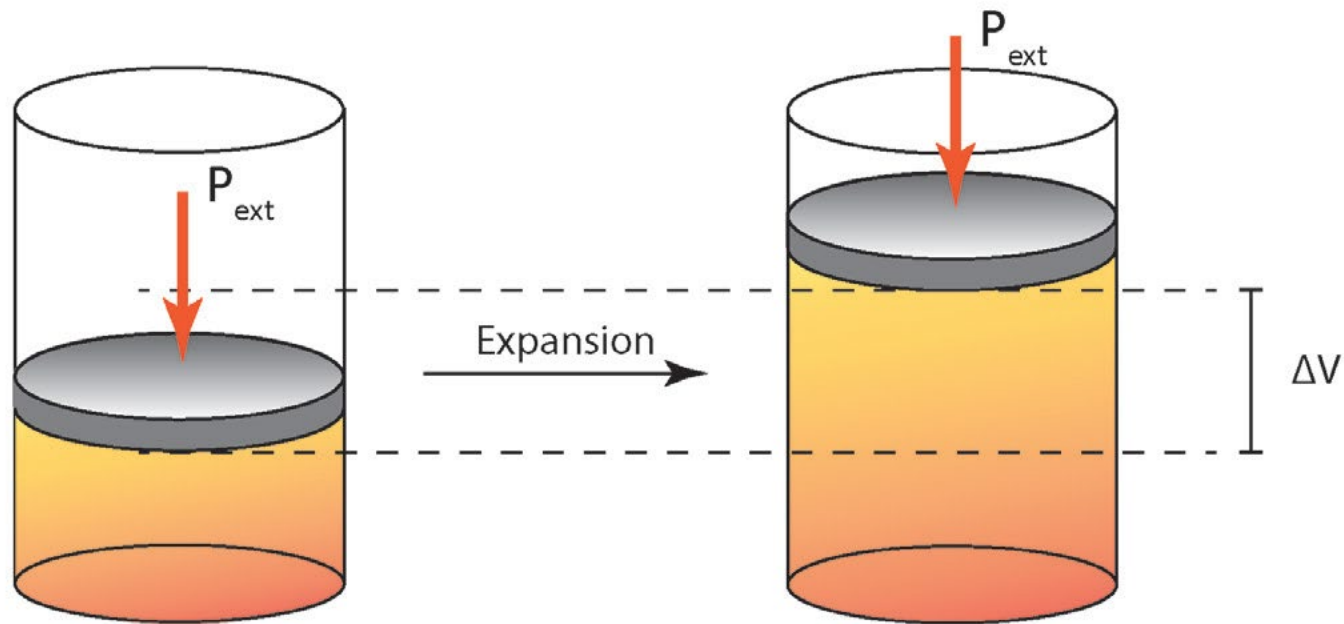 ❑ Electrical work (moving a charge in an electric field)

PV Work

Calculation of Expansion Work:

In general: $\boxed{dw = -P_{ext}\, dV}$ $\implies$ $\boxed{w = \int_{V_{initial}}^{V_{final}} (-P_{ext})\, dV}$

P_{ex} is the external pressure exerted on the gas, **NOT** the internal gas pressure (P)!

Work in a Gas Expansion Process

Sign Convention for Work

- There are two different sign conventions actively used for work, causing a difference in writing the First Law.

- In chemistry, the sign convention is:

  ❑ <u>Negative</u> for work done <u>by the system</u> on the surroundings (<u>system loses energy</u>)

  ❑ <u>Positive</u> for work done <u>by the surrounding</u> on the system (<u>system gains energy</u>)

- In engineering and physics, the opposite sign convention is used. For example, a car engine does positive work in the engineering convention and negative work in the chemistry convention.

In CHEM 154, we will use the chemistry convention.

The Physicist's point of view vs. the Chemist's point of view

Physicist:
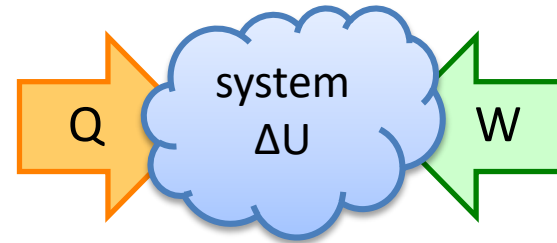What can the system do
for me?

$\Delta U = Q - W$
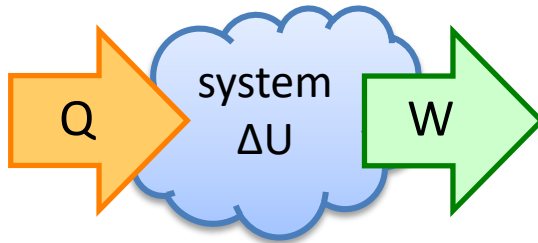
Chemist:
What is my system
doing?

$\Delta U = Q + W$

Which physical process led to work being done <u>BY the system</u>?

A) Melting of ice

B) Boiling of water

C) Both melting of ice and boiling of water

D) Neither process

Which physical process led to work being done <u>BY the system</u>?

A) Melting of ice

✓ B) Boiling of water

C) Both melting of ice and boiling of water

D) Neither process

Compression with $P_{ext} = 4$ atm from $V_{inital} = 40$ L to $V_{final} = 10$ L

$$w = - \int_{V_{initial}}^{V_{final}} P_{ext} dV = -P_{ext} \int_{V_{initial}}^{V_{final}} dV = -P_{ext}\left(V_{final} - V_{initial}\right)$$
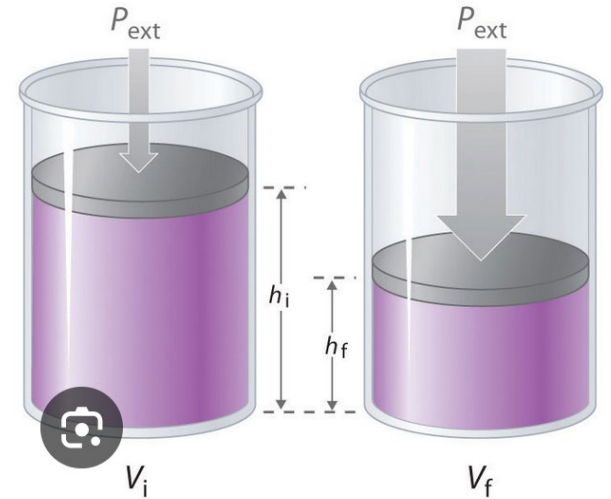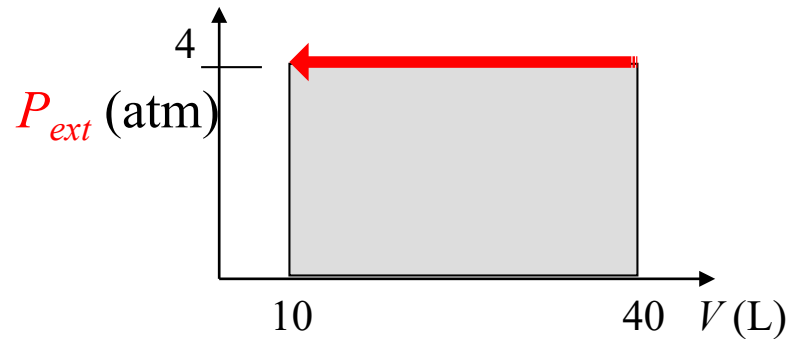
The grey area corresponds to the work exchanged.

$$w = -P_{ext}\left(V_{final} - V_{initial}\right)$$

$$= -4 \text{ atm}\left(10\text{ L} - 40\text{ L}\right) =$$

$$-4\left(101325\right)\text{Pa}\left(\frac{10}{1000} - \frac{40}{1000}\right)m^3 = 12159 J$$

Work in a Chemical Reaction at constant P_{ext}

$$w \equiv -P_{\text{ext}}\,\Delta V$$

If $\Delta V > 0$ (expansion), w < 0.

If $\Delta V < 0$ (contraction), w > 0.

– This equation is valid only at ***constant external pressure***!

– Expansion is work by system (negative)

– Contraction is work on system (positive)

– Chemists sign convention is always positive if **system** gains energy and negative if **system** loses energy (be it heat or work)

A quantity of <u>0.850 moles</u> of an <u>ideal gas</u> initially at a pressure of <u>15.0 atm and 300 K</u> is allowed to expand until its final pressure is <u>1.00 atm</u> and final temperature is <u>300 K</u>. Calculate the work done, in kJ, when the expansion is done against a constant external pressure of 1 atm . (*Hint: Use the ideal gas law.*)

Is this process reversible or irreversible (explain)
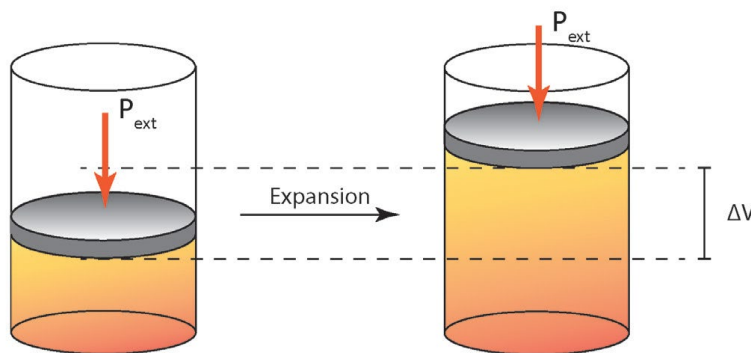
Worksheet Question #3

- Expansion with a constant external pressure $P_{ext} = P_f = 1.00 \ atm$

$$w = -\int_{V_i}^{V_f} P_{ext} dV = -P_{ext} \int_{V_i}^{V_f} dV = -P_{ext}\left(V_f - V_i\right)$$

- For an ideal gas, $V_i = \dfrac{nRT}{P_i}$ and $V_f = \dfrac{nRT}{P_f}$

Therefore, $w = -nRTP_f \left(\dfrac{1}{P_f} - \dfrac{1}{P_i}\right)$

$$= -(0.850 \ mol)(0.08206 \ L \ atm \ mol^{-1} \ K^{-1})(300 \ K)(1.00 \ atm)$$

$$\times \left(\dfrac{1}{1.00 atm} - \dfrac{1}{15.0 atm}\right)$$

$$= -19.5 \ L \ atm \left(101.325 \ \dfrac{J}{L \ atm}\right) = -1.98 \ kJ$$

- This process is irreversible.

Worksheet Question #4

Work may be done by a system or on the system during phase changes. Calculate the work done (in J) for:

a) The complete conversion of 1 mol of ice to water at 273 K and 1 atm. The molar volumes of ice and water at 273 K are 0.0196 L mol^{-1} and 0.0180 L mol^{-1}, respectively.

b) The complete conversion of 1 mol of water to steam at 373 K and 1 atm. The molar volumes of water and steam at 373 K are 0.0188 L mol^{-1} and 30.61 L mol^{-1}, respectively.

c) Compare and contrast your answers to part a and b based on chemical/physical structural changes.

Calculate the work done (in J) for:

a) The complete conversion of 1 mol of <u>ice to water</u> at <u>273 K and 1 atm</u>. The molar volumes of ice and water at 273 K are 0.0196 L mol^{-1} and 0.0180 L mol^{-1}, respectively.

$$P_{ext} = \text{constant} = 1 \text{ atm}$$
$$w = -P_{ext}\Delta V$$
$$= -(1 \text{ atm})(1 \text{ mol})(0.0180 \text{ L mol}^{-1} - 0.0196 \text{ L mol}^{-1})$$
$$= -(1 \text{ atm})(1 \text{ mol})(-0.0016 \text{ L mol}^{-1})$$
$$= 0.0016 \text{ L atm} \left(101.325 \frac{J}{\text{L atm}}\right) = 0.162 \, J$$

Worksheet Question #4

b) The complete conversion of 1 mol of <u>water to steam</u> at <u>373 K and 1 atm</u>. The molar volumes of water and steam at 373 K are 0.0188 L mol^{-1} and 30.61 L mol^{-1}, respectively.

$$P_{ext} = \text{constant} = 1 \text{ atm}$$

$$w = -P_{ext}\Delta V$$
$$= -(1\ atm)(1\ mol)(30.61\ L\ mol^{-1} - 0.0188\ L\ mol^{-1})$$
$$= -(1\ atm)(1\ mol)(30.5912\ L\ mol^{-1})$$
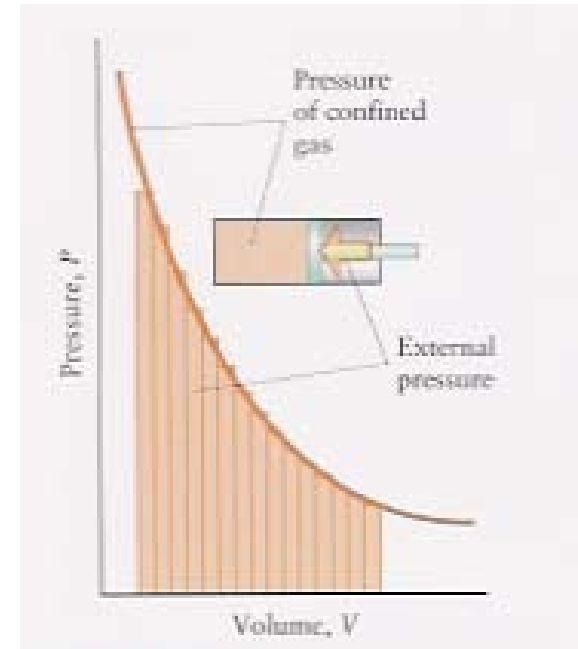$$= -30.5912\ L\ atm\left(101.325\ \frac{J}{L\ atm}\right) = -3100 \text{ J}$$

Reversible Isothermal Compression of an *Ideal Gas*:

- an Ideal Gas: $\boxed{PV = nRT \implies P_{gas} = \dfrac{nRT}{V}}$

- Reversible: $\boldsymbol{P_{ext} = P_{gas}}$

$$\boxed{w = - \int_{V_{initial}}^{V_{final}} P_{ext}\, dV} = - \int_{V_{initial}}^{V_{final}} P_{gas}\, dV$$

$$= -nRT \int_{V_{initial}}^{V_{final}} \frac{dV}{V} = -nRT \ln\left(\frac{V_{final}}{V_{initial}}\right)$$

- Since the internal energy of an *ideal gas* ($U \propto T$) does not change in an isothermal process ($\Delta U = 0$), it follows that:

$$\Delta U = q + w = 0 \implies q = -w$$

# Reversible and Irreversible Processes

Irreversible Process:

- The system is not always in equilibrium. The process cannot be reversed.
- At the end of a *cycle*, the system can be returned to its initial state, but the surroundings have not and have experienced a permanent change.

Reversible Process:

- The system is always in equilibrium. The process can be reversed by an infinitesimal change of its properties.
- At the end of a *cycle*, both the system and surroundings can be returned to their initial states without any permanent change to either.
- Sometimes, this is referred to as a quasi-static process.
- The direction of the process is not predetermined.

State functions

- A **state function is** a physical property that depends ONLY on the present state of the system and is independent of how the state was prepared and the past history of the system, *e.g.*, density, internal energy U, pressure p, volume V, temperature T, etc.
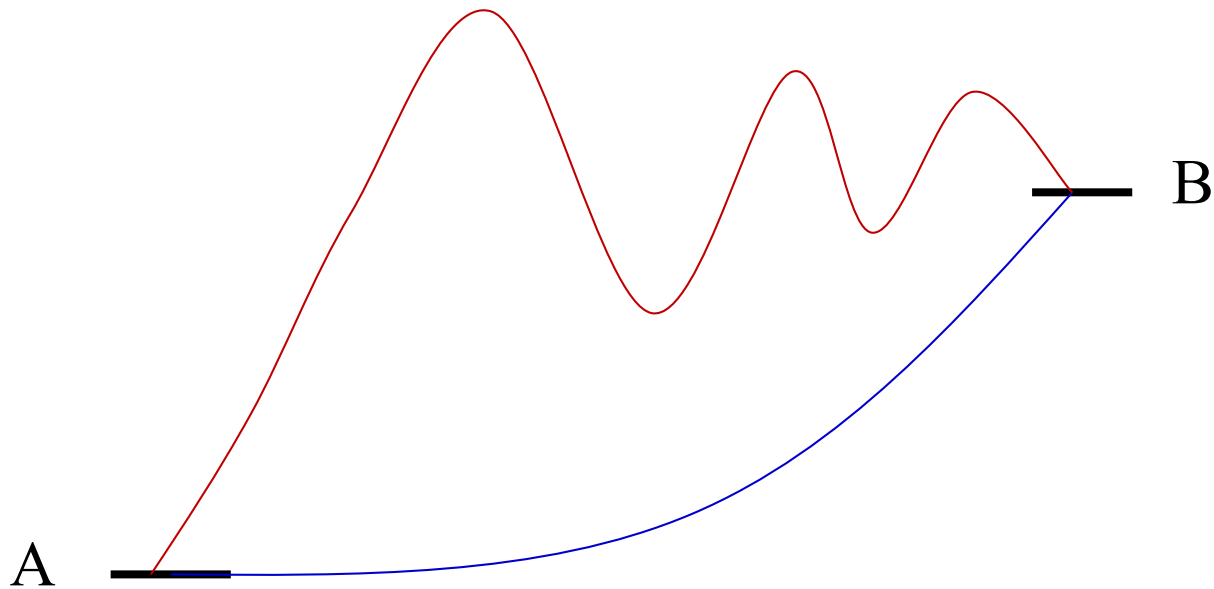
Z is a state function if $Z(B) - Z(A)$ = constant, for all paths A $\rightarrow$ B.

State functions

T - Temperature

P - Pressure

V - Volume

U – Internal Energy

H - Enthalpy

S - Entropy

G – Gibb's Energy

For a one-component **closed** system, if 2 of the values are fixed, you can determine any of the remaining variables.

In general, capitalized variables are usually state functions.

Changing Equilibrium State of System

A process or path changes the system from one equilibrium state to another.

Some Types of Process	Condition
Isothermal	Constant Temperature
Isobaric	Constant Pressure
Isochoric	Constant Volume
Adiabatic	No Heat Flow (q=0)

– Path functions depend on the process (path) .

– Heat and work are path functions – different amounts of heat flow and work can accomplish the same internal energy change.

Reversible Processes

- A process is reversible if the system remains at equilibrium throughout the **entire** process, and if a small perturbation can stop the process and reverse it.

- An irreversible process is any process that is not reversible.

- We will see in Unit 8 that the calculation of entropy is fundamentally linked with reversible processes.

The <u>combustion</u> of <u>4.54 g of Sucrose</u> in a piston <u>releases 75 kJ</u> of energy. <u>62 kJ</u> of the energy is <u>absorbed by the surroundings</u>, and the rest is used to <u>expand the volume</u> of the piston. Determine ΔU, q, and w for the system. The molar mass of sucrose is 342.30 g mol^{-1}.

A) ΔU = -75 kJ, w = -13 kJ, and q = -62 kJ

B) ΔU = -75 kJ, w = -137 kJ, and q = +62 kJ

C) ΔU = +75 kJ, w = +137 kJ, and q = -62 kJ

D) ΔU = +75 kJ, w = +13 kJ, and q = +62 kJ

E) None of the above

Clicker Question

The <u>combustion</u> of <u>4.54 g of Sucrose</u> in a piston <u>releases 75 kJ</u> of energy. <u>62 kJ</u> of the energy is <u>absorbed by the surroundings</u>, and the rest is used to <u>expand the volume</u> of the piston. Determine ΔU, q, and w for the system. The molar mass of sucrose is 342.30 g mol^{-1}.

✓ A) ΔU = -75 kJ, w = -13 kJ, and q = -62 kJ

B) ΔU = -75 kJ, w = -137 kJ, and q = +62 kJ

C) ΔU = +75 kJ, w = +137 kJ, and q = -62 kJ

D) ΔU = +75 kJ, w = +13 kJ, and q = +62 kJ

E) None of the above

ΔU = -75 kJ

q = -62 kJ

w = ΔU −q = -75-(-62) = -13 kJ

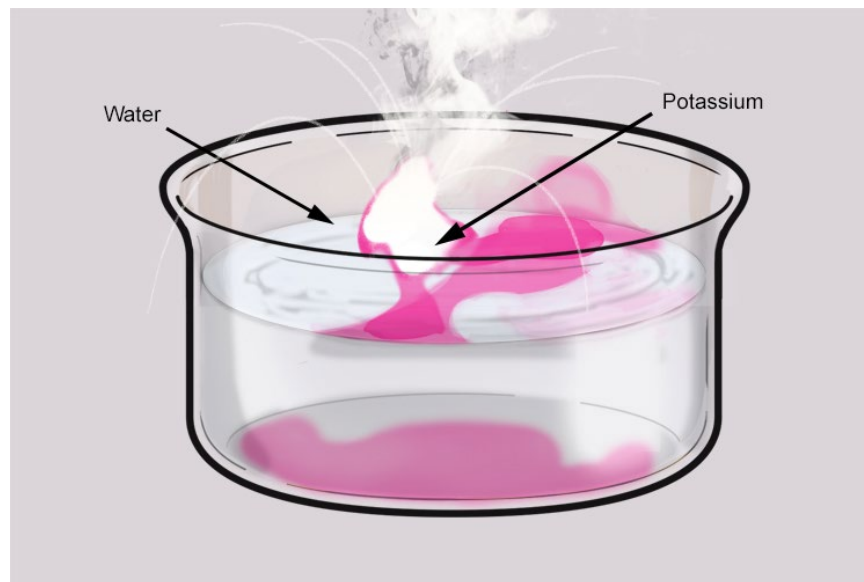A piece of potassium metal is added to water in a beaker. The reaction that takes place is:

$$2\ K(s) + 2\ H_2O(l) \rightarrow 2\ KOH(aq) + H_2(g)$$

A piece of <u>potassium metal is added to water</u> in a beaker. The reaction that takes place is:

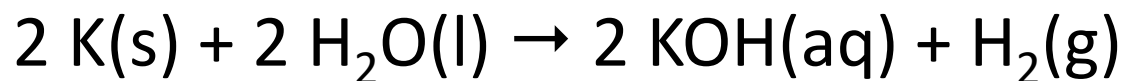$$2 \text{ K(s)} + 2 \text{ H}_2\text{O(l)} \rightarrow 2 \text{ KOH(aq)} + \text{H}_2\text{(g)}$$

Predict the signs of q and w *(Answers given in this order).*

A) + / -
B) + / +
C) - / +
D) - / -

Clicker Question

A piece of potassium metal is added to water in a beaker. The reaction that takes place is:

$$2\ K(s) + 2\ H_2O(l) \rightarrow 2\ KOH(aq) + H_2(g)$$

Predict the signs of q and w *(Answers given in this order).*

A) + / -
B) + / +
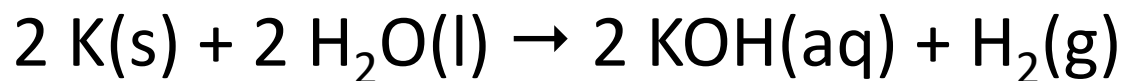C) - / +
✓ D) - / -   • Heat – exothermic
                • Work negative (producing gas molecules)

A piece of potassium metal is added to water in a beaker. The reaction that takes place is:

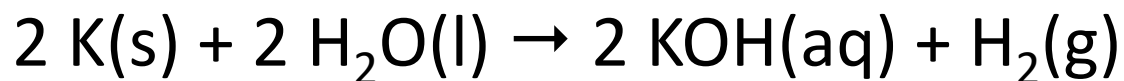$$2\ K(s) + 2\ H_2O(l) \rightarrow 2\ KOH(aq) + H_2(g)$$

What is the sign of ΔU?

A) +

B) -

C) Cannot be determined

A piece of potassium metal is added to water in a beaker. The reaction that takes place is:

$$2\ K(s) + 2\ H_2O(l) \rightarrow 2\ KOH(aq) + H_2(g)$$

What is the sign of ΔU?

A) +

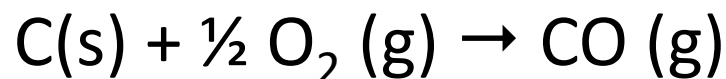✔ B) -

C) Cannot be determined

both w and q are negative

Consider the following reaction performed in a sealed and rigid container:

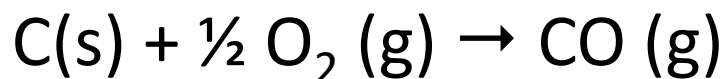$$C(s) + \tfrac{1}{2}\, O_2\,(g) \rightarrow CO\,(g)$$

The heat evolved for the reaction as written is <u>-110.42 kJ</u> at <u>298 K and 1 atm</u> constant pressure. R = 8.3145 J mol^{-1} K^{-1}.

What will happen to the pressure in the container as the reaction proceeds?

A) Increase
B) Stay the same
C) Decrease

Consider the following reaction performed in a sealed and rigid container:

$$C(s) + \tfrac{1}{2} O_2 (g) \rightarrow CO (g)$$

The heat evolved for the reaction as written is -110.42 kJ at 298 K and 1 atm constant pressure. R = 8.3145 J mol^{-1} K^{-1}.

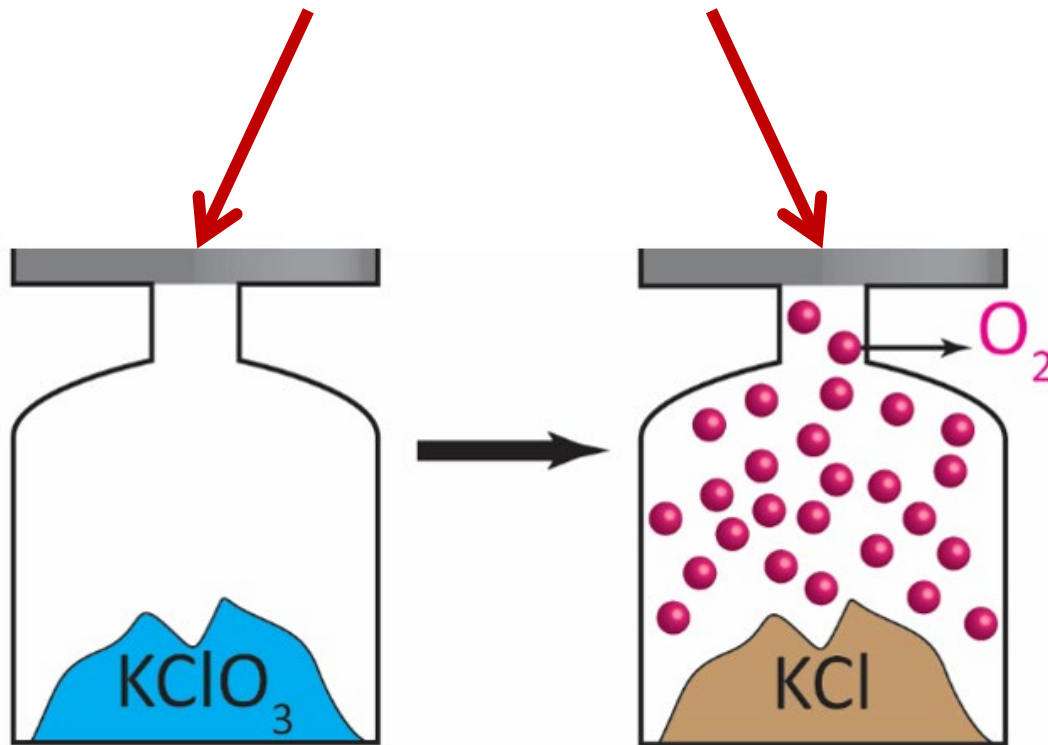What will happen to the pressure in the container as the reaction proceeds?

✓ A) Increase
B) Stay the same
C) Decrease

Gas produced over course of reaction. In a fixed container the pressure inside will increase.

Constant Volume Process

Sealed rigid containers

$$2\ KClO_3(s) \rightarrow 2\ KCl(s) + 3\ O_2(g)$$

$$\Delta U = q + w$$

How much work can the reaction perform?

$\Delta V = 0$
Since $w = w_{PV} = -P_{ext}\Delta V$,
then $w = 0$

$$\boxed{\Delta U = q = q_V}$$

Special designation for constant volume

Clicker Question

A certain chemical reaction <u>absorbs 10.1 kJ of heat</u> under **constant volume** conditions and <u>absorbs 8.4 kJ of heat</u> under **constant pressure** conditions. What is ΔU for the chemical reaction?

A) -10.1 kJ
B) -8.4 kJ
C) +1.7 kJ
D) +9.4 kJ
E) +10.1 kJ

A certain chemical reaction <u>absorbs 10.1 kJ of heat</u> under **constant volume** conditions and <u>absorbs 8.4 kJ of heat</u> under **constant pressure** conditions. What is ΔU for the chemical reaction?
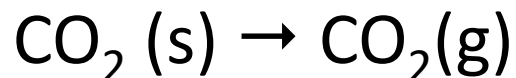
A) -10.1 kJ
B) -8.4 kJ
C) +1.7 kJ
D) +9.4 kJ
✔ E) +10.1 kJ

$$\Delta U = q_V$$

The <u>sublimation of dry ice</u> is described by the following reaction:

$$CO_2 \text{ (s)} \rightarrow CO_2\text{(g)}$$

The reaction can be done in an <u>open petri dish</u> (<u>constant pressure</u>) or in a stoppered flask (<u>constant volume</u>). Which situation will result in the greater energy transfer in the form of heat?

A) Constant pressure
B) Constant volume
C) Both are the same

The sublimation of dry ice is described by the following reaction:

$$CO_2 \ (s) \rightarrow CO_2(g)$$

The reaction can be done in an open petri dish (constant pressure) or in a stoppered flask (constant volume). Which situation will result in the greater energy transfer in the form of heat?

✓ A) Constant pressure
B) Constant volume
C) Both are the same