2- Heat Capacities

Classical physics the principle could be used to calculate the heat capacity of a solid .

The energy of an atom as it oscillates a bout its mean position in a solid is KT for each direction of displacement .

As each atom can oscillate in three dimensions , the average energy of each atom is 3KT for N atoms the total energy is $3N_AKT$, N_A= Avogadro number constant = 6.02×10^{23} mol^{-1}

The contribution of this motion to the molar internal energy is therefore .

Um= 3NaKT= 3RT

Because N_A K= R ….R= gases constant , K= Boltzmann constant

The heat capacity at constant volume is denoted C_v and is defined formally as .

$C_v = (dU/ dT)_v$

Is the predicted to be $C_v = (dU/ dT)_v = 3R$

It possible to measure heat capacities at low temperatures .

It was found that the molar heat capacities of all metals are lower than 3R at low temperatures .

Einstein calculated the contribution of the oscillations of the atoms to the total molar energy of the metal and obtained .

$$U_m = \frac{3\,NA\,h\nu}{e^{\frac{h\nu}{KT}} - 1}$$

In place of the classical expression 3RT .that the heat capacity by differentiating U_m with respect to T.

The resulting expression is now known as the Einstein formula .

$$Cv = 3R\left(\frac{h\nu}{KT}\right)^2 \frac{e^{h\nu/2KT}}{e^{\frac{h\nu}{KT}} - 1}$$

At high temperatures when $T > h\nu/K$ the result is $Cv = 3R$ because

$$\left(\frac{h\nu}{KT}\right)^2 \frac{e^{h\nu/2KT}}{e^{\frac{h\nu}{KT}} - 1} = 1$$

At low temperatures when $T < h\nu/K$ the result is

$$C_v = 3R\left(\frac{h\nu}{KT}\, e^{-\frac{h\nu}{2KT}}\right)^2$$

- We see that Einstein's formula accounts for the accounts for the decrease of heat capacity at low temperatures .
- The physical reason for that at low temperatures only a few oscillators possess enough energy to oscillate significantly at higher temperatures ,there is enough energy available for all the oscillators to become active all 3 N oscillators contribute ,and the heat capacity approaches its classical value .
- Einstein's assumption that all the atom oscillate with the same frequency , where as in fact the oscillate over range of frequencies from zero up to a maximum v.

3- photoelectric effect

- Light shining a metal causes emission of electrons. The energy of a wave is proportional to its intensity and not related to its frequency .
- So the electromagnetic, wave picture of light leads one to expect that the kinetic energy of an emitted photoelectron would increase as the light intensity increases but would not change as the light frequency changes .
- Instead ,one observes that the kinetic energy of an emitted electron is independent of the lights intensity but increases as the light s frequency increases .

When an electron in the metal absorbs a photon , part of the absorbed photon energy is used to overcome the forces holding the electron in the metal , and the remainder appears as kinetic energy of the electron after it has left the metal .

Conservation of energy gives.

$E = Q + E_k$

$hv = Q + E_K$

Q= work function is the minimum energy needed by an electron to escape the metal.

E_k= maximum kinetic energy of an emitted electron .

An increase in the lights frequency v increases the photon energy and hence increases the kinetic energy of the emitted electron .

An increase in light intensity at fixed frequency increases the rate at which photons strike the metal and hence increases the rate of emission of electrons , but does not change the kinetic energy of each emitted electron .

The photoelectric effect shows that light can exhibit particle like behavior in addition to the wave like behavior it shows in diffraction experiments.

Further evidence for the particle -like character of radiation comes from the measurement of the energies of electrons produced in the photoelectric effect .

This effect is the ejection of electrons from metals when they are exposed to ultra-violet radiation .

The experimental characteristics of the photoelectric effect are as follows:

1-No electrons are ejected , unless the frequency of the radiation exceeds a threshold value characteristic of the metal .

2-Electrons are ejected immediately if the frequency is above threshold.

3-Electron emission occurs less than 1ms sec. after the illumination starts independent of the light intensity .

Classical theory predicts a light intensity dependent emission time.

4-The kinetic energy of the electrons depends only on the frequency of the light but independent of the intensity .

Classical theory predicts that kinetic energy depends on the light intensity.

These observations strongly suggest that the photoelectric effect depends on the ejection of an electron when it is involved in a collision with a particle -like projectile that carries enough energy to eject the electron from the metal .

If we suppose that the projectile is a photon of energy hv. Then the conservation of energy requires that the kinetic energy of the ejected electron should obey.

$E = Q + E_k$

$E_k = 1/2\ m_e v^2$

$Q = h\nu_0$

$h\nu = Q + 1/2\ m_e v^2$

the energy required to remove an electron from the metal to infinity. photo ejection cannot occur if $h\nu < Q$ because the photon brings insufficient energy.

h=Planck constant $= 6.62 \times 10^{-34}$ J.s

m_e = mass electron $= 9.1 \times 10^{-31}$ kg

c=velocity of light $= 3 \times 10^{8}$ m.s^{-1}

Q= work function (1 eV= 1.6×10^{-19} J)

V= velocity of electron emitted

V_0= Threshold frequency