

The First Law of Thermodynamics: Internal Energy, Heat, and Work

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The First Law of Thermodynamics

Chemical reactions almost always involve a transfer of energy between the reaction and the surrounding area.

"Thermodynamics" is the study of these energy transfers.

"Thermo" = heat "dynamics" = change

The First Law of Thermodynamics and the Transfer of Energy

The transfer of energy between a chemical reaction system and its surroundings occurs and work or heat.

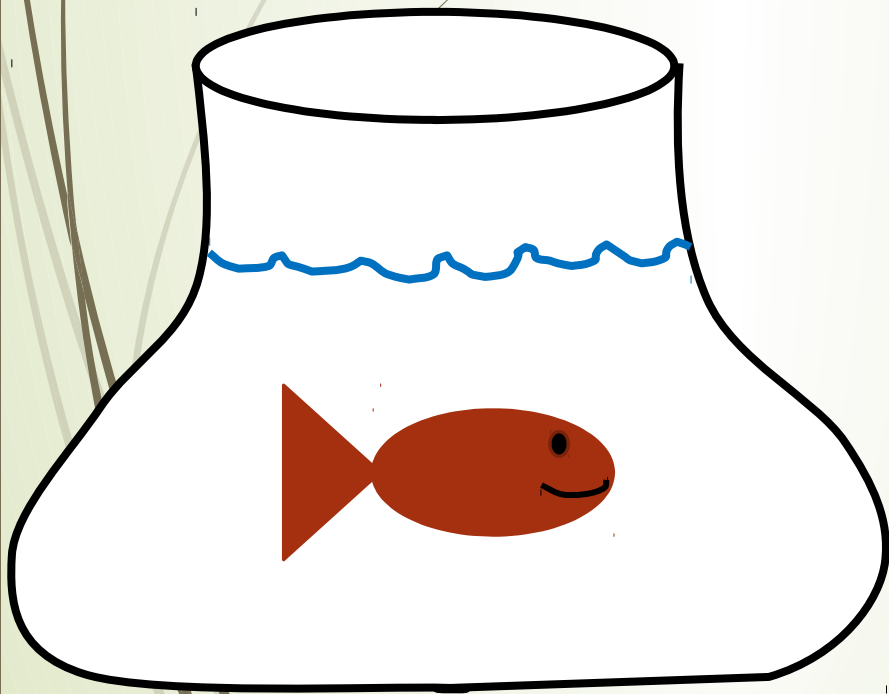
The system is defined as the chemical reaction itself (or whatever you are interested in).

The surroundings are the part of the universe with which the system can exchange energy or matter.

System versus Surroundings

Example: How could you define the system and the surroundings?

The system is defined as whatever you are interested in.



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System versus Surroundings

Example: How could you define the system and the surroundings?

The system is defined as whatever you are interested in.

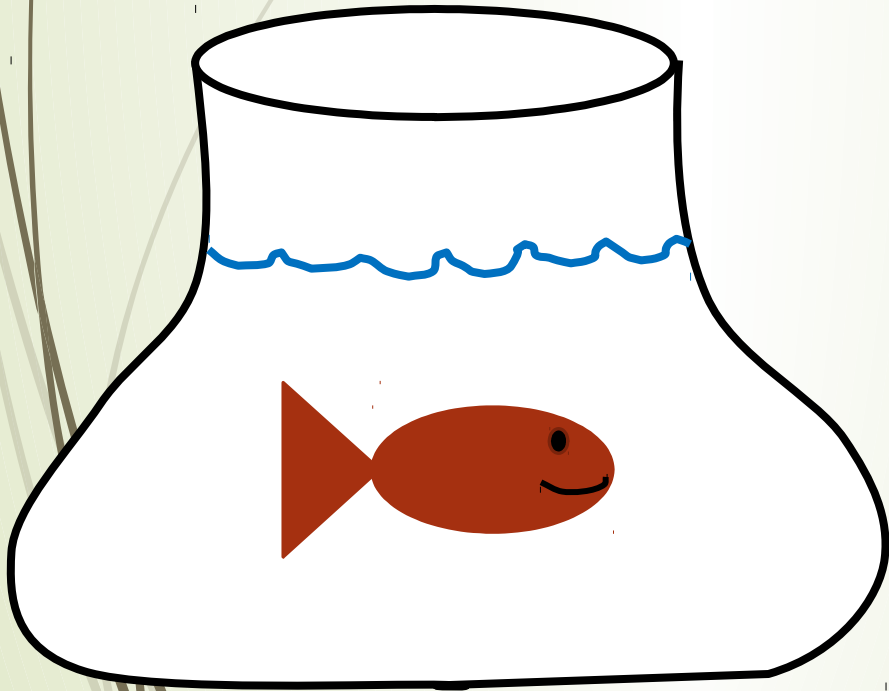
We could define the system as just the fish

the fish + water, OR

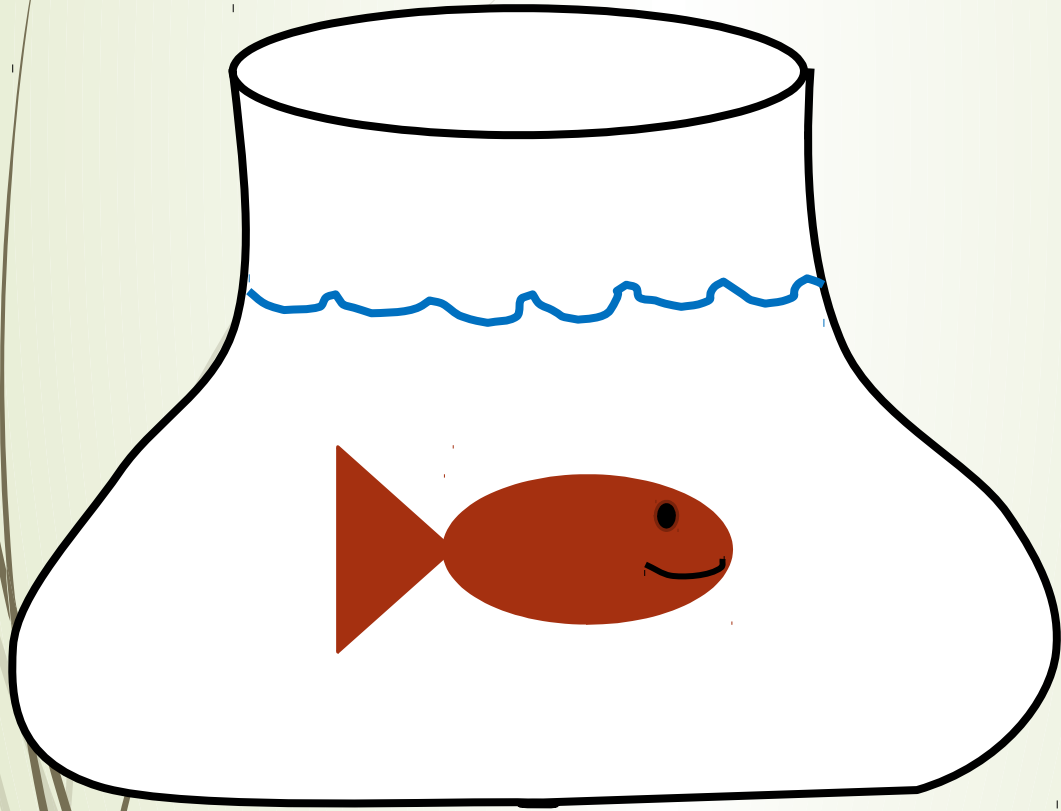
the fish + water + bowl

The surroundings are the part of the universe with which the system can exchange energy or matter.

The surroundings will depend on how we defined the system!



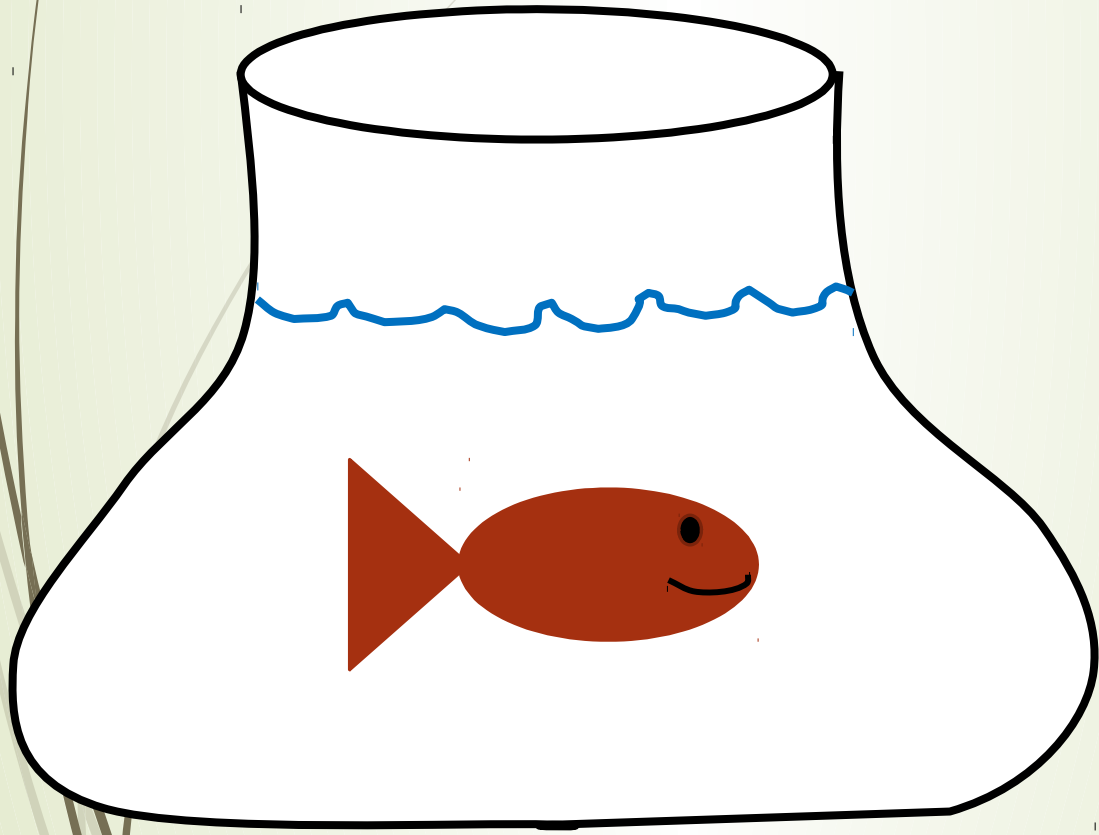
Systems can be Open or Closed



A closed system cannot exchange mass with its surroundings, but it can exchange energy!

If we put an airtight lid on the fishbowl, it would be a closed system.

Systems can be Open or Closed



An open system does exchange mass with its surroundings!

If we identify the system as the "fish only", then the fish eats, acquires O_2 , ... with the surroundings.

Back to chemical reactions...

The First Law of Thermodynamics: Work and Heat

□ The transfer of energy between a chemical reaction system and its surroundings occurs and work or heat.

$$\Delta U = q + w$$

ΔU (or ΔE) is the change in internal energy of the system

q is heat and w is work

The Internal Energy (ΔE or ΔU)

$$\Delta U = q + w$$

ΔU (or ΔE) is the difference in energy between reactants and products in a chemical reaction.

ΔU (or ΔE) is the sum of all of the kinetic and potential energies of all particles in the system.

These can be changed by work, heat, or both.

The Internal Energy (ΔU or ΔE)

$$\Delta U = q + w$$

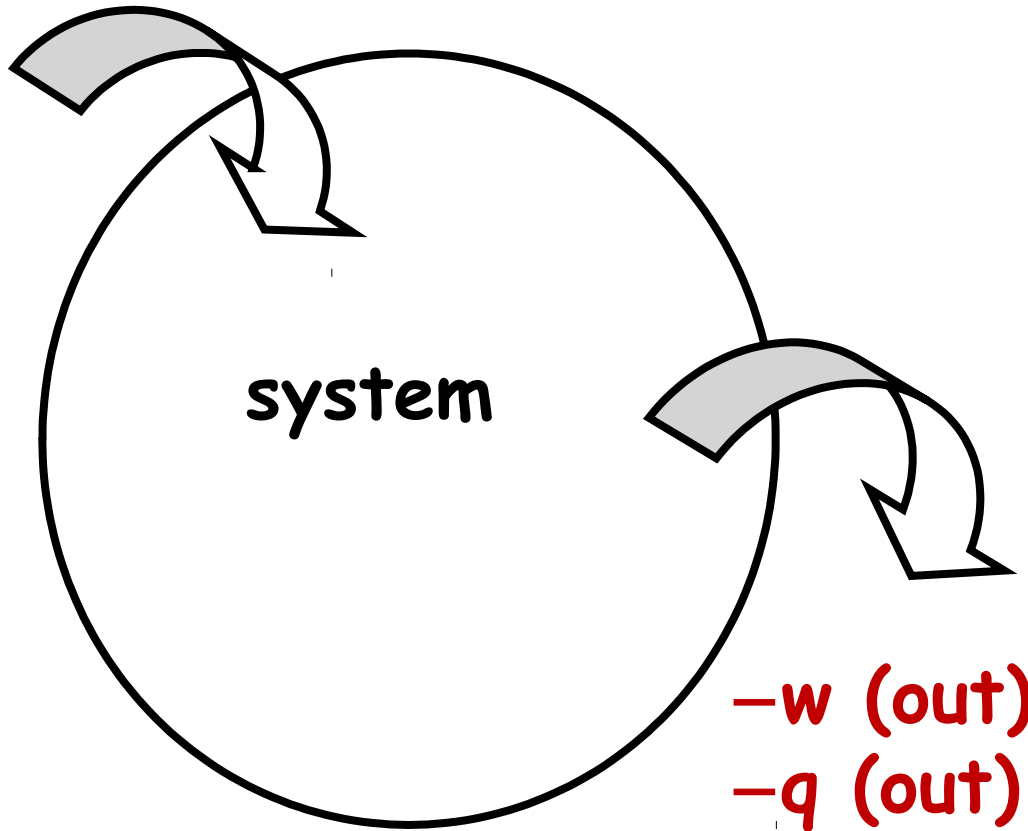
Work, w , is the mechanical transfer of energy from one thing to another

Heat, q , is the energy transferred from a hot object to a cold one upon contact.

All energy transfers can be classified as either heat or work.

Internal Energy U, Work, and Heat

+w (in)
+q (in)



surroundings

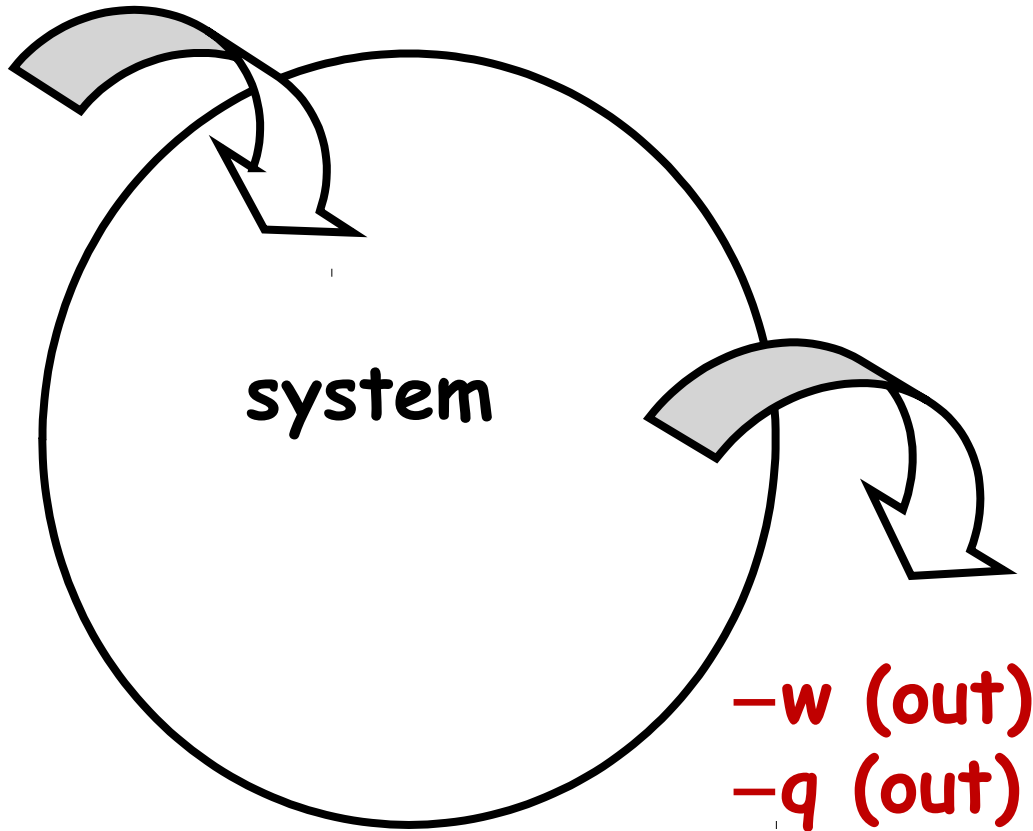
$$\Delta U = q + w$$

+w for work done on
the system by the
surroundings

-w for work done by
the system on the
surroundings

Internal Energy U, Work, and Heat

+w (in)
+q (in)



surroundings

$$\Delta U = q + w$$

+q for heat added (or absorbed) into the system **from the surroundings**

-q for heat **released by the system** to the surroundings

The Internal Energy (ΔE or ΔU)

$$\Delta U = q + w$$

A few more points:

Recall that energy is conserved.

If ΔU does not equal zero in a thermodynamic process, then energy must have been **transferred into or out of the system** in the form of **heat and/or work**.

A Brief Discussion of PV Work

□ **Work, w ,** is the mechanical transfer of energy from one thing to another.

$$\text{Work} = \text{Force} \times \text{Displacement}$$

Pressure is a force over a unit area.

$$P = \frac{\text{Force}}{\text{Area}}$$

A Brief Discussion of PV Work

One equation for work is $w = -P_{\text{ext}}\Delta V$

Where ΔV is the change in volume

$$\Delta V = V_f - V_i$$

P_{ext} is the external pressure the system expands against.

Example: Calculating PV Work

How much work is required to compress a gas from 7.3 L to 3.0 L by exerting a constant pressure of 1.8 atm?

Example: Calculating PV Work

□ How much work is required to compress a gas from 7.3 L to 3.0 L by exerting a constant pressure of 1.8 atm?

Are we doing work on the system, or is the system doing work?

Use the equation for PV work

$$w = -P_{\text{ext}}\Delta V$$

Example: Calculating PV Work

How much work is required to compress a gas from 7.3 L to 3.0 L by exerting a constant pressure of 1.8 atm?

$$w = -P_{\text{ext}}\Delta V$$

We need ΔV $V_i = 7.3 \text{ L}$ and $V_f = 3.0 \text{ L}$

$$\Delta V = V_f - V_i = 3.0 \text{ L} - 7.3 \text{ L} = -4.3 \text{ L}$$

P_{ext} is the external pressure the system expands against.

Example: Calculating PV Work

How much work is required to compress a gas from 7.3 L to 3.0 L by exerting a constant pressure of 1.8 atm?

$$w = -P_{\text{ext}}\Delta V$$

$$\Delta V = -4.3 \text{ L} \quad P_{\text{ext}} = 1.8 \text{ atm}$$

Plug in

$$w = -P_{\text{ext}}\Delta V = -(1.8 \text{ atm})(-4.3 \text{ L})$$
$$w = +7.74 \text{ L} \cdot \text{atm}$$

We need SI units... Convert "L·atm" to J

Example: Calculating PV Work

How much work is required to compress a gas from 7.3 L to 3.0 L by exerting a constant pressure of 1.8 atm?

$$w = -P_{\text{ext}}\Delta V$$

$$w = +7.74 \text{ L} \cdot \text{atm}$$

Convert "L·atm" to J $\Rightarrow 1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$

$$+7.74 \text{ L} \cdot \text{atm} \left(\frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} \right) = 784 \text{ J} \quad 2 \text{ sig figs, } 780 \text{ J}$$

(work was done on the system, +w)


Heat (q)

**Exothermic reactions (or processes)
release heat**

$-q$ for an exothermic reaction

**Endothermic reactions (or processes)
absorb heat**

$+q$ for an endothermic reaction




What You Should Be Able to Do (so far)

Describe and be able to use the First Law and the equation for ΔU (ΔE)

Define and/or identify the system and the surroundings for various scenarios.

Describe and identify whether a given system is open or closed.



What You Should Be Able to Do (so far)

Identify when the system is doing work or having work done on it.

Be able to calculate PV work for a given process.

Identify an exothermic or endothermic process using q .