



Welcome to Chemistry 154!

Chemistry for Engineering



Reminders

- **Worksheet: Unit 7 (Qs 1 – 6)**
Due Nov. 7th at 11:59pm
- **Achieve Assignment #7** (Due Nov. 13th at 11:59pm)
- **Quiz #3 (Today, Nov. 2nd)**

Instructor Office Hours

Monday and Friday 7-8pm via Zoom (All Lectures Site)

Real gases

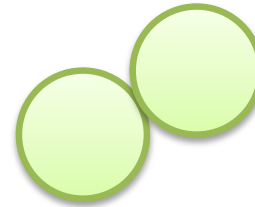
The ideal gas model assumes molecules do not interact. Real molecules **do** have interactions.

At low densities (low pressure), molecules in the gas spend little time close together so the effect of any interactions is negligible and the ideal gas equation can be quite accurate.

At high densities (high pressure), interactions start to have an effect and more accurate gas equations are needed, such as the virial equation or the van der Waals equation.

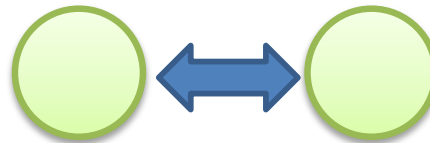
van der Waals equation

a and b are determined experimentally



[b] L/mol
Accounts for
volume of particle

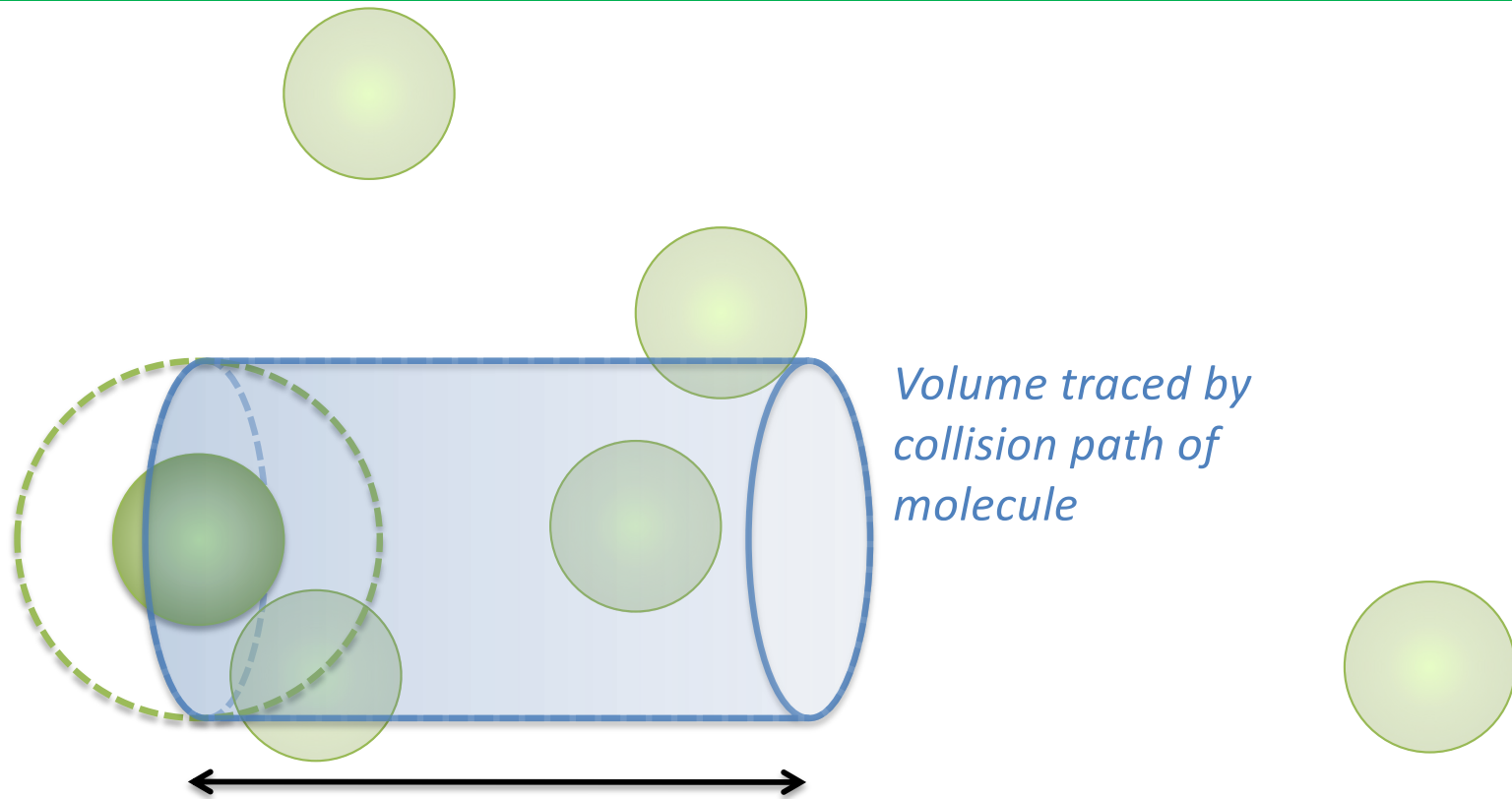
$$\left(P + a \left(\frac{n}{V} \right)^2 \right) (V - nb) = nRT$$



[a] bar L²/mol²

Also accounts for interactions among particles
(pressure is a force per area)

Real gases



Average distance travelled/unit time = \bar{v}

$$\textcircled{Z} = \underbrace{\frac{P}{PRT}}_{\downarrow} = \frac{1}{1 - pb} - \frac{\textcircled{aP}}{RT}$$

compressibility factor

accounts for volume of particle

accounts for interactions

this is a function of P now

for ideal gas: $PV = nRT$

$$\frac{PV}{nRT} = 1$$

$$\therefore P = \frac{n}{V}$$

$$\therefore Z = \frac{P}{PRT} = 1$$

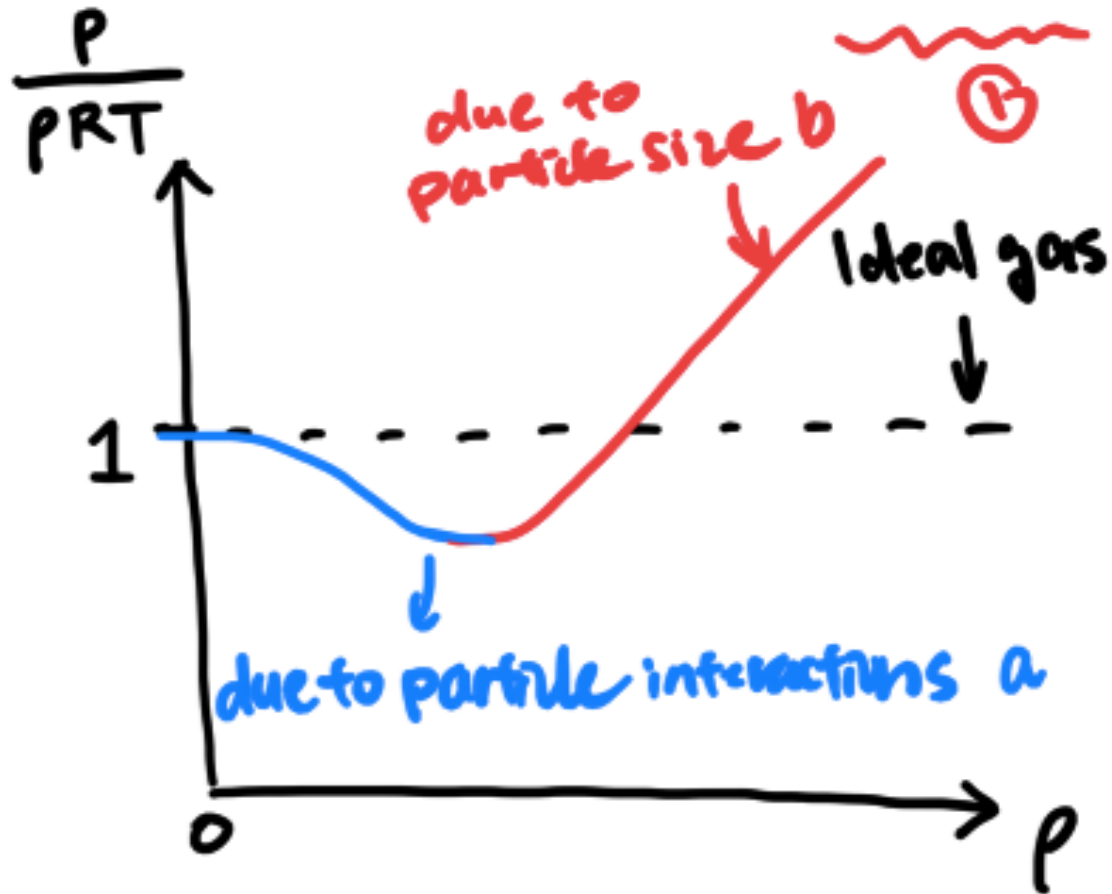
$Z=1 \rightarrow$ ideal gas

when $P=0$, $Z=1$

$$\hookrightarrow \frac{1}{1 - pb} - \frac{aP}{RT} = 1 = Z \text{ for ideal gas}$$

$$Z = \frac{P}{PRT} = \frac{1}{1 - pb} - \frac{aP}{RT}$$

both terms on the right depend on P



At the beginning, as P gets away from 0, effect from term ② dominates. That's why the curve becomes negative.

$\therefore a$ is proportional to the dip.

As P increases further,

term ① becomes bigger. this increases the curve.

$\therefore b$ is proportional to the increase.

We can measure compressibility factor z

Gases can deviate from ideal gas behaviour ($z=1$) in different ways:

- Positive deviation:

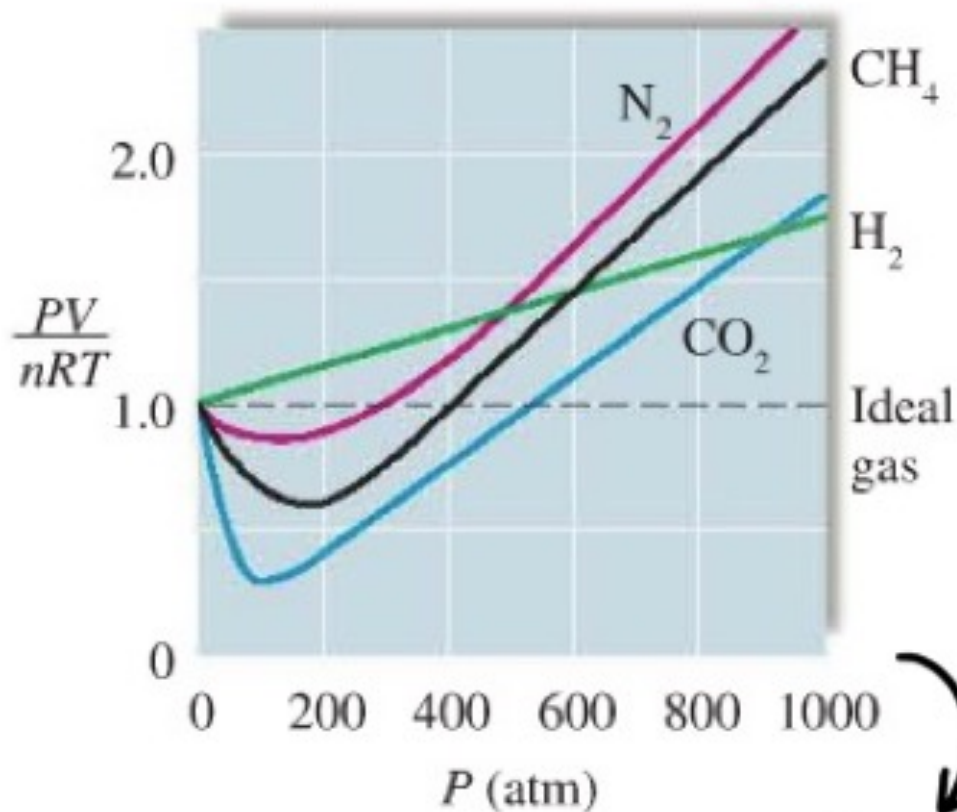
↳ from particle sizes, quantified by factor " b "

- Negative deviation:

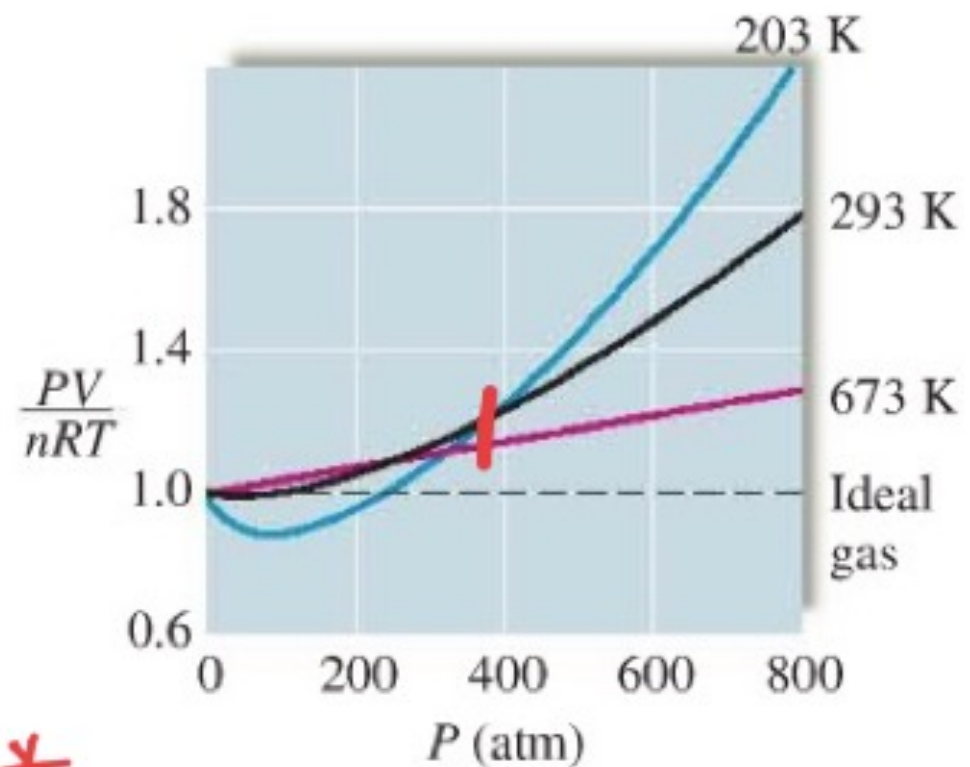
↳ from intermolecular forces, quantified by factor " a "

Compressibility factor (Z) ^{temperature and pressure dependent}

- Compressibility factor is the ratio of PV/nRT
- Compressibility factor for ideal gases = 1



Z is also not gas independent



* gases display ideal gas behaviour at low pressures and high temperatures

Unit 7
Energy and Chemistry
(aka Thermodynamics)

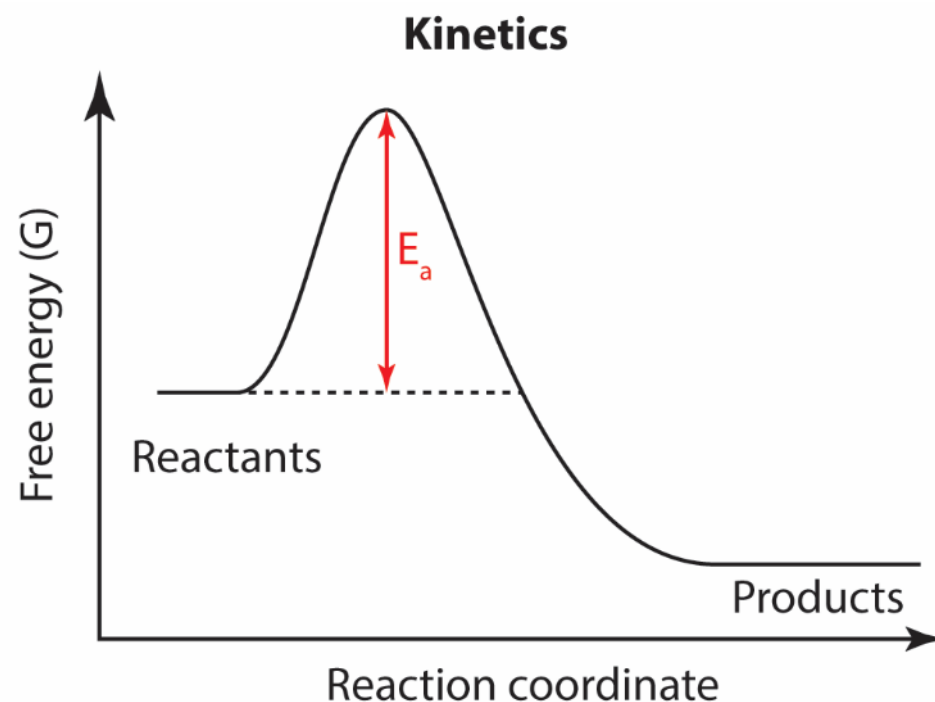
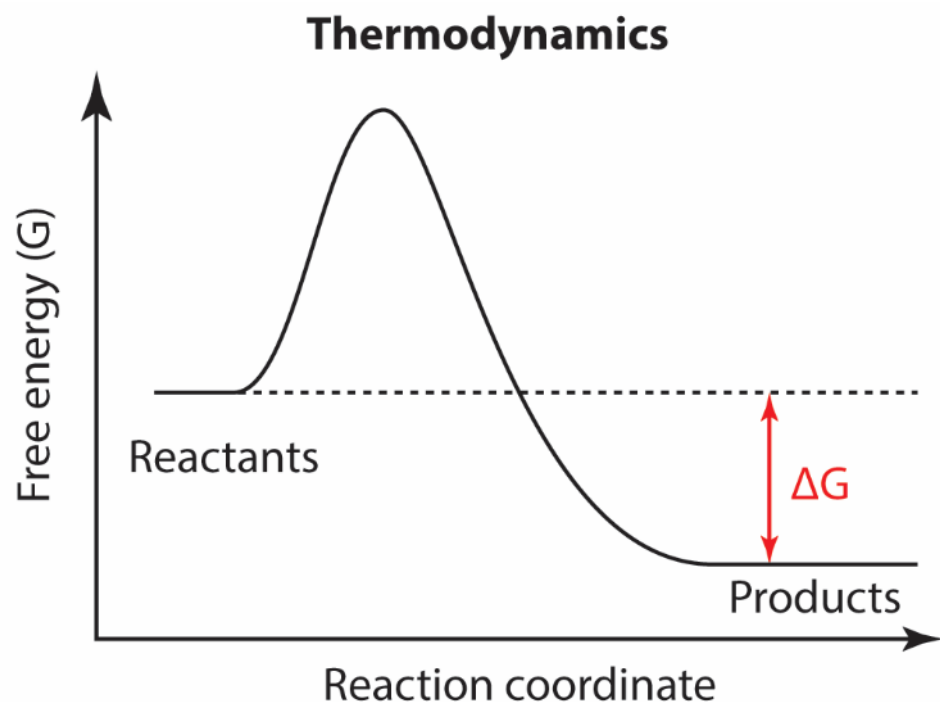
(aka Physics, meet Chemistry)

Learning Objectives

After mastering this unit you will be able to:

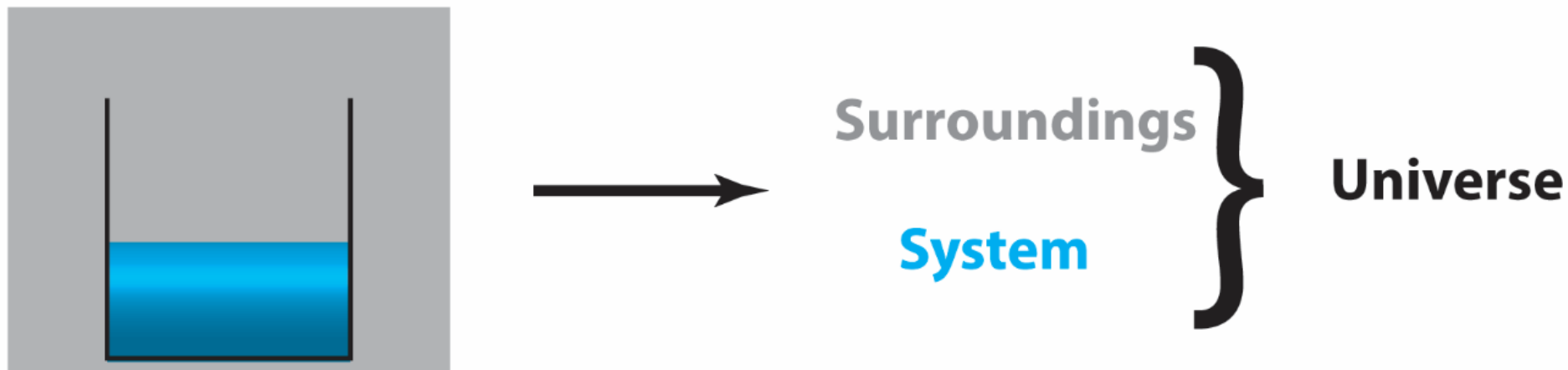
- Define work and heat using standard sign conventions.
- Define state functions and explain their importance.
- State the first law of thermodynamics in words and as an equation.
- Use calorimetric data to obtain values for ΔU and ΔH for chemical reactions.
- Define ΔH_f° and write formation reactions for compounds.
- Explain Hess's law in your own words.
- Calculate ΔH° for chemical reactions from tabulated data.

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: What we're interested in

Surroundings: Everything else (usually what we're NOT interested in)

Universe: System + Surroundings

Open, closed, isolated system

Closed System:

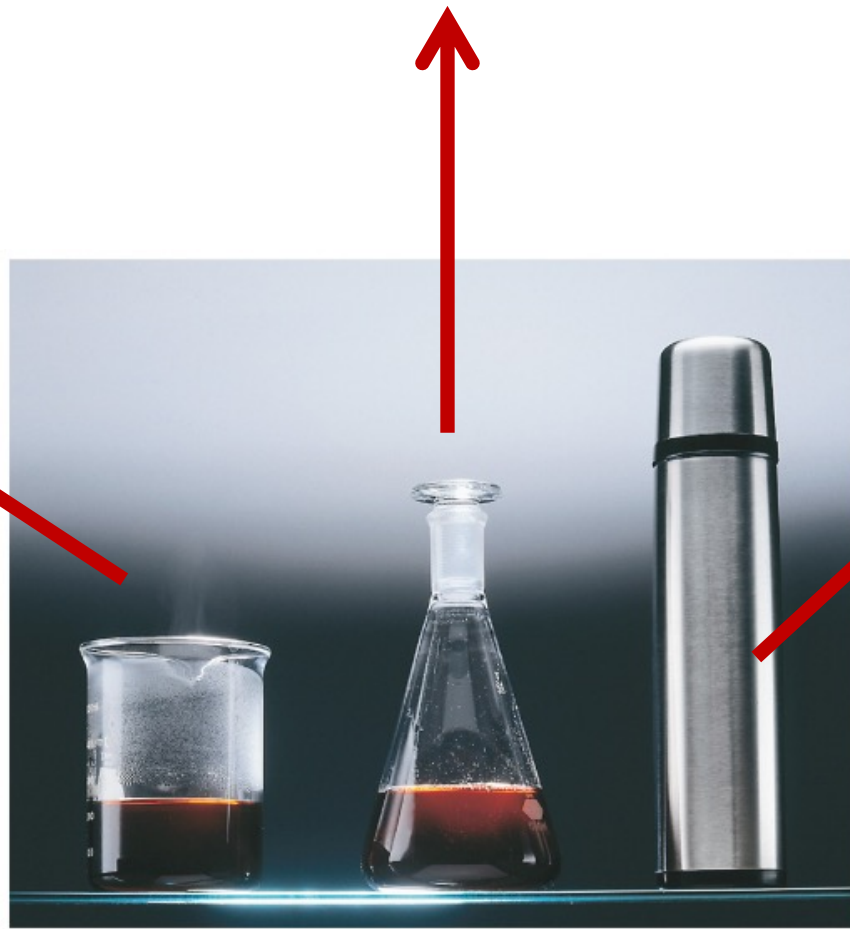
Heat exchange, no matter exchange

Open system:

Heat + matter exchange

Isolated system:

No heat exchange, no matter exchange



Extensive vs. Intensive Properties

- Extensive properties scale with the size (quantity) of the system.
- Intensive properties do NOT scale with the size (quantity) of the system.
- The ratio of two extensive thermodynamic properties is an **intensive** property. *

$$\frac{\text{mass}}{\text{volume}} = \text{density} \leftarrow \text{intensive}$$

mass. volume

Worksheet Question #1

From the following list of variables/properties, circle any answers that are an **EXTENSIVE** variables/properties.

- Density
- Number of moles
- Heat Capacity
- Total Energy
- Concentration
- Volume
- Temperature
- Pressure
- Mass
- Viscosity Coefficient
- Diffusion Coefficient

Click ANY answer on your clicker when you have finished this worksheet question.

Worksheet Question #1

From the following list of variables/properties, circle any answers that are an **EXTENSIVE** variable (property).

- Density
- Number of moles
- Heat Capacity
- Total Energy
- Concentration
- Volume
- Temperature
- Pressure
- Mass
- Viscosity Coefficient
- Diffusion Coefficient

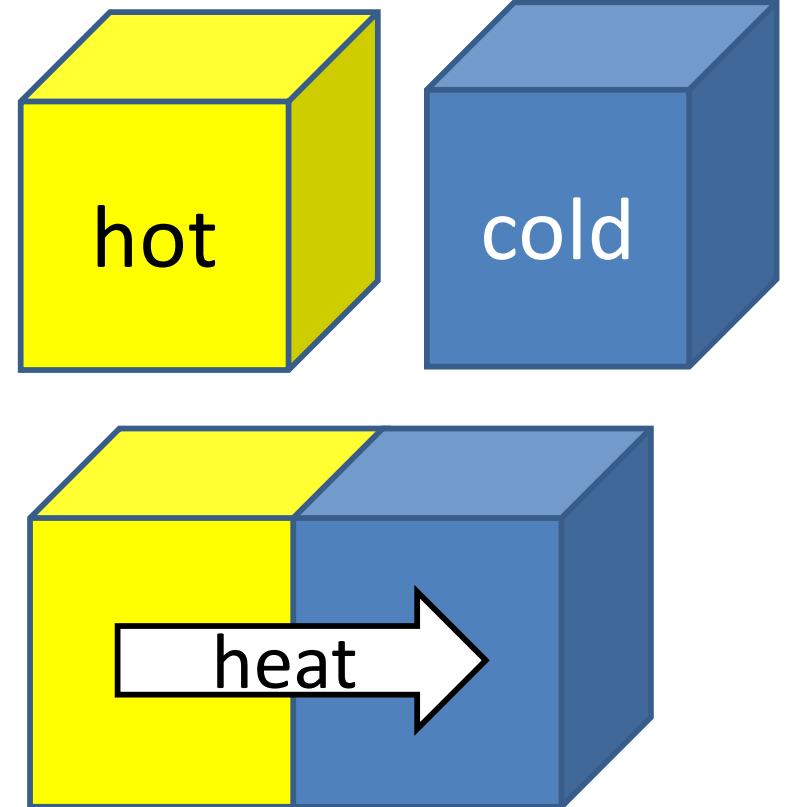
Items in red are **EXTENSIVE** variables.

Move energy
to change
the state of
a system.



Heat (q)

- Heat is the energy transferred between the system and surroundings which cannot be attributed to work.
- Example: energy transfer from a hot object to a cold object.



Sign convention:

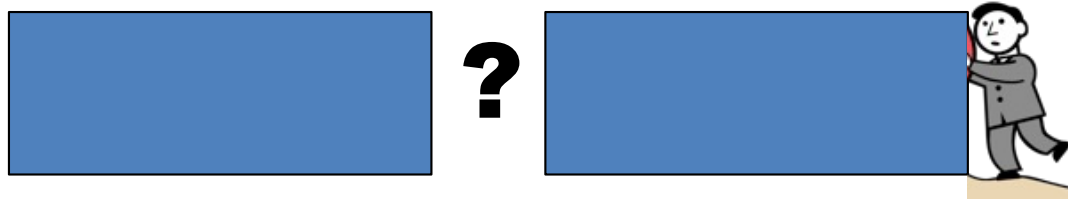
Positive for heat flow from surroundings to system (endothermic)

Negative for heat flow from system to surroundings (exothermic)

2 Room Temperature blocks

What will happen when we put together two blocks, each at room temperature:

- A. Nothing.
- B. Heat flows, but the temperature does not change.
- C. The temperature increases because there is more heat available.
- D. The temperature decreases because there is more material to spread the heat over.
- E. None of the above.



Heat Capacity and Specific Heat

Heat capacity: Quantity of heat required to change the temperature of a substance (with no phase changes occurring)

Heat capacity depends on the type of substance.

Under constant pressure conditions:

$C_{p,m}$ = Molar heat capacity ($\text{J mol}^{-1} \text{K}^{-1}$)

c_p = Specific heat capacity ($\text{J g}^{-1} \text{K}^{-1}$)

Heat and Temperature Changes

Heat capacity depends on:

1. Amount of temperature change (ΔT)
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 ₂ O (s)	2.09	37.7
H ₂ O (l)	4.18	75.3
H ₂ O (g)	2.03	36.4

Values for H₂O 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 ₂ O (s)	2.09	37.7

$$\begin{aligned}C_{p,m} &= c_p \times \text{molar mass} \\&= 2.09 \frac{\text{J}}{\text{g} \cdot \text{K}} \times 18 \frac{\text{g}}{\text{mol}} \\&= 37.7 \frac{\text{J}}{\text{mol} \cdot \text{K}}\end{aligned}$$

Clicker Question

$$-50 \text{ J} = (1 \text{ mol})(C_{p,m, \text{iron}}) \Delta T_{\text{iron}} = (1 \text{ mol})(C_{p,m, \text{mercury}}) \Delta T_{\text{mercury}}$$

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.

therefore, ΔT_{iron} is larger than $\Delta T_{\text{mercury}}$

- ☒ 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.

Worksheet Question #2

Homework

A CHEM 154 student is interested in commercializing a hot pack that takes advantage of the exothermic dissolution of CaCl_2 in water. To this end, the student collects the data...

Mass of CaCl_2 (g)	22
Mass of water (g)	95
T_i ($^{\circ}\text{C}$)	25
T_f ($^{\circ}\text{C}$)	66

- How much CaCl_2 must the student weigh to heat 30mL of water at 5° to 30°C ? ($c_p = 4.184 \text{ J g}^{-1} \text{ K}^{-1}$)
- Would switching the solvent from water to methanol ($c_p = 1.7 \text{ J g}^{-1} \text{ K}^{-1}$) make the hot pack work better than with water? What other factors must the CHEM 154 student consider?

Work (w)

Work is the energy transferred between system and surroundings attributable due a force times a distance (in a general sense). 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)

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:

- ☐ Negative for work done by the system on the surroundings (system loses energy)
- ☐ Positive for work done by the surrounding on the system (system gains energy)

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.

Clicker

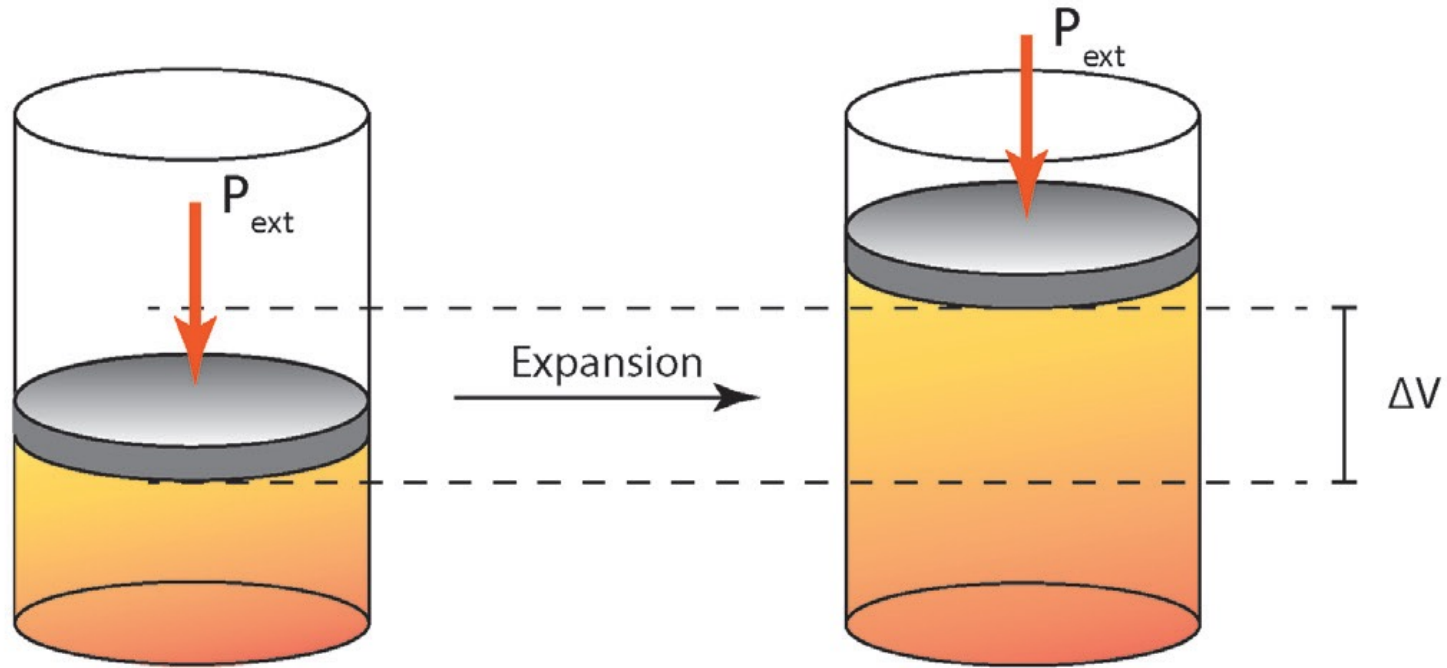
A system does work on the surroundings. What is the sign of w ?

A. $w_{sys} > 0$

B. $w_{sys} = 0$

C. $w_{sys} < 0$

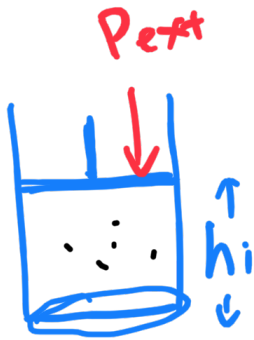
Work in a Gas Expansion Process



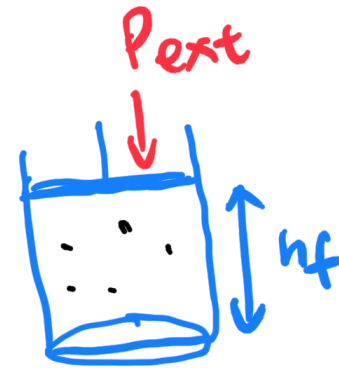
$$\text{Force} = \text{Pressure} \times \text{Area}$$

$$\text{Work} = \text{force} \times \text{distance}$$

$$W = P_{\text{ext}} \times A \times (h_f - h_i)$$



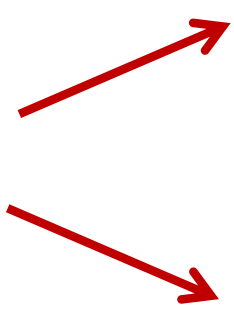
expansion
→



$$W_{\text{sys}} = -P_{\text{ext}} \Delta V$$

Work in a Chemical Reaction: PV work

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



If ΔV is positive
expansion = -ve work

If ΔV is negative
contraction = +ve work

- This equation valid at ***constant 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)

Worksheet Question #3

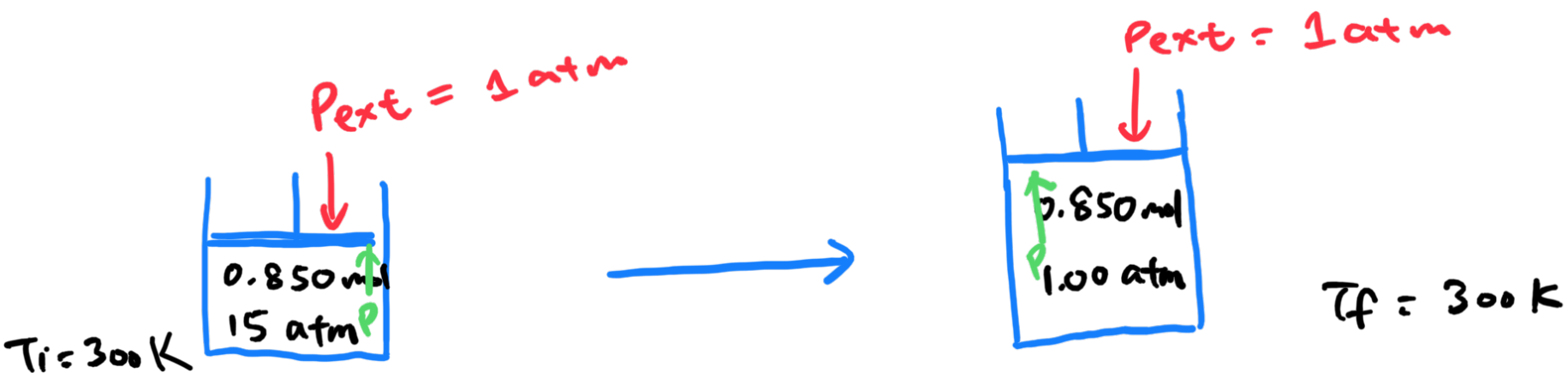
A quantity of 0.850 moles of an ideal gas initially at a pressure of 15.0 atm and 300 K is allowed to expand isothermally until its final pressure is 1.00 atm. Calculate the work done, in kJ, when the expansion is done against a constant external pressure. (*Hint: Use the ideal gas law.*)

Is this process reversible or irreversible (explain)

Unit conversion hint: 1 L atm = 101.325 Joules

Click ANY answer on your clicker when you have finished this worksheet question.

this process is irreversible, why? Homework



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

$$= -P_{\text{ext}} (V_f - V_i)$$

$$= -P_{\text{ext}} \left(\frac{nRT}{P_f} - \frac{nRT}{P_i} \right)$$

$$= -\underline{nRT} P_{\text{ext}} \left(\frac{1}{P_f} - \frac{1}{P_i} \right)$$

Ideal gas

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$W = \boxed{-1.98 \text{ kJ}}$$

Worksheet Question #4

Homework

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 $0.0196 \text{ L mol}^{-1}$ and $0.0180 \text{ L mol}^{-1}$, 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 $0.0188 \text{ L mol}^{-1}$ and 30.61 L mol^{-1} , respectively.
- c) Compare and contrast your answers to part a and b based on chemical/physical structural changes.

Internal Energy (U)

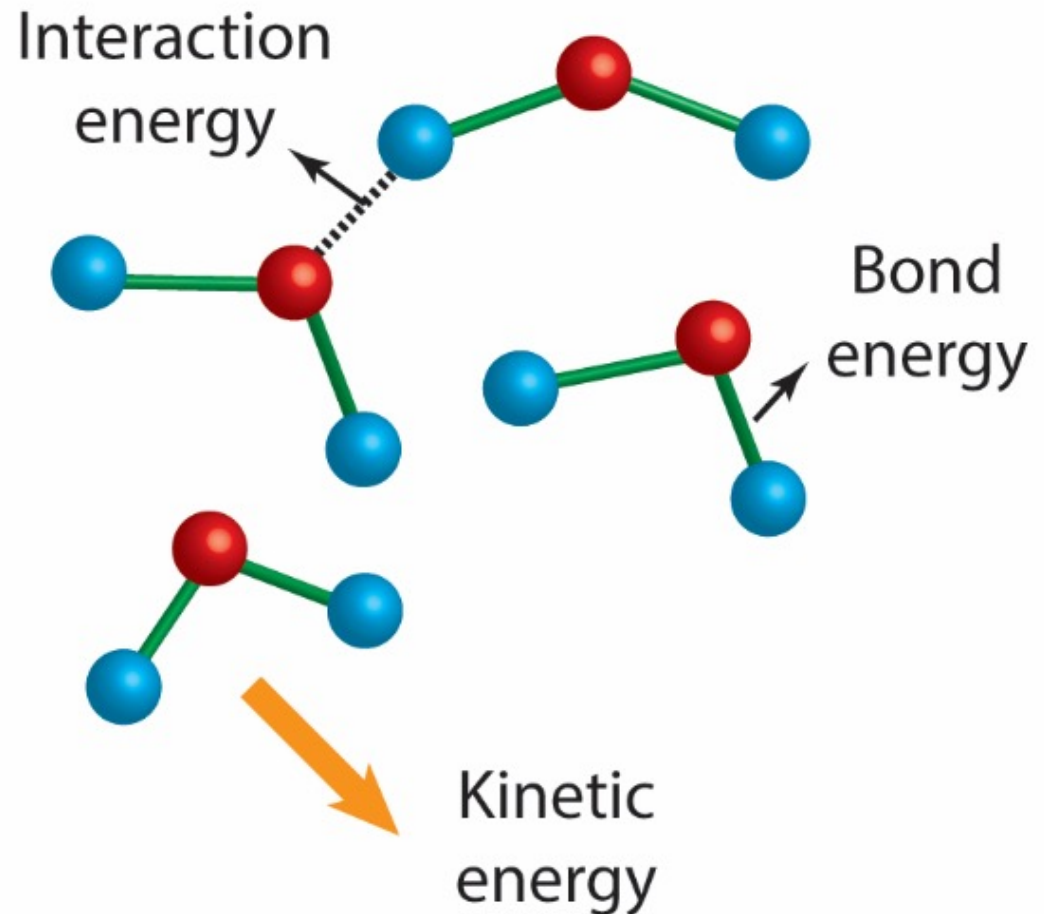
U is the total energy (sum of kinetic and potential energies) of all the particles in the system (translations or rotations of the whole system are not included in U)

Kinetic (thermal) energy

- Translational
- Rotational
- Vibrational

Chemical energy

- Bond energies
- Intermolecular interact



1st Law of Thermodynamics (for closed system)

$$\Delta U = q + w$$

ΔU = Change in Internal Energy

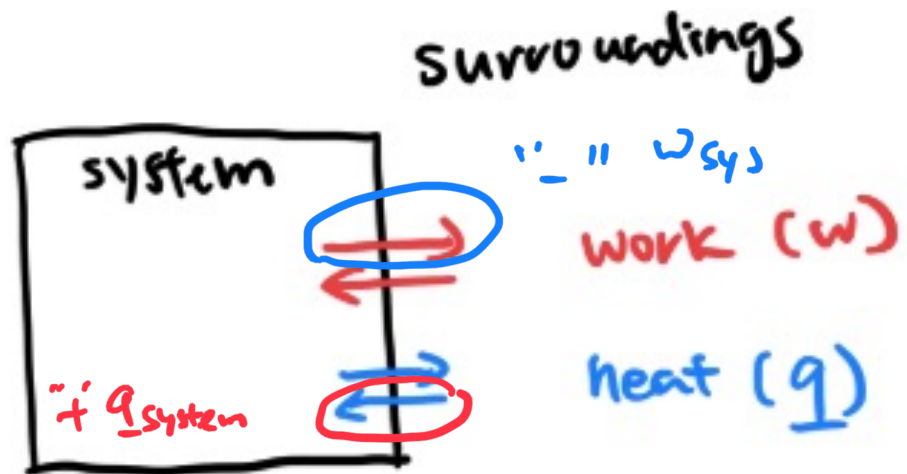
q = heat

w = work

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

Because 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.

Move energy
to change
the state of
a system.



1st Law of Thermodynamics

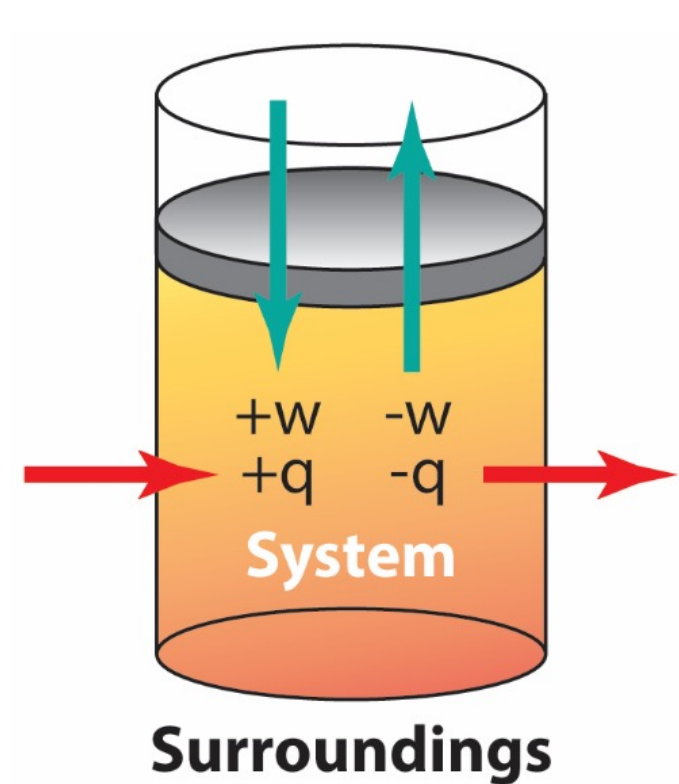
$$\Delta U = q + w$$

ΔU = Change in Internal Energy

q = heat

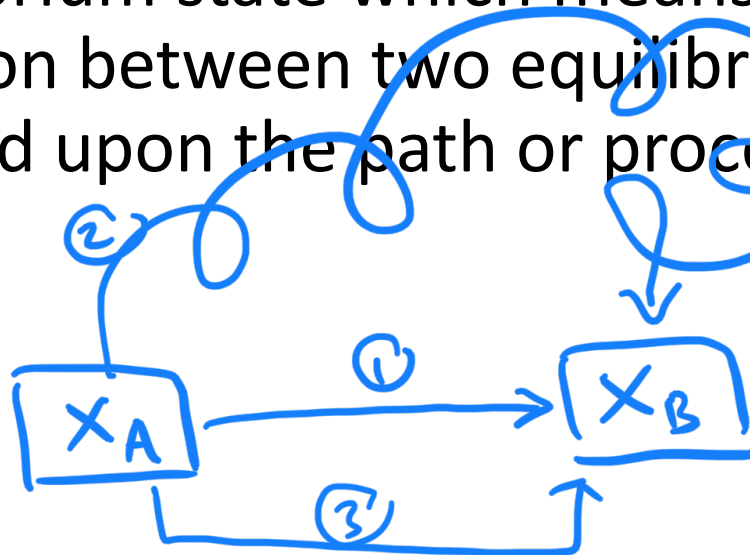
w = work

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)



State functions

- A system at equilibrium is characterized by thermodynamic variables (like a point on a phase diagram).
- This equilibrium state is the same regardless of how it was prepared (does not depend upon its past history).
- A state function has a unique value for each equilibrium state which means the difference in a state function between two equilibrium states does not depend upon the path or process used to produce them.



$$\Delta X = X_B - X_A$$

NOT path dependent.

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.