LESSON 12

IUU

ISAAC NEWTON ______ 1643-1727

$\square \Delta(mv) = F\Delta t \in$

DEUTSCHE BUNDESPOST PHYSICS 168 LUIS ANCHORDOQUI

Temperature and Kinetic Theory of Gases

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Atomic Theory of Matter

On microscopic scale, arrangements of molecules in solids, liquids, and gases are quite different



Temperature and Thermometers

Temperature is a measure of how hot or cold something is

Most materials expand when heated

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Temperature and Thermometers (cont'd)



Temperature is generally measured using either Fahrenheit or Celsius scale

Freezing point of water is 0°C = 32°F boiling point is 100°C = 212°F

$$T_{C} = \frac{5}{9} (T_{F} - 32^{\circ})$$
$$T_{F} = \frac{9}{5} T_{C} + 32^{\circ}$$

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Thermal Expansion

Linear expansion occurs when an object is heated



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Volume expansion is similar except that it is relevant for liquids and gases as well as solids:

$$\Delta V = eta V_0 \, \Delta T$$
 , coefficient of volume expansion

For uniform solids 🖛 $\beta\,\approx\,3\,\alpha$

Equation of state and Boyle's law



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Gas Laws and Absolute Temperature

Volume is linearly proportional to temperature, as long as temperature is somewhat above condensation point and pressure is constant:

 $V \propto T$

Extrapolating volume becomes zero at -273.15°C

this temperature is called absolute zero



Gas Laws and Absolute Temperature (cont'd)

Concept of absolute zero allows us to define a third temperature scale absolute (or Kelvin) scale

> This scale starts with 0 K at absolute zero but otherwise is same as Celsius scale

Freezing point of water is 273.15 K and boiling point is 373.15 K

When volume is constant 🖛 pressure is directly proportional to temperature

 $P \propto T$

Temperature of various places and phenomena

Temperature (K)



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Ideal Gas Law

We can combine three relations just derived into a single relation: $PV \, \propto \, T$

What about amount of gas present?

If temperature and pressure are constant

volume is proportional to amount of gas:



 $PV \propto mT$

Relative Atomic Mass Scale



- masses of atoms are expressed relative to

the mass of a Carbon-12 atom.

Why is there a need for the scale?

atoms are too small to be weighed directly.
inconvenient to express masses of atoms in terms of kg.

So what does it imply?

- 1 atom of ¹²C = 12
- 1/12 the mass of a ¹²C atom = 1





Atomic mass \Rightarrow mass of an atom in atomic mass units (u)

By definition: 1 atom $^{12}\mbox{C}$ "weighs" 12 u

On this scale ${}^{1}H$ = 1.008 u ${}^{16}O$ = 16.00 u



Mole (mol): A unit to count numbers of particles

Dozen = 12





Mole — amount of a substance that contains as many elementary entities as there are atoms in exactly 12.00 grams of ¹²C

 $1 \text{ mol} = N_A = 6.022 \text{ x} 10^{23}$

*N*_A ► Avogadro's number

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Ideal Gas Law (cont'd)

A mole (mol) is defined as number of grams of a substance that is numerically equal to molecular mass of substance

 $1 \mod H_2$ has a mass of 2 g

 $1 \mod N_2$ has a mass of $28 \ g$

 $1 \mod CO_2$ has a mass of 44 g

Number of moles in a certain mass of material:

 $n (mol) = \frac{mass (grams)}{Molecular mass (g/mol)}$

Ideal Gas Law (cont'd)

We can now write ideal gas law 🖛

$$PV = n RT$$
number of moles universal gas constant
$$R = 8.315 J/(\text{mol} \cdot K)$$

$$= 0.0821 (L \cdot \text{atm})/(\text{mol} \cdot K)$$

 $= 1.99 \operatorname{calories}/(\operatorname{mol} \cdot K)$

Ideal Gas Law in Terms of Molecules: Avogadro's Number

Since gas constant is universal number of molecules in one mole is same for all gases That number is called Avogadro's number:

$$N_A = 6.02 \times 10^{23}$$

Number of molecules in a gas is number of moles times Avogadro's number:

$$N = n N_A$$

Ideal Gas Law in Terms of Molecules: Avogadro's Number

Therefore we can write:

$$PV = NkT$$

$$k = \frac{R}{N_A} = \frac{8.315 \, J/\text{mol} \cdot K}{6.02 \times 10^{23} \, / \,\text{mol}} = 1.38 \times 10^{-23} \, J/K$$

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Assumptions of kinetic theory:

OLarge number of molecules moving in random directions with a variety of speeds

OMolecules are far apart on average

OMolecules obey laws of classical mechanics and interact only when colliding

OCollisions are perfectly elastic

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Force exerted on the wall by collision of one molecule is

$$F = \frac{\Delta(mv)}{\Delta t} = \frac{2 m v_x}{2l/v_x} = \frac{m v_x^2}{l}$$

Then force due to all N molecules colliding with that wall is





(b)

0

Averages of squares of speeds in all three directions are equal:

$$F = \frac{m}{l} N \frac{\bar{v}^2}{3}$$

So pressure is
$$\blacksquare$$
 $P = \frac{F}{A} = \frac{1}{3} \frac{N m \bar{v}^2}{Al} = \frac{1}{3} \frac{N m \bar{v}^2}{V}$

Rewriting
$$\blacktriangleright PV = \frac{2}{3}N\left(\frac{1}{2}m\bar{v}^2\right)$$

so $\blacktriangleright \langle KE \rangle = \overline{KE} = \frac{1}{2}m\bar{v}^2 = \frac{3}{2}kT$

Average translational kinetic energy of molecules in an ideal gas is directly proportional to temperature of gas

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We can invert this to find average speed of molecules in a gas as a function of temperature



Mean Free Path

Average speed of molecules in a gas at normal pressure is several hundred meters per second yet if somebody across room from you opens a perfume bottle you do not detect odor for several minutes

Reason for time delay 🖛 perfume molecules do not travel directly towards you but instead travel a zigzag path due to collisions with air molecules

Average distance $\,\lambda$ travelled by a molecule between collisions

is called its mean free path

Mean Free Path (cont'd)

Consider one gas molecule of radius r moving with speed vthrough a region of stationary molecules Moving molecule will collide with another molecule of radius rif centers of two molecules come within a distance $d = r_1 + r_2$ from each other r_2 ŗ. If all molecules are of same type ·--- $= r_1 + r_2$ d = molecular diameterLuis Anchordogui

Mean Free Path (cont'd)

As molecule moves it will collide with any molecule whose center is in a circle of radius dAfter a time t molecule moves a distance vt and collides with every molecule in cylindrical volume $\pi d^2 vt$ Diameter d Number of molecules in this volume is $rackstarrow n_V \pi d^2 vt$ Number density Area = πd^2 number of molecules per unit volume $racksin n_V = N/V$ After each collision direction of molecule changes so path actually zigs and zags Total path length divided by number of collisions is mean free path $\lambda = \frac{vt}{n_V \pi d^2 vt} = \frac{\mathbf{1}}{n_V \pi d^2}$ Anchordoqui

Mean Free Path (cont'd)

Our previous calculation of mean free path assumes that all but one of gas molecules are stationary which is not a realistic situation When motion of all molecules is taken into account mean free path becomes

$$\lambda = \frac{1}{\sqrt{2} n_V \pi d^2}$$

Average time between collisions is called collision time τ

Reciprocal of collision time is equal to average number of collisions per second

Then if v_{av} is average speed \blacksquare average distance travelled between collisions is

$$\lambda = \frac{v_{av}}{\tau}$$

What is heat?

 Subjective sensation (familiar to everyone): when you touch something hot *heat* goes into your hand and burns it

We talk of tansfer of heat
 e.g. reading from one object (the radiator) to another (your hand)

Fact that radiator is hot

expressed as "radiator is @ high temperature"

 Heat and work are mutually convertible: you can do work and get heat or use heat and do work (a car engine or steam engine)

- The catch is register when you go from heat to useful work you never achieve 100% conversion there is always some heat wasted
- Thermal energy random motion of molecules in matter sample which constitutes form of kinetic energy

Temperature reasure of average kinetic energy/molecule
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- Heat is *also* kinetic energy regime moving energy
- It is kinetic energy of zillions of atoms in material vibrating (in solid) or zapping around (in gas) in a random way going nowehere in particular
- Heat is random energy of atoms and molecules
- This is very different from organized energy
- It is like throwing bag of hot popcorn (organized energy)
 vs. letting them pop around inside popper (random energy)
- Popcorn popping very quickly has a lot of heat energy

- Total heat energy of material depends on two things:
 - bow many atomos there are
 - how energetic each atom is (on average)
- Heat energy Q can be expressed as product of number of atoms N and average randon energy of single atom $\langle \varepsilon \rangle$

 $Q = N \left< \varepsilon \right>$

• *Temperature* redirect measurement of second factor:

average energy of an atom

- High temperature means peppy atoms
- Low temperature means sluggish atoms
- When atoms are so sluggish that they don't move you've hit bottom in temperature scale \mathbb{R} absoulte zero which is $T = -273^{\circ}$ C \mathbb{R} very cold!

- When you push your hand across table (mechanical energy)
- you set molecules at surface of table into random vibration and create heat energy (friction in this case)



- You touch hot poker readly vibrrating atoms on surface of poker bombard molecules of your skin
- these start vibrating reactions which tell your brain: "It's hot, let go!"



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Laws of Thermodynamics

Via work or via heat, every energy transfer

happen can!

THERMODYNAMICS - (developed in 19th century)

Phenomenological theory

to describe equilibrium properties of macroscopic systems

based on few macroscopically measurable quantities

A thermodynamic system

A thermodynamic system is a body of matter and/or radiation confined in space by walls (with defined permeabilities) which separate it from its sourroundings Isolated System Closed System Open System Exchange of energy Exchange of matter Heat Heat Heat Open system Closed system Isolated system Luis Anchordogui
Internal energy of system

Internal energy ${\bf U}$ of a system is total of all kinds of energy possessed by particles that make up system



Usually internal energy consists of sum of potential and kinetic energies of working gas molecules **Thermal Equilibrium: Zeroth Law of Thermodynamics**

Two objects placed in thermal contact will eventually come to same temperature When they do we say they are in thermal equilibrium

In the process of reaching thermal equilibrium heat Q is transferred from one body to the other

Zeroth law of thermodynamics says that if 2 objects are each in equilibrium with a 3 object they are also in thermal equilibrium with each other

Thermodynamics

First Law

Energy of universe is constant

Energy can be neither created nor destroyed

so while energy can be converted to another form

total energy remains constant



This is merely a statement of conservation of energy

First law of Thermodynamics

First law of thermodynamics is application of conservation of energy principle to heat and thermodynamic processes

> Change in internal energy of a system is equal to heat added to system minus work done by system

$$\Delta U = Q - W$$

Change inheat addedwork doneinternal energyto systemby system

Energy can't be created or destroyed 🖛 it can only change form

First law of thermodynamics

Net heat put into a system is equal to change in internal energy of system plus work done BY system

$$\Delta Q = \Delta U + \Delta W$$
 $\Delta = (final - initial)$

Conversely, work done ON a system is equal to change in internal energy plus heat lost in process



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Application of first law of thermodynamics

Example 1

In figure, gas absorbs 400 J of heat and at same time does 120 J of work

What is change in internal energy of system?

Apply First Law:

on piston



Application of first law of thermodynamics (cont'd)

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Application of first law of thermodynamics (cont'd)

Energy is conserved

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 $400\,\mathrm{J}\,\mathrm{of}$ input thermal energy is used to perform

is used to perform $120\,\mathrm{J}$ of external work,

increasing internal energy of system by $\,280\,J$

$$Q_{in} = 400 \, J$$

Increase in internal energy is $\clubsuit \Delta U = +280 \, J$



 $W_{out} = 120 \, J$

It is common experience that a cup of hot coffee left in a cooler room

eventually cools off



This process satisfies first law of thermodynamics since amount of energy lost by coffee is equal to amount gained by surrounding air

Now let us consider reverse process-hot coffee getting even

hotter in a cooler room as a result of heat transfer from room air We all know that this process never takes place

Yet, doing so would not violate first law as long as amount of energy lost by air is equal to amount gained by coffee

It is clear from above that processes proceed in a certain direction and not in reverse direction

First law places no restriction on direction of a process, but satisfying first law does not ensure that that process will actually occur

This inadequacy of first law to identify whether a process can take place is remedied by introducing another general principle, second law of thermodynamic

Second Law of Thermodynamics



Clausius statement:

A process whose only net result is to absorb heat from a cold reservoir and release the same amount of heat to a hot reservoir is impossible

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Entropy

A measure of disorder of a system

Systems tend to change from a state of low entropy

to a state of higher entropy

F If left to themselves, systems tend to increase their entropy







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Four thermodynamic processes Isochoric Process $-\Delta V = 0$, $\Delta W = 0$ Isobaric Process \blacksquare $\Delta P = 0$ Isothermal Process $-\Delta T = 0$, $\Delta U = 0$ Adiabatic Process - $\Delta Q = 0$

$$\Delta Q = \Delta U + \Delta W$$

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Isochoric process

CONSTANT VOLUME $\Delta V = 0, \Delta W = 0$ $\Delta Q = \Delta U + \Delta W^0$ so that $\Delta Q = \Delta U$



HEAT IN = INCREASE IN INTERNAL ENERGY

HEAT OUT = DECREASE IN INTERNAL ENERGY

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Isochoric example







Heat input increases \boldsymbol{P} with constant \boldsymbol{V}

400 J heat input increases internal energy by 400 J and zero work is done



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Heat input increases V with constant P

400 J heat does 120 J of work increases internal energy by 280 J



with constant ${\rm P}$

Work = Area under PV curve

Work = $P \Delta V$

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Isothermal process





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 $\Delta U = \Delta T = 0$

 $\begin{array}{ll} 400 \ \mathrm{J} \ \mathrm{of} \ \mathrm{energy} \ \mathrm{is} \ \mathrm{absorbed} \ \mathrm{by} \ \mathrm{gas} & \qquad \mbox{Isothermal Work} \\ \mathrm{as} \ 400 \ \mathrm{J} \ \mathrm{of} \ \mathrm{work} \ \mathrm{is} \ \mathrm{done} \ \mathrm{on} \ \mathrm{gas} & \qquad \mbox{W} = \ \mathrm{nR} \ \mathrm{T} \ \mathrm{ln} \ \frac{\mathrm{V}_{\mathrm{B}}}{\mathrm{V}_{\mathrm{A}}} \end{array}$

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Adiabatic process



Adiabatic example



 $\Delta Q = 0$

Expanding gas does work with zero heat loss $Work = -\Delta U$

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Adiabatic expansion



 $400 \,\mathrm{J}$ of WORK is done,

DECREASING internal energy by $400 \, \mathrm{J}$

Net heat exchange is ZERO

$$\Delta Q = 0$$

Luis Anchordoqui Thursday, November 19, 20 $P_A V_A^{\gamma} = P_B V_B^{\gamma}$

REMEMBER, FOR ANY PROCESS INVOLVING AN IDEAL GAS



$\Delta Q = \Delta U + \Delta W$

 $\Delta U \,=\, n C_V \, \Delta T$

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Example problem

A 2-L sample of Oxygen gas has an initial temperature and pressure of $200\,K\,$ and $1\,atm\,$ Gas undergoes four processes:

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 $\checkmark AB$: Heated at constant V to $400\,\mathrm{K}$

✓ BC : Heated at constant P to $800 \, {\rm K}$

 $\checkmark CD$: Cooled at constant V back to $1\,atm$

 $\checkmark DA$: Cooled at constant P back to $200\,\mathrm{K}$

PV-DIAGRAM FOR PROBLEM

How many moles of O_2 are present? Consider point AB 400 K P_B PV = nRT $800\,\mathrm{K}$ $200\,\mathrm{K}$ 1 atm 2Ln = $\frac{PV}{RT}$ = $\frac{(101.300 \text{ Pa})(0.002 \text{ m}^3)}{(8.314 \text{ J/mol} \cdot \text{K})(200 \text{ K})}$ = 0.122 mol

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Process AB 🖛 Isochoric

What is pressure at point B ?



 $P_B = 2 \operatorname{atm}$ or $203 \operatorname{kPa}$

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Process AB \blacktriangleright $\Delta Q = \Delta U + \Delta W$

Analyze first law for ishochoric process AB



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Process BC 🖛 Isobaric

What is Volume at point C(& D)?



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Finding ΔU for process BC

Process BC is <code>ISOBARIC</code>



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Finding ΔW for process BC





$$\Delta W = (2 \text{ atm})(4 \text{ L} - 2 \text{ L}) = 4 \text{ atm} \text{ L} = 405 \text{ J}$$

 $\Delta W = +405 \text{ J}$

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Finding ΔQ for process BC



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Process CD 🖛 Isochoric

What is temperature at point D?


Process CD \blacktriangleright $\Delta Q = \Delta U + \Delta W$

Analyze first law for $\ensuremath{\texttt{ISOCHORIC}}$ process CD



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Finding ΔU for process DA

Process $DA \mbox{ is } \mbox{ ISOBARIC }$



 $\Delta U = (0.122 \,\mathrm{mol})(21.1 \,\mathrm{J/mol}\,\mathrm{K})(400 \,\mathrm{K} - 200 \,\mathrm{K})$

$$\Delta U = -514 \, J$$

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Finding ΔW for process DA

Work depends on change in \boldsymbol{V}

 $\Delta P = 0$ $800\,\mathrm{K}$ $400\,\mathrm{K}$ 2 atm $200\,\mathrm{K}$ 400 K A 1 atm Work = $P \Delta V$ $4 \mathrm{L}$ 2L $\Delta W = (1 \text{ atm})(2 \text{ L} - 4 \text{ L}) = -2 \text{ atm} \text{ L} = -203 \text{ J}$ $\Delta W = -203 J$

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Finding ΔQ for process DA

Analyze first law for DA



 $\Delta Q = -717 J \qquad \Delta U = -514 J \qquad \Delta W = -203 J$

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PROBLEM SUMMARY

For all processes $\blacktriangleright \quad \Delta Q = \Delta U + \Delta W$

PROCESS	ΔQ	ΔU	ΔW
AB	$514\mathrm{J}$	$514\mathrm{J}$	0
BC	$1433\mathrm{J}$	$1028\mathrm{J}$	$405\mathrm{J}$
CD	$-1028\mathrm{J}$	$-1028\mathrm{J}$	0
DA	$-717\mathrm{J}$	$-514\mathrm{J}$	$-203\mathrm{J}$
TOTALS	$202\mathrm{J}$	0	$202\mathrm{J}$





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