

**University of Leicester**  
**Department of Physics and Astronomy**  
**Lecture Notes**  
**1st Year Basic Thermodynamics**

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# 1 Syllabus - Basic Thermodynamics - 112-1

The material is covered in the following sections of Tipler Mosca 6th Edition:

## Chapter 17

- 17-1 Thermal equilibrium and temperature
- 17-1 Temperature scales
- 17-2 Gas thermometers and the absolute temperature scale
- (20-3 Phase diagrams)
- 17-3 The ideal gas law
- 17-4 The kinetic theory of gases - the Equipartition Theorem

## Chapter 18

- 18-1 Heat capacity and specific heat
- 18-2 Phase changes and latent heat
- 18-3 Joule's experiment - First law of thermodynamics
- 18-4 Internal energy
- 18-5 Work and PV diagrams for a gas
- 18-6 Heat capacities of gases - equipartition
- 18-7 Heat capacities of solids
- 18-8 Failure of equipartition
- 18-9 Quasi static adiabatic changes

## 2 Introduction

What is heat? What is temperature?

Some days are cold, some days are hot but what is it about cold air which is different from hot air?

We are all familiar with stuff which is hot and stuff which is cold. If we have something which is cold (soup from a tin) and we want to heat it up we put it in contact with something which is hot (the ring of a cooker)... Cut to the chase.

- Heat is a form of energy.
- This energy is associated with random motion or jiggle of atoms, molecules or, more generally, microscopic entities of all sorts.
- Temperature is a measure of the AVERAGE energy associated with the random motion or jiggle of individual particles.
- Heat is the sum of the random motion or jiggle energy of very many particles.
- Heat moves around because the particles collide or interact with one another.

Errr... That's it! In this course you will start to learn about how you measure temperature and how heat moves about - thermodynamics.

Both temperature and heat are associated with RANDOM motion. There are large variations in the energy associated with this random motion of individual particles but temperature and heat don't seem to be random and don't normally fluctuate. This is because for macroscopic system we are averaging over a very large number of particles. Typically of order Avagado's number of particles,  $N_A = 6.022 \times 10^{23}$ . With such a large summation involved in the averaging the fluctuations are negligible!

## 3 Zeroth law of thermodynamics, temperature and temperature scales

Two objects are defined to have the same temperature if they are in thermal equilibrium with each other.

The zeroth law of thermodynamics states:

If two objects are in thermal equilibrium with a third, then they are in thermal equilibrium with each other.

In other words temperature is *transferable* and you can use a system called a thermometer to measure the temperature of other systems in a consistent, unambiguous way.

As temperature changes so physical properties of an object change. We can set up a temperature scale using a so-called thermometric property, e.g. expansion of a solid, liquid or gas.

We can use phase transitions to provide fixed points of a temperature scale. e.g. melting ice, a mixture of ice and water in thermal equilibrium (here think of solid ice as one system and liquid water as another), at 1 atmosphere defines  $0^\circ\text{C}$  and boiling water, a mixture of liquid water and gaseous steam in thermal equilibrium, at 1 atmosphere defines  $100^\circ\text{C}$ .

Using a thermometric property  $F_t$  we define the Celcius temperature scale as:

$$t_C = \frac{F_t - F_0}{F_{100} - F_0} \times 100$$

or rewriting in the more familiar form of a linear equation:

$$t_C = mF_t + c$$

where the gradient  $m = 100/(F_{100} - F_0)$  and intercept  $c = -F_0 \times 100/(F_{100} - F_0)$ .

In general different properties  $F_t$  will produce slightly different scales but they will agree at the ice point temperature and steam point temperature.

## 4 Gas thermometers and the ideal-gas temperature scale

In a constant-volume gas thermometer the thermometric property is the pressure of a fixed volume of gas. Look up details of how such a thermometer is constructed in Tipler. Then

$$t_C = \frac{P_t - P_0}{P_{100} - P_0} \times 100$$

When the gas density is very low all gas thermometers give the same value of any temperature independent of the type of gas.

We can invert this equation to find  $P_t$  as a function of  $t_C$ :

$$P_t = t_C \times \frac{P_{100} - P_0}{100} + P_0$$

The pressure will drop to zero at a temperature:

$$t_Z = -100 \times \frac{P_0}{P_{100} - P_0}$$

This limit is  $t_Z = -273.15$  whatever the type of gas used. At absolute zero temperature the gas molecules stop moving/jiggling. The amplitude of the jiggle goes to zero. You can't get colder than that!

We define the ideal-gas temperature scale such that the temperature of the triple point of water (the unique combination of temperature and pressure at which ice, water and steam coexist) is 273.16 kelvins (K). Look-up phase diagrams in chapter 20-3. Then if the pressure at the triple point is  $P_3$ :

$$T = \frac{273.16}{P_3} P$$

The second reference point is now  $T = 0$  when the pressure  $P = 0$ . This defines an absolute zero since you can't have a negative gas pressure.

## 5 The ideal-gas law

Boyle's law (found experimentally) for a low-density gas at constant temperature is

$$PV = \text{constant}$$

It was also found experimentally (by Charles and Gay-Lussac) that the absolute temperature of a low-density gas is proportional to its volume at constant pressure.

We can combine these with the definition of the ideal-gas temperature scale to give:

$$PV = CT$$

where  $C$  is some constant which depends on how much gas we have. If we have  $N$  molecules of gas:

$$PV = NkT$$

where  $k$  is Boltzmann's constant. If we have  $n$  moles of the gas ( $n$  times Avagadro's number of molecules) then:

$$PV = nRT$$

where  $R$  is the universal gas constant. Such a relationship between the variables  $P$ ,  $V$  and  $T$  is called an equation of state. The above is the equation of state for an ideal-gas. In such a gas there is no force between the molecules.

Note that the product  $PV$  has units of work or energy (Joules) so Boltzmann's constant and the universal gas constant both have units of Joules per K.

## 6 Heat capacity and specific heat

Heat (units of energy, see below under Joule's experiment) is required to increase the jiggle of the particles, i.e. heat is required to increase the temperature. The amount of heat required to raise the temperature of a substance is proportional to the temperature change and the amount of substance.

$$\Delta Q = mc\Delta T$$

where  $c$  is the specific heat (the heat capacity per unit mass).

The molar specific heat is  $c' = mc/n = Mc$  where  $n$  is the number of moles and  $M$  is the molar mass.

The specific heat can tell us something about the internal structure of a substance.

## 7 Phase changes and latent heat

fusion - liquid to solid

melting - solid to liquid

vapourization - liquid to gas

condensation - gas to liquid

sublimation - solid to gas

During a phase change (for a pure substance) the temperature remains constant. This temperature depends on the pressure. During a phase change the internal structure of the substance changes and this involves the exchange of heat.

Heat must usually be supplied for melting, vapourization and sublimation.

Heat is usually released in fusion and condensation.

The amount of heat is proportional to the amount of substance.

$$\Delta Q = mL$$

where  $L$  is the latent heat of fusion or latent heat of vapourization. Latent heat tells us something about the forces between the molecules.

## 8 Joule's experiment

Look-up in section 18-3. Equivalence of heat and work. Heat has units of energy.

## 9 First law of thermodynamics

For an isolated system

$$Q = \Delta U + W$$

where

- positive  $Q$  is the heat flow INTO the system
- negative  $Q$  is the heat flow OUT OF the system
- $\Delta U$  is the change in internal energy of the system
- positive  $W$  is work done BY the system
- negative  $W$  is work done ON the system

This is simply a statement of the conservation of energy. There is an equivalence between heat and work - Joule's experiment - we can increase the temperature of something by doing work. Note: I have used the symbol  $U$  for internal energy not  $E_{int}$ . Every text book in the Universe except for Tipler uses  $U$ !

## 10 The internal energy of an ideal gas

In an ideal gas the internal energy is associated with the translational energy of the particles (kinetic energy). Look-up chapter 17-4 on kinetic theory of gases. There are 3 degrees of freedom because the gas particles can move independently in 3 directions.

$$U = \frac{3}{2}nRT$$

where  $n$  is the number of moles,  $R$  is the universal gas constant and  $T$  is the absolute temperature. Here we are quantifying the thermal jiggle, associated with a given temperature, in an ideal gas.

The average kinetic energy of atoms or molecules is

$$KE = \frac{1}{2}mv^2$$

where  $m$  is the atomic or molecular mass and  $v$  is the root mean square velocity of the particles. If we have a mole of material then the total mass is  $M = N_A m$  the molar mass or the mass of Avagadro's number of particles. Equating the internal energy of an ideal gas to the kinetic energy we have for 1 mole

$$\frac{1}{2}Mv^2 = \frac{3}{2}RT$$

Therefore the root mean square (rms) velocity of gas molecules at temperature  $T$  is

$$v = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3kT}{m}}$$

We can use either the Universal gas constant and the molar mass or Boltzman's constant,  $k$ , and the mass of a single molecule/particle.

## 11 Work and the PV diagram for a gas

The differential of the mechanical work done by a gas is:

$$dW = PdV$$

where  $P$  is the pressure and  $dV$  is the differential increase in the volume of the gas. The gas does work against the external pressure.

The total work done in some change is then:

$$W = \int_{V_1}^{V_2} PdV$$

isochoric change - constant volume -  $W_{isochoric} = 0$ .

isobaric expansion - constant pressure -  $W_{isobaric} = P\Delta V$ .

isothermal expansion - constant temperature -  $P = nRT/V$  therefore:

$$\int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$W_{isothermal} = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \frac{V_2}{V_1}$$

## 12 Heat capacities of gases

If a substance expands when heated then the heat capacity at constant pressure is greater than the heat capacity at constant volume because work is done as the substance expands (against an external pressure). This difference is large for gases.

At constant volume

$$\Delta Q = C_v \Delta T = \Delta U$$

Since  $\Delta W = 0$  in the first law of thermodynamics. Taking the limit as  $\Delta T \rightarrow 0$  we have:

$$C_v = \frac{dU}{dT}$$

At constant pressure

$$\Delta Q = C_p \Delta T = \Delta U + \Delta W = \Delta U + P \Delta V$$

For an infinitesimal change this becomes:

$$C_p dT = dU + P dV$$

Substituting for  $dU$  using  $C_v$  we get:

$$C_p dT = C_v dT + P dV$$

For an ideal gas  $PV = nRT$ . Taking differentials of both sides gives  $PdV + VdP = nRdT$ . At constant pressure  $dP = 0$  so

$$C_p dT = C_v dT + nRdT$$

Therefore for an ideal gas  $C_p - C_v = nR$ .

## 13 Equipartition theorem

The internal energy for each degree of freedom is  $\frac{1}{2}RT$  per mole or  $\frac{1}{2}kT$  per particle.

For  $n$  moles of a monoatomic gas  $C_v = \frac{3}{2}nR$ ,  $C_p = \frac{5}{2}nR$

For gases which contain diatomic molecules  $C_v = \frac{5}{2}nR$ ,  $C_p = \frac{7}{2}nR$ .

The extra degrees of freedom arise from rotations of the molecule. Note that rotation about the line of centres doesn't seem to contribute?!

See above where we calculated the rms velocity of gas molecules at temperature  $T$  using the internal energy of an ideal gas. We can get the same answer using equipartition and 3 degree of freedom associated with the kinetic energy of translation for each particle of mass  $m$ .

$$\frac{1}{2}mv^2 = \frac{3}{2}kT$$

So the rms velocity is as before

$$v = \sqrt{\frac{3kT}{m}}$$

## 14 Heat capacities of solids

Dulong-Petit law  $c' = 3R$  - elemental or monatomic solids. There are 6 degrees of freedom associated with each atom - 3 for the motion of the atom and 3 for the motion of the bonds (springs) between the atoms. These bonds are actually the valence electrons.

## 15 Failure of equipartition

The equipartition theorem fails because of quantization of energy levels. The energy associated with each degree of freedom can only take discrete values. The energy levels are populated by collisions in a gas or vibrations in a solid. The typical energy involved in such collisions is  $kT$  where  $k$  is Boltzmann's constant. If the gap between the quantized energy levels is  $\Delta E > kT$  then equipartition breaks down since collisions can no longer excite the higher energy levels.

## 16 Quasi-static adiabatic expansion of a gas

A quasi-static process is one that proceeds very slowly so that thermal equilibrium is always established.

A process in which no heat flows into or out of a system is called an adiabatic process.

Using the first law of thermodynamics:

$$dQ = dU + dW = C_v dT + PdV = 0$$

For an ideal gas  $P = nRT/V$  so:

$$C_v dT + nRT \frac{dV}{V} = 0$$

$$\frac{dT}{T} + \frac{nR}{C_v} \frac{dV}{V} = 0$$

But  $nR/C_v = (C_p - C_v)/C_v = \gamma - 1$  where

$$\gamma = \frac{C_p}{C_v}$$

the ratio of the specific heats. We have

$$\frac{dT}{T} + (\gamma - 1) \frac{dV}{V} = 0$$

Integrating gives:

$$\ln T + (\gamma - 1) \ln V = \text{constant}$$

$$TV^{\gamma-1} = \text{constant}$$

Using  $PV = nRT$  we have

$$\frac{PV}{nR}V^{\gamma-1} = \text{constant}$$

or

$$PV^\gamma = \text{constant}$$

for a quasi-static adiabatic change.

The work done can be calculated using the first law of thermodynamics. Because  $dQ = 0$  we have:

$$dW = -dU = -C_v dT$$

$$W_{\text{adiabatic}} = \int -C_v dT = -C_v \Delta T = -C_v(T_2 - T_1)$$

Using  $PV = nRT$ ,  $nR = C_p - C_v$  and  $\gamma = C_p/C_v$  we get

$$W_{\text{adiabatic}} = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$