

# Internal Energy

## CHEM 361A: Introduction to Physical Chemistry

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### Lecture 3

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Learning Objective: Quantify the internal energy of a gas and discuss how energy is transferred to/from the gas to its surroundings through work and heat.

References:

- Atkins and de Paula Focus 2A-2C
- Chang §3.8 - §4.2

# Translational Kinetic Energy

The **translational kinetic energy** of a molecule of gas is

$$E_k = \frac{1}{2} m \langle v^2 \rangle$$

We saw in the previous lecture that

$$\langle v^2 \rangle = \frac{3RT}{M}$$

So

$$E_k = \frac{1}{2} m \frac{3RT}{M} = \frac{3}{2} \frac{RT}{N_A} = \frac{3}{2} k_B T$$

where Boltzmann's Constant ( $k_B = 1.380658 \times 10^{-23} \text{ J K}^{-1}$ ) and  $k_B = R/N_A$ .

# Equipartition of Energy Theorem

- According to the **equipartition of energy theorem**, the energy of a molecule is equally divided among all types of motion or degrees of freedom.
- There are  $3N$  degrees of freedom in any molecule and each contributes  $\frac{1}{2}k_B T$  to the total energy.

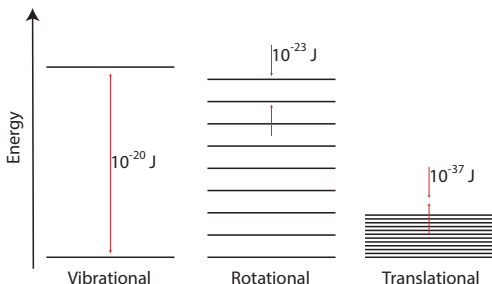
- For one mole of gas

Species	Translation	Rotation	Vibration
Atom	$\frac{3}{2}RT$	-	-
Linear Molecule	$\frac{3}{2}RT$	$RT$	$(3N-5)RT$
Nonlinear Molecule	$\frac{3}{2}RT$	$\frac{3}{2}RT$	$(3N-6)RT$

- This means that to determine the total energy of a mole of gas, just sum across a row (translational, rotational and vibrational energies).

# When Equipartition Fails

- For equipartition to hold, the system must have enough energy to evenly distribute between all the states of the different degrees of freedom



- Different degrees of freedom have different energy gaps between states.

# When Equipartition Fails - Boltzmann Distribution Law

The ratio of the population in any two energy levels is given by the **Boltzmann Distribution Law**:

$$\frac{N_2}{N_1} = e^{-\frac{\Delta E}{k_B T}}$$

Using the energy separations in the previous slide

- At  $T = 293 \text{ K}$

- Rotation

$$\frac{N_2}{N_1} = e^{-\frac{1 \times 10^{-23}}{k_B(293)}} = 0.998$$

- Vibration

$$\frac{N_2}{N_1} = e^{-\frac{1 \times 10^{-20}}{k_B(293)}} = 0.084$$

- At  $T = 3000 \text{ K}$

- Rotation

$$\frac{N_2}{N_1} = e^{-\frac{1 \times 10^{-23}}{k_B(3000)}} \approx 1$$

- Vibration

$$\frac{N_2}{N_1} = e^{-\frac{1 \times 10^{-20}}{k_B(3000)}} = 0.786$$

# Internal Energy and the First Law of Thermodynamics

**The First Law of Thermodynamics** states that the internal energy of an isolated system is constant.

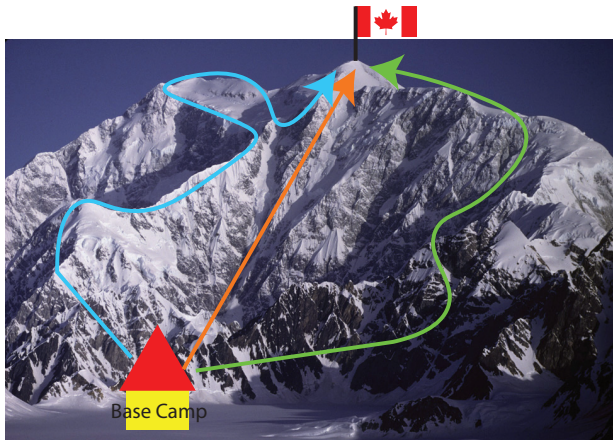
- This is closely related to the law of conservation of energy
- This law essentially states that work cannot be done without consuming fuel

The total energy of a system is quantified as the **Internal Energy**,  $U$ . We will focus on the change in internal energy:

$$\Delta U = w + q$$

# State Functions

Altitude (like internal energy) is a state function



Regardless of the path taken, the change in altitude between the base camp and the peak is the same.



# Systems and Surroundings

We need to define where reactions take place:

- **The Surroundings:** From where we make observations. It also acts as a very large reservoir adsorbing/delivering pressure, volume and heat while remaining unchanged.
- **The System:** The part of the world where we have interest. Three types of systems exist:
  - ① An **Open System** can exchange both energy and matter with the surroundings.
  - ② A **Closed System** can only exchange energy with the surroundings.
  - ③ An **Isolated System** can not exchange energy or matter with the surroundings.

The transfer of energy between the system and the surroundings is quantified as work and heat.

# Work and Heat

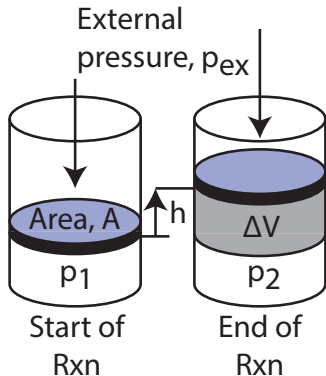
- **Work**,  $w$ , is a transfer of energy that causes or utilises uniform motion of atoms in the surroundings.
  - It is energy used to cause motion against an opposing force.
- **Heat**,  $q$ , is a transfer of energy that causes or utilises chaotic motion in the surroundings.
  - It is energy in transit as a result of a temperature difference.
  - A process is **exothermic** when the system *releases* energy.
  - A process is **endothermic** when the system *adsorbs* energy.

A note on sign conventions:  $w$  and  $q$  are positive if energy enters the system (as work and heat, respectively)

# Transfer of Energy - Expansion Work

Many reactions form gases. Expansion work is done to make room for these gases against an external pressure. The work done by the system is quantified as:

$$w = \int_{V_i}^{V_f} -p_{ex} dV$$

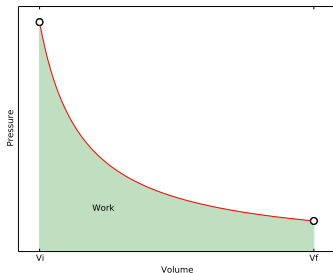


- The minimum work is done when  $p_{ex} = 0$  (free expansion).
- The maximum work is done when  $p_{ex}$  is only infinitesimally less than the pressure in the system.

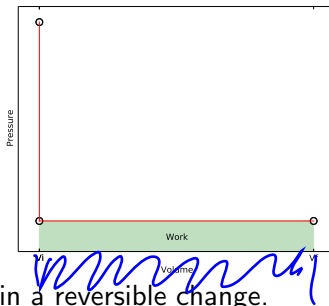
# Work of Reversible Isothermal Expansion of a Perfect Gas

A process is **reversible** when a change can be reversed by an infinitesimal change in a variable.

Reversible Isothermal Expansion



Non-reversible expansion



Maximum expansion work is achieved in a reversible change.

# Quantifying Reversible, Isothermal Expansion Work

When the system expands through an infinitesimal volume,  $dV$ , the infinitesimal work,  $dw$ , done is:

$$dw = -p_{\text{ex}}dV$$

At each stage, the external pressure is the same as the current pressure,  $p$ , of the gas. Applying the ideal gas law gives:

$$dw = -pdV = -\frac{nRT}{V}dV$$

Integrating between  $V_f$  and  $V_i$  gives:

$$w = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

# Calculating Work Problems

- 1 Determine the work done by a gas expanding from  $3 \text{ dm}^3$  to  $5 \text{ dm}^3$  against an external pressure of  $100 \text{ kPa}$ .
- 2 Calculate the work done with  $1.0 \text{ mol}$  of  $\text{Ar(g)}$  confined in a cylinder of volume  $1.0 \text{ dm}^3$  at  $25^\circ\text{C}$  expands isothermally and reversibly to  $2.0 \text{ dm}^3$

# Transfer of Energy - Heat

The heat transferred in a process is quantified as:

$$q = \int_{T_i}^{T_f} C dT$$

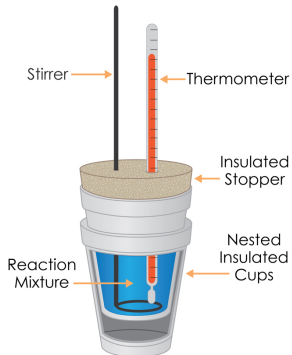
It is convenient to write the heat capacity,  $C$ , as:

- **Specific Heat Capacity**,  $C_s$ : The heat capacity divided by the mass of the sample ( $C_s = C/m$ )
- **Molar Heat Capacity**,  $C_m$ : The heat capacity divided by the mols of the sample ( $C_m = C/n$ )
- **Heat Capacity at Constant Pressure**,  $C_p$ : The heat capacity when the sample is kept at a constant pressure (fx. water in an open container)
- **Heat Capacity at Constant Volume**,  $C_V$ : The heat capacity when the sample is kept at a constant volume (fx. a gas in a rigid container)

# Calorimeters

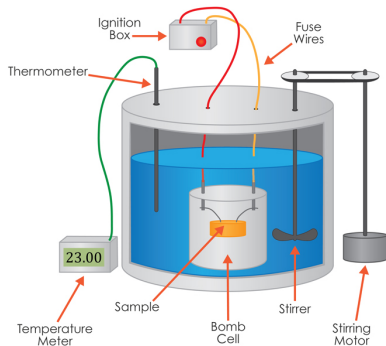
## Constant pressure calorimetry

### Coffee Cup Calorimeter



## Constant volume calorimetry

### Bomb Calorimeter



Images from: [goo.gl/5QIGWG](http://goo.gl/5QIGWG)

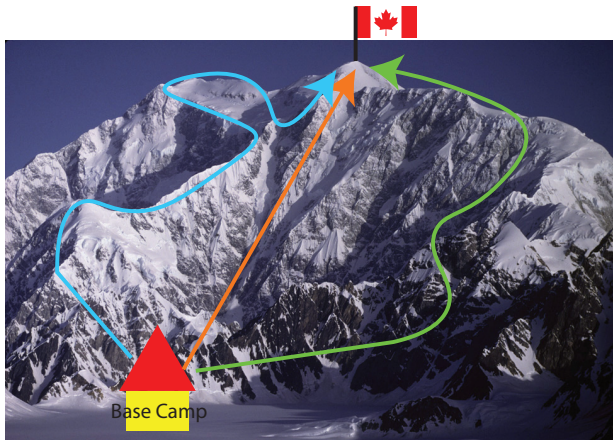


# Heat Capacity Problem

- 1 It takes 330 J of energy to raise the temperature of 24.6 g of benzene from 21.0° C to 28.7° C at constant pressure. What is the molar heat capacity of benzene at constant pressure?

# Path Functions

The distance traveled (like work and heat) is a path function



The path taken directly affects distance traveled (like heat and work) so each segment must be accounted for.

# Calculating $\Delta U$ at Constant Volume

At constant volume, no expansion work can be performed:

$$\Delta U = q_V + w = \int C_V dT - \int p_{\text{ex}} dV \xrightarrow{0}$$

This means that for constant volume processes

$$\Delta U = q_V$$

A bomb calorimeter can be used in this scenario to determine  $\Delta U$ :

$$C_V = \frac{\Delta U}{\Delta T} \implies C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

# Calculating $\Delta U$ at Constant Temperature

Because the Internal Energy,  $U$ , is determined by the temperature of the gas, if there is no change in temperature, then there is no change in internal energy. For example, for the expansion of one mole of a mono-atomic, ideal gas:

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial\left(\frac{3}{2}RT\right)}{\partial V}\right)_T = 0$$

Using this, we can relate  $q$  to the change in volume as the gas expands isothermally.

$$\Delta U = q + w = 0 \quad \rightarrow \quad q = -w$$

Therefore, if the isothermal process is reversible:

$$q = nRT \ln \frac{V_f}{V_i}$$

# Change in Internal Energy Problem

- 1 Nutritionalists are interested in the use of energy by the human body. Calorimeters have been constructed for people and can measure their energy output. Supposed a person does 622 kJ of work on an exercise bike and loses 82 kJ of energy as heat. What is  $\Delta U$  of the person.
- 2 Pretend that we are heating one mole of a monoatomic ideal gas at a constant volume from 293 K to 300 K. Determine the  $q$ ,  $w$ , and  $\Delta U$  for this process.

# Summary

- The internal energy of a substance is quantified by the equal distribution of energy over the occupied degrees of freedom
- The First law of thermodynamics states that the internal energy of an isolated system is constant
- Internal energy is a state function meaning that  $\Delta U$  is independent of the path taken
- Heat and Work, which are path functions, can be used to determine the change in internal energy. They represent transfers of energy between the system and the surroundings
- In order to maximize work the expansion/compression must be done reversibly
- For isothermal processes  $\Delta U=0$
- For constant volume processes

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V$$