Chapter 4
Thermodynamics and Statistical Physics

4.1 Basic Concepts and Formulae

Kinetic theory of gases

Pressure

$$p = \frac{1}{3}\rho < v^2 > \tag{4.1}$$

Root-mean-square velocity

$$v_{\text{rms}} = \sqrt{3P/\rho} \tag{4.2}$$

$$v_{\text{rms}} = \sqrt{3kT/m} = \sqrt{3RT/M} \tag{4.3}$$

Average speed

$$< v >= \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} \tag{4.4}$$

Most probable speed

$$v_p = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}} \tag{4.5}$$

where m is the mass of the molecule, M is the molar weight, ρ the gas density, $k = 1.38 \times 10^{-23}/\text{K}$, the Boltzmann constant, $R = 8.31$ J/mol-K, is the universal gas constant, and K is the Kelvin (absolute) temperature.

$$v_p :< v >: v_{\text{rms}} :: \sqrt{2} : \sqrt{8/\pi} : \sqrt{3} \tag{4.6}$$

The Maxwell distribution

$$N(\nu)\mathrm{d}\nu = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\nu^2 e^{-m\nu^2/2kT}\,\mathrm{dv} \tag{4.7}$$

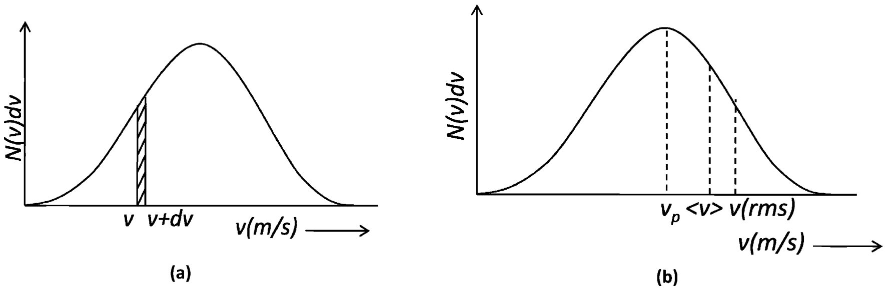

Fig. 4.1 The Maxwell distribution

Flux

$$\emptyset = \frac{1}{4}n < \nu > \quad \text{(number of molecules striking unit area per second)} \tag{4.8}$$

where n is the number of molecules per unit volume.

Mean free path (M.F.P)

$$\lambda = \frac{1}{\sqrt{2}\pi n\sigma^2} \tag{4.9}$$

where n is the number of molecules per unit volume and σ is the diameter of the molecule.

Collision frequency

$$f = \frac{< \nu >}{\lambda} \tag{4.10}$$

Viscosity of gas (η)

$$\eta = \frac{1}{3}\rho\lambda < \nu > \tag{4.11}$$

Thermal conductivity (K)

$$K = \eta C_\nu \tag{4.12}$$

where C_ν is the specific heat at constant volume.

Coefficient of diffusion (D)

$$D = \frac{\eta}{\rho} \tag{4.13}$$

Clausius Clepeyron equation

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L}{T(\nu_2 - \nu_1)} \tag{4.14}$$

where ν_1 and ν_2 are the initial and final specific volumes (volume per unit mass) and L is the latent heat.

Vander Waal's equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad \text{(for one mole of gas)} \tag{4.15}$$

The Stefan-Boltzmann law

$$E = \sigma T^4 \tag{4.16}$$

If a blackbody at absolute temperature T be surrounded by another blackbody at absolute temperature T_0, the amount of energy E lost per second per square metre of the former is

$$E = \sigma(T^4 - T_0^4) \tag{4.17}$$

where $\sigma = 5.67 \times 10^{-8}$ W/m^2.K^4 is known as Stefan-Boltzmann constant.

Maxwell's thermodynamic relations

$$\text{First relation: } \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{4.18}$$

$$\text{Second relation: } \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{4.19}$$

$$\text{Third relation: } \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{4.20}$$

$$\text{Fourth relation: } \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{4.21}$$

Thermodynamical potentials

(i) Internal energy (U)
(ii) Free energy (F)
(iii) Gibb's function (G)
(iv) Enthalpy (H)

$$H = U + PV \tag{4.22}$$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \tag{4.23}$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \tag{4.24}$$

$$\left(\frac{\partial H}{\partial P}\right)_S = V \tag{4.25}$$

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \tag{4.26}$$

The Joule-Kelvin effect

$$\Delta T = \frac{\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]\Delta P}{C_P} \tag{4.27}$$

Black body radiation

$$P_{\text{radiatio}} = \frac{u}{3} \tag{4.28}$$

where u is the radiation density

Wein's displacement law

$$\lambda_m T = 0.29 \text{ cm - K} \tag{4.29}$$

Planck's radiation law

$$u_\nu d\nu = \frac{8\pi h\nu^3 d\nu}{c^3(e^{h\nu/kT} - 1)} \tag{4.30}$$

$$u_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} . \frac{1}{(e^{hc/\lambda kT} - 1)} \tag{4.31}$$

$$\sigma = \frac{2}{15} . \frac{\pi^5 k^4}{h^3 c^2} \tag{4.32}$$

$$\Delta S = \frac{\Delta Q}{T} \tag{4.33}$$

$$\Delta S = k\ln(\Delta W) \tag{4.34}$$

where W is the number of accessible states.
Probability for finding a particle in the nth state at temperature T

$$P(n, T) = \frac{e^{-E_n/kT}}{\Sigma_{n=0}^{\infty} e^{-E_n/kT}} \tag{4.35}$$

Stirling's approximation

$$n! = \sqrt{2\pi n}\, n^n e^{-n} \tag{4.36}$$

4.2 Problems

4.2.1 Kinetic Theory of Gases

4.1 Derive the formula for the velocity distribution of gas molecules of mass m at Kelvin temperature T.

4.2 Assuming that low energy neutrons are in thermal equilibrium with the surroundings without absorption and that the Maxwellian distribution for velocities is valid, deduce their energy distribution.

4.3 In Problem 4.1 show that the average speed of gas molecule $< v >= \sqrt{8kT/\pi m}$.

4.4 Show that for Maxwellian distribution of velocities of gas molecules, the root mean square of speed $< v^2 >^{1/2} = (3kT/m)^{1/2}$

4.5 (a) Show that in Problem 4.1 the most probable speed of the gas molecules $v_p = (2kT/m)^{1/2}$
(b) Show that the ratio $v_p :< v >:< v^2 >^{1/2} :: \sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$

4.6 Estimate the rms velocity of hydrogen molecules at NTP and at 127°C
[Sri Venkateswara University 2001]

4.7 Find the rms speed for molecules of a gas with density of 0.3 g/l of a pressure of 300 mm of mercury.
[Nagarjuna University 2004]

4.8 The Maxwell's distribution for velocities of molecules is given by $N(v)\mathrm{d}v = 2\pi N(m/2\pi kT)^{3/2} v^2 \exp(-mv^2/2kT)\mathrm{d}v$

Calculate the value of $< 1/v >$

4.9 The Maxwell's distribution of velocities is given in Problem 4.8. Show that the probability distribution of molecular velocities in terms of the most probable velocity between α and $\alpha + \mathrm{d}\alpha$ is given by

$$N(\alpha)\mathrm{d}\alpha = \frac{4N}{\sqrt{\pi}}\alpha^2 e^{-\alpha^2}\mathrm{d}\alpha$$

where, $\alpha = v/v_p$ and $v_p = (2kT/m)^{1/2}$.

4.10 Calculate the fraction of the oxygen molecule with velocities between 199 m/s and 201 m/s at 27°C

4.11 Assuming that the hydrogen molecules have a root-mean-square speed of 1,270 m/s at 300 K, calculate the rms at 600 K.

4.12 Clausius had assumed that all molecules move with velocity v with respect to the container. Under this assumption show that the mean relative velocity $< v_{\mathrm{rel}} >$ of one molecule with another is given by $< v_{\mathrm{rel}} >= 4v/3$.

4.13 Estimate the temperature at which the root-mean-square of nitrogen molecule in earth's atmosphere equals the escape velocity from earth's gravitational field. Take the mass of nitrogen molecule = 23.24 amu, and radius of earth = 6,400 km.

4.14 Calculate the fraction of gas molecules which have the mean-free-path in the range λ to 2λ.

4.15 If ρ is the density, $< v >$ the mean speed and λ the mean free path of the gas molecules, then show that the coefficient of viscosity is given by $\eta = \frac{1}{3}\rho < v > \lambda$.

4.16 At STP, the rms velocity of the molecules of a gas is 10^5 cm/s. The molecular density is $3 \times 10^{25}\ \mathrm{m}^{-3}$ and the diameter (σ) of the molecule 2.5×10^{-10} m. Find the mean-free-path and the collision frequency.

[Nagarjuna University 2000]

4.17 When a gas expands adiabatically its volume is doubled while its Kelvin temperature is decreased by a factor of 1.32. Calculate the number of degrees of freedom for the gas molecules.

4.18 What is the temperature at which an ideal gas whose molecules have an average kinetic energy of 1 eV?

4.19 (a) If γ is the ratio of the specific heats and n is the degrees of freedom then show that for a perfect gas

$\gamma = 1 + 2/n$

(b) Calculate γ for monatomic and diatomic molecules without vibration.

4.20 If K is the thermal conductivity, η the coefficient of viscosity, C_v the specific heat at constant volume and γ the ratio of specific heats then show that for the general case of any molecule

$$\frac{K}{\eta C_v} = \frac{1}{4}(9\gamma - 5)$$

4.2.2 Maxwell's Thermodynamic Relations

4.21 Obtain Maxwell's Thermodynamic Relations

(a) $\left(\frac{\partial s}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

(b) $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

4.22 Obtain Maxwell's thermodynamic relation.

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

4.23 Obtain Maxwell's thermodynamic relation.

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

4.24 Using Maxwell's thermodynamic relations deduce Clausius Clapeyron equation

$$\left(\frac{\partial p}{\partial T}\right)_{\text{saturation}} = \frac{L}{T(\nu_2 - \nu_1)}$$

where p refers to the saturation vapor pressure, L is the latent heat, T the temperature, ν_1 and ν_2 are the specific volumes (volume per unit mass) of the liquid and vapor, respectively.

4.25 Calculate the latent heat of vaporization of water from the following data: $T = 373.2\,\text{K}$, $\nu_1 = 1\,\text{cm}^3$, $\nu_2 = 1,674\,\text{cm}^3$, $\mathrm{d}p/\mathrm{d}T = 2.71\,\text{cm}$ of mercury K^{-1}

4.26 Using the thermodynamic relation

$$\left(\frac{\partial s}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V,$$

derive the Stefan-Boltzmann law of radiation.

4.27 Use the thermodynamic relations to show that for an ideal gas $C_P - C_V = R$.

4.28 For an imperfect gas, Vander Waal's equation is obeyed

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

with the approximation $b/V \ll 1$, show that

$$C_P - C_V \cong R\left(1 + \frac{2a}{RTV}\right)$$

4.29 If E is the isothermal bulk modulus, α the coefficient of volume expansion then show that

$$C_P - C_V = TE\alpha^2 V$$

4.30 Obtain the following $T\mathrm{d}s$ equation
$T\mathrm{d}s = C_V\mathrm{d}T + T\alpha E_T\mathrm{d}V$

where $E_T = -V\left(\frac{\partial P}{\partial V}\right)_T$ is the isothermal elasticity and $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ is the volume coefficient of expansion, S is the entropy and T the Kelvin temperature.

4.31 Obtain the equation
$T\mathrm{d}s = C_p\mathrm{d}T - TV\alpha\mathrm{d}p$

4.32 Obtain the equation

$$T\mathrm{d}s = C_V\left(\frac{\partial T}{\partial P}\right)_V \mathrm{d}P + C_P\left(\frac{\partial T}{\partial V}\right)_P \mathrm{d}V$$

4.33 Obtain the formula for the Joule–Thompson effect

$$\Delta T = \frac{[T(\partial V/\partial T)_P - V]\Delta P}{C_P}$$

4.34 (a) Show that for a perfect gas governed by the equation of state $PV = RT$ the Joule-Thompson effect does not take place.
(b) Show that for an imperfect gas governed by the equation of state $\left(P + \frac{a}{V^2}\right)$ $(V - b) = RT$, the Joule-Thompson effect is given by

$$\Delta T = \frac{1}{C_P}\left(\frac{2a}{RT} - b\right)\Delta P.$$

4.35 Explain graphically the condition for realizing cooling in the Joule-Thompson effect using the concept of the inversion temperature.

4.36 Prove that for any substance the ratio of the adiabatic and isothermal elasticities is equal to the ratio of the two specific heats.

4.37 Prove that the ratio of the adiabatic to the isobaric pressure coefficient of expansion is $1/(1 - \gamma)$.

4.38 Show that the ratio of the adiabatic to the isochoric pressure coefficient is $\gamma/(\gamma - 1)$.

4.39 If U is the internal energy then show that for an ideal gas $(\partial U/\partial V)_T = 0$.
[Nagarjuna University 2004]

4.40 Find the change in boiling point when the pressure on water at 100°C is increased by 2 atmospheres. ($L = 540\,\mathrm{Calg}^{-1}$, volume of 1 g of steam = 1,677 cc)
[Nagarjuna University 2000]

4.41 If 1 g of water freezes into ice, the change in its specific volume is 0.091 cc Calculate the pressure required to be applied to freeze 10 g of water at −1°C.
[Sri Venkateswara University 1999]

4.42 Calculate the change of melting point of naphthalene per atmospheric change of pressure, given melting point = 80°C, latent heat = 35.5 cal/g, density of solid = 1.145 g/*cc* and density of liquid = 0.981 g/cc

[University of Calcutta]

4.43 The total energy of blackbody radiation in a cavity of volume V at temperature T is given by $u = aVT^4$, where $a = 4\sigma/c$ is a constant.

(a) Obtain an expression for the entropy S in terms of T, V and a.
(b) Using the expression for the free energy F, show that the pressure $P = \frac{1}{3}u$.

4.44 Given that the specific heat of Copper is 387 J/kg K^{-1}, calculate the atomic mass of Copper in amu using Dulong Petit law.

4.2.3 Statistical Distributions

4.45 Calculate the ratio of the number of molecules in the lowest two rotational states in a gas of H_2 at 50 K (take inter atomic distance = 1.05 A°)

[University of Cambridge, Tripos 2004]

4.46 Consider a photon gas in equilibrium contained in a cubical box of volume $V = a^3$. Calculate the number of allowed normal modes of frequency ω in the interval dω.

4.47 Show that for very large numbers, the Stirling's approximation gives
$n! \cong \sqrt{2\pi n}\, n^n e^{-n}$

4.48 Show that the rotational level with the highest population is given by

$$\mathrm{J\,max(pop)} = \frac{\sqrt{I_0 kT}}{\hbar} - \frac{1}{2}$$

4.49 Assuming that the moment of inertia of the H_2 molecule is 4.64×10^{-48} kg-m^2, find the relative population of the $J = 0, 1, 2$ and 3 rotational states at 400 K.

4.50 In Problem 4.49, at what temperature would the population for the rotational states $J = 2$ and $J = 3$ be equal.

4.51 Calculate the relative numbers of hydrogen atoms in the chromosphere with the principal quantum numbers $n = 1, 2, 3$ and 4 at temperature 6,000 K.

4.52 Calculate the probability that an allowed state is occupied if it lies above the Fermi level by kT, by $5kT$, by $10\,kT$.

4.53 If n is the number of conduction electrons per unit volume and m the electron mass then show that the Fermi energy is given by the expression

$$E_\mathrm{F} = \frac{h^2}{8m}\left(\frac{3n}{\pi}\right)^{2/3}$$

4.54 The probability for occupying the Fermi level $P_F = 1/2$. If the probability for occupying a level ΔE above E_F is P_+ and that for a level ΔE below E_F is P_-, then show that for $\frac{\Delta E}{kT} \ll 1$, P_F is the mean of P_+ and P_-

4.55 Find the number of ways in which two particles can be distributed in six states if

(a) the particles are distinguishable
(b) the particles are indistinguishable and obey Bose-Einstein statistics
(c) the particles are indistinguishable and only one particle can occupy any one state.

4.56 From observations on the intensities of lines in the optical spectrum of nitrogen in a flame the population of various vibrationally excited molecules relative to the ground state is found as follows:

v	0	1	2	3
N_v/N_0	1.000	0.210	0.043	0.009

Show that the gas is in thermodynamic equilibrium in the flame and calculate the temperature of the gas ($\theta_v = 3{,}350$ K)

4.57 How much heat (in eV) must be added to a system at 27°C for the number of accessible states to increase by a factor of 10^8?

4.58 The counting rate of Alpha particles from a certain radioactive source shows a normal distribution with a mean value of 10^4 per second and a standard deviation of 100 per second. What percentage of counts will have values

(a) between 9,900 and 10,100
(b) between 9,800 and 10,200
(c) between 9,700 and 10,300

4.59 A system has non-degenerate energy levels with energy $E = \left(n + \frac{1}{2}\right)\hbar\omega$, where $\hbar\omega = 8.625 \times 10^{-5}$ eV, and $n = 0,\ 1,\ 2,\ 3\ldots$ Calculate the probability that the system is in the $n = 10$ state if it is in contact with a heat bath at room temperature ($T = 300$ K). What will be the probability for the limiting cases of very low temperature and very high temperature?

4.60 Derive Boltzmann's formula for the probability of atoms in thermal equilibrium occupying a state E at absolute temperature T.

4.2.4 Blackbody Radiation

4.61 A wire of length 1 m and radius 1 mm is heated via an electric current to produce 1 kW of radiant power. Treating the wire as a perfect blackbody and ignoring any end effects, calculate the temperature of the wire.

[University of London]

4.62 When the sun is directly overhead, the thermal energy incident on the earth is 1.4 kWm^{-2}. Assuming that the sun behaves like a perfect blackbody of radius 7×10^5 km, which is 1.5×10^8 km from the earth show that the total intensity of radiation emitted from the sun is $6.4 \times 10^7\ \text{Wm}^{-2}$ and hence estimate the sun's temperature.

[University of London]

4.63 If u is the energy density of radiation then show that the radiation pressure is given by $P_{\text{rad}} = u/3$.

4.64 If the temperature difference between the source and surroundings is small then show that the Stefan's law reduces to Newton's law of cooling.

4.65 The pressure inside the sun is estimated to be of the order of 400 million atmospheres. Estimate the temperature corresponding to such a pressure assuming it to result from the radiation.

4.66 The mass of the sun is 2×10^{30} Kg, its radius 7×10^8 m and its effective surface temperature 5,700 K.

(a) Calculate the mass of the sun lost per second by radiation.
(b) Calculate the time necessary for the mass of the sun to diminish by 1%.

4.67 Compare the rate of fall of temperature of two solid spheres of the same material and similar surfaces, where the radius of one surface is four times of the other and when the Kelvin temperature of the large sphere is twice that of the small one (Assume that the temperature of the spheres is so high that absorption from the surroundings may be ignored).

[University of London]

4.68 A cavity radiator has its maximum spectral radiance at a wavelength of 1.0 μm in the infrared region of the spectrum. The temperature of the body is now increased so that the radiant intensity of the body is doubled.

(a) What is the new temperature?
(b) At what wavelength will the spectral radiance have its maximum value? (Wien's constant $b = 2.897 \times 10^{-3}$ m-K)

4.69 In the quantum theory of blackbody radiation Planck assumed that the oscillators are allowed to have energy, $0,\ \varepsilon,\ 2\varepsilon \ldots$ Show that the mean energy of the oscillator is $\bar{\varepsilon} = \varepsilon/[\exp(\varepsilon/kT) - 1]$ where $\varepsilon = h\nu$

4.70 Planck's formula for the blackbody radiation is

$$u_\lambda \mathrm{d}\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1} \mathrm{d}\lambda$$

(a) Show that for long wavelengths and high temperatures it reduces to Rayleigh-Jeans law.
(b) Show that for short wavelengths it reduces to Wien's distribution law

4.71 Starting from Planck's formula for blackbody radiation deduce Wien's displacement law and calculate Wien's constant b, assuming the values of h, c and k.

4.72 Using Planck's formula for blackbody radiation show that Stefan's constant

$$\sigma = \frac{2}{15}\frac{\pi^5 k^4}{h^3 c^2} = 5.67 \times 10^{-8}\ \text{W.m}^{-2}.\text{K}^{-4}$$

4.73 A blackbody has its cavity of cubical shape. Determine the number of modes of vibration per unit volume in the wavelength region 4,990–5,010 A°.

[Osmania University 2004]

4.74 A cavity kept at 4,000 K has a circular aperture 5.0 mm diameter. Calculate (a) the power radiated in the visible region (0.4–0.7 μm) from the aperture (b) the number of photons emitted per second in the visible region

4.75 Planck's formula for the black body radiation is

$$u_\lambda \mathrm{d}\lambda = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda kT} - 1}\mathrm{d}\lambda$$

Express this formula in terms of frequency.

4.76 Estimate the temperature T_E of the earth, assuming that it is in radiation equilibrium with the sun (assume the radius of sun $R_s = 7 \times 10^8$ m, the earth-sun distance $r = 1.5 \times 10^{11}$ m, the temperature of solar surface $T_s = 5{,}800$ K)

4.77 Calculate the solar constant, that is the radiation power received by 1 m^2 of earth's surface. (Assume the sun's radius $R_s = 7 \times 10^8$ m, the earth-sun distance $r = 1.5 \times 10^{11}$ m, the earth's radius $R_E = 6.4 \times 10^6$ m, sun's surface temperature, $T_s = 5{,}800$ K and Stefan-Boltzmann constant $\sigma = 5.7 \times 10^{-8} \frac{\text{W}}{\text{m}^2} - \text{K}^4$).

4.78 A nuclear bomb at the instant of explosion may be approximated to a blackbody of radius 0.3 m with a surface temperature of 10^7 K. Show that the bomb emits a power of 6.4×10^{20} W.

4.3 Solutions

4.3.1 Kinetic Theory of Gases

4.1 Consider a two-body collision between two similar gas molecules of initial velocity v_1 and v_2. After the collision, let the final velocities be v_3 and v_4. The probability for the occurrence of such a collision will be proportional to the number of molecules per unit volume having these velocities, that is to the product $f(v_1)f(v_2)$. Thus the number of each collisions per unit volume per unit time is $c\ f(v_1)f(v_2)$ where c is a constant. Similarly, the number of inverse collisions per unit volume per unit time is $c'\ f(v_3)f(v_4)$ where c' is also a constant. Since the gas is in equilibrium and the velocity distribution is unchanged by collisions, these two rates must be equal. Further in the centre of mass these two collisions appear to be equivalent so that $c' = c$. We can then write

$$f(v_1)f(v_2) = f(v_3)f(v_4)$$
$$\text{or} \ln f(v_1) + \ln f(v_2) = \ln f(v_3) + \ln f(v_4) \tag{1}$$

Since kinetic energy is conserved

$$v_1^2 + v_2^2 = v_3^2 + v_4^2 \tag{2}$$

Equations (1) and (2) are satisfied if

$$\ln f(v) \propto v^2 \tag{3}$$
$$\text{or} f(v) = A\exp(-\alpha v^2) \tag{4}$$

where A and α are constants. The negative sign is essential to ensure that no molecule can have infinite energy.

Let $N(v)\mathrm{d}v$ be the number of molecules per unit volume with speeds v to $+\mathrm{d}v$, irrespective of direction. As the velocity distribution is assumed to be spherically symmetrical, $N(v)\mathrm{d}v$ is equal to the number of velocity vectors whose tips end up in the volume of the shell defined by the radii v and $+\mathrm{d}v$, so that

$$N(v)\mathrm{d}v = 4\pi v^2 f(v)\mathrm{d}v \tag{5}$$

Using (4) in (5)

$$N(v)\mathrm{d}v = 4\pi A v^2 exp(-\alpha v^2) \tag{6}$$

We can now determine A and α. If N is the total number of molecules per unit volume,

$$N = \int_0^\infty N(v)\mathrm{d}v \tag{7}$$

Using (6) in (7)

$$N = 4\pi A \int_0^\infty v^2 \exp(-\alpha v^2)\,\mathrm{d}v = 4\pi A(1/4)(\pi/\alpha^3)^{1/2}$$
$$\text{or } N = A(\pi/\alpha)^{3/2} \tag{8}$$

If E is the total kinetic energy of the molecules per unit volume

$$E = \frac{1}{2}m\int_0^\infty v^2 N(v)\mathrm{d}v = \frac{4\pi Am}{2}\int_0^\infty v^4 \exp(-\alpha v^2)\mathrm{d}v$$
$$\text{or } E = (3mA/4)(\pi^3/\alpha^5)^{1/2} \tag{9}$$

where gamma functions have been used for the evaluation of the two integrals. Further,

$$E = 3NkT/2 \tag{10}$$

Combining (8), (9) and (10)

$$\alpha = \frac{m}{2kT} \tag{11}$$

$$\text{and} \quad A = N(\alpha/\pi)^{3/2} = N(m/2\pi kT)^{3/2} \tag{12}$$

Using (11) and (12) in (5)

$$N(\nu)\mathrm{d}\nu = 4\pi N(m/2\pi kT)^{3/2}\nu^2 exp(-m\nu^2/2kT)\mathrm{d}\nu$$

4.2 $N(\nu)\mathrm{d}\nu = 4\pi N(m/2\pi kT)^{3/2}\nu^2 exp(-m\nu^2/2kT)\mathrm{d}\nu$ (1)

Put $E = \frac{1}{2}m\nu^2$, $\mathrm{d}E = m\nu \mathrm{d}\nu$ (2)

Use (2) in (1) and simplify to obtain

$$N(E)\mathrm{d}E = \frac{2\pi N E^{1/2}}{(\pi kT)^{3/2}} \exp\left(-\frac{E}{kT}\right)\mathrm{d}E$$

4.3 The average speed

$$< \nu >= \frac{\int_0^\infty \nu N(\nu)\mathrm{d}\nu}{N} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty \nu^3 \exp(-m\nu^2/2kT)\mathrm{d}\nu \tag{1}$$

where we have used the Maxwellian distribution

$$\text{Put } \alpha = \frac{m}{2kT} \tag{2}$$

$$\text{so that } \int_0^\infty \nu^3 e^{-\alpha\nu^2}\mathrm{d}\nu = \frac{1}{2\alpha^2} \tag{3}$$

Combining (1), (2) and (3)

$$< \nu >= \left(\frac{8kT}{\pi m}\right)^{1/2} = \sqrt{\frac{8RT}{M}} \tag{4}$$

where m is the mass of the molecule, M is the molecular weight and R the gas constant.

4.4 $< \nu^2 >= \dfrac{\int_0^\infty \nu^2 N(\nu)\mathrm{d}\nu}{N} = 4\pi\left(\dfrac{m}{2\pi kT}\right)^{3/2}\displaystyle\int_0^\infty \nu^4 \exp(-m\nu^2/2kT)\mathrm{d}\nu$

with $\alpha = \dfrac{m}{2kT}$ and $x = \alpha\nu^2$; $\mathrm{d}x = 2\alpha\nu\mathrm{d}\nu$

The integral, $I = \displaystyle\int_0^\infty \nu^4 e^{-\alpha\nu^2}\mathrm{d}\nu = \frac{1}{2\alpha^{5/2}}\int_0^\infty x^{3/2}e^{-x}\mathrm{d}x = \frac{3\sqrt{\pi}}{8\alpha^{5/2}}$

Therefore, $< \nu^2 >= 4\pi\left(\dfrac{m}{2\pi kT}\right)^{3/2}\dfrac{3\sqrt{\pi}}{8\left(\frac{m}{2kT}\right)^{5/2}} = \dfrac{3kT}{m}$

$$< \nu^2 >^{1/2}= (3kT/m)^{1/2}$$

4.5 (a) v_p is found by maximizing the Maxwellian distribution.

$$\frac{d}{dv}[v^2 \exp(-mv^2/2kT)] = 0$$

$$\exp(-mv^2/kT)[2v - mv^3/kT] = 0$$

whence $v = v_p = (2kT/m)^{1/2}$

(b) $v_p :< v >:< v^2 >^{1/2} :: (2kT/m)^{1/2} : (8kT/\pi m)^{1/2} : (3kT/m)^{1/2}$
$= \sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$

4.6 $$< v^2 >^{1/2} = \left(\frac{3kT}{m}\right)^{1/2} = \left(\frac{3 \times 1.38 \times 10^{-23} \times 273}{1.67 \times 10^{-27}}\right)^{1/2}$$

= 2,601 m/s at N.T.P

$$< v^2 >^{1/2} = \left(\frac{3 \times 1.38 \times 10^{-23} \times 400}{1.67 \times 10^{-27}}\right)^{1/2} = 3{,}149 \text{ m/s at } 127^\circ\text{C.}$$

4.7 $$< v^2 >^{1/2} = \left(\frac{3p}{\rho}\right)^{1/2} = \left(\frac{3 \times (300/760) \times 1.013 \times 10^5}{0.3}\right)^{1/2} = 632\,\text{m/s}$$

4.8 $$< \frac{1}{v} > = \frac{1}{N}\int_0^\infty \frac{1}{v} N(v)\,dv$$

$$= \frac{1}{N}\int_0^\infty \frac{1}{v} .4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp(-mv^2/2kT)\,dv$$

Set $mv^2/2kT = x; v dv = kT\ dx/m$

$$< \frac{1}{v} > = (2m/\pi kT)^{1/2} \int_0^\infty \exp(-x)\,dx = (2m/\pi kT)^{1/2}$$

4.9 $N(v)dv = 4\pi N(m/2\pi kT)^{3/2} v^2 \exp(-mv^2/2kT)dv$ (1)

$v_p = (2kT/m)^{1/2}$ (2)

Let $v/v_p = \alpha; dv = v_p d\alpha$ (3)

Use (2) and (3) in (1)

$$N(\alpha)d\alpha = \frac{4N}{\sqrt{\pi}} \alpha^2 \exp(-\alpha^2)d\alpha$$

4.10 Fraction

$$f = \frac{N(v)dv}{N} = 4\pi \left[\frac{m}{2\pi kT}\right]^{3/2} v^2 \exp(-mv^2/2kT)dv$$

$$v = \frac{199 + 201}{2} = 200\,\text{m/s}$$

$dv = 201 - 199 = 2\,\text{m/s}$

$$f = 4\pi\left(\frac{32 \times 1.67 \times 10^{-27}}{2\pi \times 1.38 \times 10^{-23} \times 300}\right)^{3/2}(200)^2$$
$$\exp\left(-\frac{32 \times 1.67 \times 10^{-27} \times 200^2}{2 \times 1.38 \times 10^{-23} \times 300}\right) \times (2)$$
$$= 2.29 \times 10^{-3}$$

4.11 $< v^2 >^{1/2} = \left(\frac{3kT}{m}\right)^{1/2}$

$$v_{\text{rms}}(600\ \text{K}) = [v_{\text{rms}}(300\ \text{K})](600/300)^{1/2}$$
$$= 1270 \times \sqrt{2} = 1{,}796\ \text{m/s}$$

4.12 Relative velocity v_{rel} of one molecule and another making an angle θ is

$v_{\text{rel}} = (v^2 + v^2 - 2(v)(v)\cos\theta)^{1/2} = 2v\sin(\theta/2)$

Now, all the direction of velocities v are equally probable. The probability $f(\theta)$ that v lies within an element of solid angle between θ and $\theta + \mathrm{d}\theta$ is given by

$f(\theta) = 2\pi\sin\theta\mathrm{d}\theta/4\pi = \frac{1}{2}\sin\theta\mathrm{d}\theta$

v_{rel} is obtained by integrating over $f(\theta)$ in the angular interval 0 to π.

$$< v_{\text{rel}} > = \int_0^\pi v_{\text{rel}} f(\theta) = \int_0^\pi 2v\sin\left(\frac{\theta}{2}\right)\left(\frac{1}{2}\sin\theta\mathrm{d}\theta\right)$$
$$= 2v\int_0^\pi \sin^2\left(\frac{\theta}{2}\right)\cos\frac{\theta}{2}\mathrm{d}\theta = 4v\int_0^\pi \sin^2\frac{\theta}{2}\mathrm{d}\left(\sin\frac{\theta}{2}\right) = 4v/3$$

4.13 $v_e = (2gR)^{1/2}$; $v_{\text{rms}} = (3kT/m)^{1/2}$

$v_{\text{rms}} = v_e$

$$T = \frac{2mgR}{3k} = \frac{2 \times (2 \times 23.24 \times 10^{-27})(9.8)(6.37 \times 10^6)}{3 \times 1.38 \times 10^{-23}}$$
$$= 1.4 \times 10^5\ \text{K}$$

4.14 Fraction of gas molecules that do not undergo collisions after path length x is $\exp(-x/\lambda)$. Therefore the fraction of molecules that has free path values between λ to 2λ is

$$f = \exp(-\lambda/\lambda) - \exp(-2\lambda/\lambda)$$
$$= \exp(-1) - \exp(-2)$$
$$= 0.37 - 0.14 = 0.23$$

4.15 Consider a volume element $\mathrm{d}V = 2\pi r^2\sin\theta\mathrm{d}\theta\mathrm{d}r$ located on a layer at a height $z = r\cos\theta$. If mu is the momentum of a molecule at the XY-plane at $z = 0$, then its value at $\mathrm{d}V$ will be $mu + \left(\frac{\mathrm{d}}{\mathrm{d}z}mu\right) r\cos\theta$ (Fig. 4.2). At an identical layer below the reference plane $\mathrm{d}A$, the momentum would be

$$mu - \left(\frac{\mathrm{d}}{\mathrm{d}z}mu\right) r\cos\theta$$

Let $\mathrm{d}n$ be the number of molecules with velocity between ν *and* $\nu + \mathrm{d}\nu$ per unit volume. The number of molecules with velocity ν *and* $\nu + \mathrm{d}\nu$ in the volume element $\mathrm{d}\nu$ is $\mathrm{d}n\mathrm{d}\nu$. Molecules within the volume element undergo collisions and are scattered in various directions.

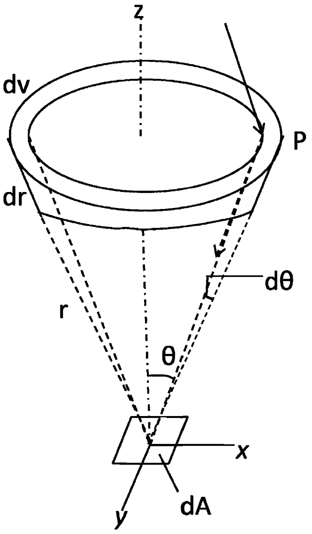

Fig. 4.2 Transport of momentum of gas molecules

Number of collisions that occur in $\mathrm{d}V$ in time $\mathrm{d}t$ will be $\frac{1}{2}\frac{\nu}{\lambda}\mathrm{d}t$. The factor $\frac{1}{2}$ is introduced to avoid counting each collision twice, since the collision between molecules 1 and 2 and that between 2 and 1 is same.

Each collision results in two new paths for the scattered molecules. Hence the number of molecules that are scattered in various directions from this volume element $\mathrm{d}V$ in time $\mathrm{d}t$ will be $2 \times \frac{1}{2}\frac{\nu}{\lambda}\mathrm{d}t \times \mathrm{d}n\mathrm{d}V$ or $\frac{\nu}{\lambda}\,\mathrm{d}t\mathrm{d}n\mathrm{d}V$.

Now the solid angle subtended by $\mathrm{d}A$ of the reference plane at $\mathrm{d}V$ is $\mathrm{d}A\cos\theta/r^2$.

Assuming the scattering to be isotropic the number of molecules moving downward toward $\mathrm{d}A$ is

$$\frac{\nu}{\lambda}\frac{\mathrm{d}t\mathrm{d}n\mathrm{d}V\mathrm{d}A\cos\theta}{4\pi r^2}$$

$$\text{or } \frac{\nu\mathrm{d}t\mathrm{d}n(2\pi r^2\sin\theta\mathrm{d}\theta\mathrm{d}r)\mathrm{d}A\cos\theta}{\lambda.4\pi r^2}$$

$$\text{or } \frac{\nu\mathrm{d}t\mathrm{d}n\mathrm{d}A\sin\theta\cos\theta}{2\lambda}$$

Transport of momentum downward from molecules in the upper hemisphere through $\mathrm{d}A$ in time $\mathrm{d}t$ is

$$P_- = \frac{\mathrm{d}A\mathrm{d}t}{2\lambda}\int_0^\infty v\mathrm{d}n\int_0^\infty e^{-r/\lambda}\mathrm{d}r\int_0^{\pi/2}\sin\theta\cos\theta\left(mu + r\cos\theta\frac{\mathrm{d}mu}{\mathrm{d}z}\right)\mathrm{d}\theta$$

The factor $e^{-r/\lambda}$ is included to ensure that the molecule in traversing the distance r toward dA does not get scattered and prevented from reaching dA.

Similarly, transport of momentum upward, from molecules in the lower hemisphere through dA in time dt is

$$P_+ = \frac{\mathrm{d}A\mathrm{d}t}{2\lambda}\int_0^\infty v\mathrm{d}n\int_0^\infty e^{-r/\lambda}\mathrm{d}r\int_0^{\pi/2}\sin\theta\cos\theta\left(mu - r\cos\theta\frac{\mathrm{d}mu}{\mathrm{d}z}\right)\mathrm{d}\theta$$

Hence net momentum transfer to the reference plane through an area dA in time dt is

$$P = P_- - P_+ = \frac{\mathrm{d}A\mathrm{d}t}{\lambda}\frac{m\mathrm{d}u}{\mathrm{d}z}\int_0^\infty v\mathrm{d}n\int_0^\infty re^{-r/\lambda}\mathrm{d}r\int_0^{\pi/2}\cos^2\theta\sin\theta\mathrm{d}\theta$$

$$= \frac{\mathrm{d}A\mathrm{d}t}{\lambda}m\frac{\mathrm{d}u}{\mathrm{d}z}n < v > \frac{\lambda^2}{3}$$

$$= \frac{m}{3}\mathrm{d}A\mathrm{d}t\frac{\mathrm{d}u}{\mathrm{d}z}\lambda n < v >$$

(the first integral gives $n < v >$, the second one λ^2 and the third one a factor 1/3)

Momentum transported per second is force

$$F = \frac{\lambda}{3}\mathrm{d}An < v > m\frac{\mathrm{d}u}{\mathrm{d}z}$$

The viscous force is

$$\eta\mathrm{d}A\frac{\mathrm{d}u}{\mathrm{d}z} = \frac{\lambda}{3}\mathrm{d}An < v > m\frac{\mathrm{d}u}{\mathrm{d}z}$$

or $\eta = \frac{1}{3}mn < v > \lambda = \frac{1}{3}\rho < v > \lambda$

where $mn = \rho =$ density of molecules.

4.16 $\lambda = \frac{1}{\sqrt{2}\pi n\sigma^2} = \frac{1}{\sqrt{2}\pi \times 3 \times 10^{25} \times (2.5 \times 10^{-10})^2}$

$= 1.2 \times 10^{-7}$ m

$$f = \frac{v}{\lambda} = \frac{1,000}{1.2 \times 10^{-7}} = 8.33 \times 10^9\ \mathrm{s}^{-1}$$

4.17 $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}, \quad \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \frac{T_1}{T_2}$

or $2^{\gamma-1} = 1.32, \quad \gamma = 1.4$

Number of degrees of freedom,

$$f = \frac{2}{\gamma - 1} = \frac{2}{1.4 - 1} = 5$$

4.18 $1\text{eV} = kT$

$$T = \frac{1eV}{k} = \frac{1.6 \times 10^{-19} J}{1.38 \times 10^{-23} J/K} = 11{,}594\,\text{K}$$

4.19 (a) For a perfect gas at temperature T, the kinetic energy from translation motion

$$\frac{1}{2}m < v_x^2 > + \frac{1}{2}m < v_y^2 > + \frac{1}{2}m < v_z^2 >= \frac{3}{2}\frac{RT}{N_0} \tag{1}$$

where R is the gas constant and N_0 is Avagadro's number. The energy of the 3 degrees of freedom of translation is therefore on the average equal to $\frac{3}{2}RT/N_0$ for each molecule. Using this result together with the principle of the equipartition of energy, it is concluded that in a system at temperature T each degree of freedom contributes, $\frac{1}{2}\frac{R}{N_0}T$ to the total energy.

If each molecule has n degrees of freedom, the total internal energy U of a gram-molecule of a perfect gas at temperature T,

$$U = \frac{1}{2}nRT \tag{2}$$

The molecular heat at constant volume C is equal to $\left(\frac{\partial U}{\partial T}\right)_v$, and is therefore given by

$$C_v = \frac{1}{2}nR \tag{3}$$

For a perfect gas

$$C_p - C_v = R \tag{4}$$

$$\text{Therefore } C_p = C_v + R = \frac{(n+2)R}{2} \tag{5}$$

$$\text{and } \gamma = \frac{C_p}{C_v} = 1 + \frac{2}{n} \tag{6}$$

(b) For monatomic molecule $n = 3$, for translation (rotation and vibration are absent), $\gamma = 1.667$.

For diatomic molecule $n = 5$ (3 from translation and only 2 from rotation as the rotation about an axis joining the centres of atoms does not contribute) and $\gamma = 1.4$

If vibration is included then $n = 7$ and $\gamma = 1.286$

4.20 According to Chapman and Enskog

$$K = \frac{\eta}{m}\left[\frac{5}{2}\frac{d\overline{E}_t}{dT} + \frac{d\overline{E}'}{dT}\right] \tag{1}$$

where $\overline{E}_t$ is the translational energy and $\overline{E}'$ the energy of other types.

If β denotes the number of degrees of freedom of the molecule due to causes other than translation, the total number of degrees of freedom of the molecule will be $3 + \beta$.

From the law of equipartition of energy we have

$$\frac{\mathrm{d}\overline{E}_t}{\mathrm{d}T} = \frac{3}{2}k; \frac{\mathrm{d}\overline{E}'}{\mathrm{d}T} = \frac{\beta}{2}k \tag{2}$$

Hence,

$$\frac{K}{\eta} = \left[\frac{5}{2}.\frac{3}{2} + \frac{\beta}{2}\right]\frac{k}{m} \tag{3}$$

We can express the result in terms of C_v and γ. From the law of equipartition of energy

$$C_v = \frac{(3+\beta)}{2}.\frac{k}{m}; \quad C_p = \frac{(5+\beta)}{2}.\frac{k}{m}$$

whence $\gamma = \dfrac{C_p}{C_v} = 1 + \dfrac{2}{3+\beta}$

$$\text{or } \beta = \frac{5-3\gamma}{\gamma-1} \tag{4}$$

Furthermore

$$C_v = \frac{k}{m(\gamma-1)} \tag{5}$$

Combining (3), (4) and (5)

$$\frac{K}{\eta C_v} = \frac{1}{4}(9\gamma - 5)$$

4.3.2 Maxwell's Thermodynamic Relations

4.21 Let $f(x, y) = 0$ (1)

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y = 0 \tag{2}$$

Equation of state can be written as $f(P, V, T) = 0$. By first law of thermodynamics

$$\mathrm{d}Q = \mathrm{d}U + \mathrm{d}W \tag{3}$$

By second law of thermodynamics

$$\mathrm{d}Q = T\mathrm{d}s \tag{4}$$

for infinitesimal reversible process

$$\mathrm{d}W = p\mathrm{d}V \tag{5}$$

Therefore,

$$\mathrm{d}U = T\mathrm{d}s - P\mathrm{d}V \tag{6}$$

where U is the internal energy, Q the heat absorbed, W the work done by the system, S the entropy, P the pressure and T the Kelvin temperature.
Let the independent variables be called x and y. Then

$$U = U(x, y); V = V(x, y); S = S(x, y) \tag{7}$$

Now,

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y \tag{8}$$

Therefore

$$\mathrm{d}U = \left(\frac{\partial U}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial U}{\partial y}\right)_x \mathrm{d}y \tag{9}$$

$$\mathrm{d}V = \left(\frac{\partial V}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial V}{\partial y}\right)_x \mathrm{d}y \tag{10}$$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial S}{\partial y}\right)_x \mathrm{d}y \tag{11}$$

Eliminating internal energy U and substituting (9), (10) and (11) in (6)

$$\left(\frac{\partial U}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial U}{\partial y}\right)_x \mathrm{d}y = T\left[\left(\frac{\partial S}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial S}{\partial y}\right)_x \mathrm{d}y\right]$$
$$-P\left[\left(\frac{\partial V}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial V}{\partial y}\right)_x \mathrm{d}y\right] \tag{12}$$

Equating the coefficients of dx and dy

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y \tag{13}$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x \tag{14}$$

Differentiating (13) with respect to y with x fixed, and differentiating (14) with respect to x with y fixed

$$\left\{\frac{\partial}{\partial y}\left(\frac{\partial U}{\partial x}\right)_y\right\}_x = \left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y + T\left\{\frac{\partial}{\partial y}\left(\frac{\partial S}{\partial x}\right)_y\right\}_x - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y - P\left\{\frac{\partial}{\partial y}\left(\frac{\partial V}{\partial x}\right)_y\right\}_x \tag{15}$$

$$\left\{\frac{\partial}{\partial x}\left(\frac{\partial U}{\partial y}\right)_x\right\}_y = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x + T\left\{\frac{\partial}{\partial x}\left(\frac{\partial S}{\partial y}\right)_x\right\}_y - \left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x - P\left\{\frac{\partial}{\partial x}\left(\frac{\partial V}{\partial y}\right)_x\right\}_y \tag{16}$$

Since the order of differentiation is immaterial, dU being a perfect differential, the left hand sides of (15) and (16) are equal. Further, since dS and dV are perfect differentials.

$$\left\{\frac{\partial}{\partial y}\left(\frac{\partial S}{\partial x}\right)_y\right\}_x = \left\{\frac{\partial}{\partial x}\left(\frac{\partial S}{\partial y}\right)_x\right\}_y \tag{17}$$

and

$$\left\{\frac{\partial}{\partial y}\left(\frac{\partial V}{\partial x}\right)_y\right\}_x = \left\{\frac{\partial}{\partial x}\left(\frac{\partial V}{\partial y}\right)_x\right\}_y \tag{18}$$

Using (15), (16), (17), and (18),

$$\left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y \tag{19}$$

Equation (19) can be written in the form of determinants

$$\begin{vmatrix} \left(\frac{\partial P}{\partial x}\right)_y & \left(\frac{\partial P}{\partial y}\right)_x \\ \left(\frac{\partial V}{\partial x}\right)_y & \left(\frac{\partial V}{\partial y}\right)_x \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial T}{\partial x}\right)_y & \left(\frac{\partial T}{\partial y}\right)_x \\ \left(\frac{\partial S}{\partial x}\right)_y & \left(\frac{\partial S}{\partial y}\right)_x \end{vmatrix} \tag{20}$$

(a) Let the temperature and volume be independent variables. Put $x = T$ and $y = V$ in (20). Then

$$\left(\frac{\partial T}{\partial x}\right)_y = \left(\frac{\partial V}{\partial y}\right)_x = 1; \quad \left(\frac{\partial T}{\partial y}\right)_x = \left(\frac{\partial V}{\partial x}\right)_y = 0$$

Since T and V are independent, we find

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{21}$$

(b) Let the temperature and pressure be independent variables. Put $x = T$ and $y = P$ in (20).

$$\left(\frac{\partial T}{\partial x}\right)_y = \left(\frac{\partial P}{\partial y}\right)_x = 1; \quad \left(\frac{\partial T}{\partial y}\right)_x = \left(\frac{\partial P}{\partial x}\right)_y = 0$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{22}$$

4.22 In Problem 4.21 let the entropy and volume be independent variables. Put $x = s$ and $y = V$ in Eq. (19)

$$\left(\frac{\partial S}{\partial x}\right)_y = \left(\frac{\partial V}{\partial y}\right)_x = 1; \quad \left(\frac{\partial S}{\partial y}\right)_x = \left(\frac{\partial V}{\partial x}\right)_y = 0 \quad \left(\frac{\partial T}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial S}\right)_V \tag{23}$$

4.23 Let the entropy and pressure be independent variables. Put $x = s$ and $y = p$ in Eq. (19) of Problem 4.21.

$$\left(\frac{\partial S}{\partial x}\right)_y = \left(\frac{\partial P}{\partial y}\right)_x = 1$$

Therefore,

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial V}{\partial S}\right)_p \tag{24}$$

4.24 Consider Maxwell's relation (21) of Problem 4.21

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{1}$$

Multiply both sides by T,

$$T\left(\frac{\partial S}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \tag{2}$$

$$\text{or} \quad \left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \tag{3}$$

which means that the latent heat of isothermal expansion is equal to the product of the absolute temperature and the rate of increase of pressure with temperature at constant volume. Apply (3) to the phase transition of a substance. Consider a vessel containing a liquid in equilibrium with its vapor. The pressure is due to the saturated vapor pressure which is a function of temperature only and is independent of the volume of liquid and vapor present. If the vessel is allowed to expand at constant temperature the vapor pressure would remain constant. However, some liquid of mass δm would evaporate to fill the extra space with vapor. If L is the latent heat absorbed per unit mass,

$$\delta Q = L\mathrm{d}m \tag{4}$$

If ν_1 and ν_2 are the specific volumes (volumes per unit mass) of the liquid and vapor respectively

$$\delta \nu = (\nu_2 - \nu_1)\mathrm{d}m \tag{5}$$

Using (4) and (5) in (3)

$$\frac{L}{\nu_2 - \nu_1} = T\left(\frac{\partial P}{\partial T}\right)_V \tag{6}$$

Here, various thermodynamic quantities refer to a mixture of the liquid and vapor in equilibrium. In this case

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial V}{\partial T}\right)_{\text{sat}}$$

since the pressure is due to the saturated vapor and is therefore independent of V, being only a function of T. Thus (6) can be written as

$$\left(\frac{\partial P}{\partial T}\right)_{\text{sat}} = \frac{L}{T(\nu_2 - \nu_1)} \quad \text{(Clapeyron's equation)} \tag{7}$$

4.25 $$L = T(\nu_2 - \nu_1)\frac{\mathrm{d}P}{\mathrm{d}T}$$
$$= 373.2(1{,}674 - 1) \times \left(\frac{2.71}{76}\right) \times 1.013 \times 10^6$$
$$= 2.255 \times 10^{10}\,\text{erg g}^{-1}$$
$$= 2.255\,\text{J/g}$$
$$= \frac{2.255}{4.18} = 539.5\,\text{cal/g}$$

4.26 $$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{1}$$

Substitute

$$\mathrm{d}S = \frac{\mathrm{d}U + P\mathrm{d}V}{T} \tag{2}$$

in (1)

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{3}$$

If u is the energy density and P the total pressure, $\left(\frac{\partial U}{\partial V}\right) = u$ and the total pressure $P = u/3$, since the radiation is diffuse. Hence (3) reduces to

$$u = \frac{T}{3}\frac{\partial u}{\partial T} - \frac{u}{3} \quad \text{or} \quad \frac{\mathrm{d}u}{u} + 4\frac{\mathrm{d}T}{T} = 0$$

Integrating,

$\ln\ u = 4\ln T + \ln a = \ln aT^4$

where $\ln a$ is the constant of integration. Thus,

$u = aT^4$

4.27 $S = f(T, V)$

where T and V are independent variables.

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Multiplying out by T and re-arranging

$$T\left(\frac{\partial S}{\partial T}\right)_p - T\left(\frac{\partial S}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Now,

$$T\left(\frac{\partial S}{\partial T}\right)_p = C_p; \quad T\left(\frac{\partial S}{\partial T}\right)_v = C_v$$

and from Maxwell's relation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

Therefore,

$$C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \tag{1}$$

For one mole of a perfect gas, $PV = RT$. Therefore

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \text{ and } \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

It follows that

$$C_p - C_v = RT$$

4.28 $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ (1)

Neglecting b in comparison with V,

$$P = \frac{RT}{V} - \frac{a}{V^2} \tag{2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \tag{3}$$

Re-writing (1)

$$PV + \frac{a}{V} = RT$$

Differentiating V with respect to T, keeping P fixed

$$P\left(\frac{\partial V}{\partial T}\right)_P - \frac{a}{V^2}\left(\frac{\partial V}{\partial T}\right)_P = R$$

or

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P - a/V^2} \tag{4}$$

Now,

$$C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \tag{5}$$

(By Problem 4.27)

Using (3) and (4) in (5)

$$\begin{aligned} C_p - C_v &= \frac{R^2 T}{V(P - a/V^2)} = R\frac{(P + a/V^2)}{(P - a/V^2)} \approx R(1 + 2a/PV^2) \\ &= R\left(1 + \frac{2a}{RTV}\right) \end{aligned}$$

4.29 If $f(x, y, z) = 0$, then it can be shown that

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{1}$$

Thus, if $f(P, V, T) = 0$

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1 \tag{1}$$

$$\text{or } \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \tag{2}$$

$$\text{and } \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \tag{3}$$

But

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \tag{4}$$

Use (2) and (3) in (4)

$$C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P^2 \tag{5}$$

$$C_P - C_V = -T\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V^2 \tag{6}$$

Equation (5) can be written in terms of the bulk modulus E at constant temperature and the coefficient of volume expansion $\propto$.

$$E = -\left(\frac{\partial P}{\partial V/V}\right); \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right) \tag{7}$$

$$C_p - C_v = TE\alpha^2 V \tag{8}$$

4.30 Taking T and V as independent variables

$$S = f(T, V)$$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + T\left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$$

Multiplying by T,

$$\begin{aligned} T\mathrm{d}S &= T\left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + T\left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V \\ &= C_V \mathrm{d}T + T\left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V \end{aligned}$$

But $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$

$$\therefore T\mathrm{d}S = C_V \mathrm{d}T + T\left(\frac{\partial P}{\partial T}\right)_V \mathrm{d}V$$

Also,

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore T\mathrm{d}S = C_V \mathrm{d}T - T\left(\frac{\partial P}{\partial V}\right)\left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}V$$

Introducing relations $\alpha = \frac{1}{V}(\partial V/\partial T)_P$ and $E_T = -V(\partial P/\partial V)_T$ for volume coefficient of expansion and isothermal elasticity

$$T\mathrm{d}S = C_V \mathrm{d}T + T\alpha E_T \mathrm{d}V$$

4.31 Taking T and P as independent variables

$$S = f(T, P)$$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial S}{\partial P}\right)_T \mathrm{d}P$$

$$\text{or } T\mathrm{d}S = T\left(\frac{\partial S}{\partial T}\right)_P \mathrm{d}T + T\left(\frac{\partial S}{\partial P}\right)_T \mathrm{d}P$$

$$= C_P\mathrm{d}T + T\left(\frac{\partial S}{\partial P}\right)_T \mathrm{d}P$$

$$\text{or } T\mathrm{d}S = C_P\mathrm{d}T - T\left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}P$$

$$= C_P\mathrm{d}T - TV\alpha\mathrm{d}P$$

4.32 Taking P and V as independent variables,

$$S = f(P, V)$$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial P}\right)_V \mathrm{d}P + \left(\frac{\partial S}{\partial V}\right)_P \mathrm{d}V$$

$$T\mathrm{d}S = T\left(\frac{\partial S}{\partial P}\right)_V \mathrm{d}P + T\left(\frac{\partial S}{\partial V}\right)_P \mathrm{d}V$$

$$= T\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V \mathrm{d}P + T\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P \mathrm{d}V$$

$$= C_V\left(\frac{\partial T}{\partial P}\right)_V \mathrm{d}P + C_P\left(\frac{\partial T}{\partial V}\right)_P \mathrm{d}V$$

4.33 In the Joule–Thompson effect heat does not enter the expanding gas, that is $\Delta Q = 0$. The net work done by the external forces on a unit mass of the gas is $(P_1V_1 - P_2V_2)$, where P_1 and P_2 refer to higher and lower pressure across the plug respectively.

$$\Delta W = P_1V_1 - P_2V_2$$

If the internal energy of unit mass is U_1 and U_2 before and after the gas passes through the plug

$$\Delta U = U_1 - U_2$$

By the first law of Thermodynamics

$$\Delta Q = 0 = \Delta W + \Delta U$$

$$\text{or} \quad U_2 - U_1 = P_1V_1 - P_2V_2$$

$$\text{or} \quad \Delta(U + PV) = 0$$

$$\text{or} \quad \Delta H = 0$$

where H is the enthalpy

$$\therefore T\Delta S + V\Delta P = 0$$

But by Problem 4.31

$$T\Delta S = C_P\Delta T - T\left(\frac{\partial V}{\partial T}\right)_P \Delta P$$

$$\therefore C_P\Delta T + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]\Delta P = 0$$

$$\text{or} \quad \Delta T = \frac{\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]\Delta P}{C_P}$$

4.34 (a) For perfect gas

$$PV = RT$$

$$P\left(\frac{\partial V}{\partial T}\right)_P = R$$

$$T\left(\frac{\partial V}{\partial T}\right)_P = \frac{TR}{P} = V$$

$$\text{or } T\left(\frac{\partial V}{\partial T}\right)_P - V = 0$$

$\therefore \Delta T = 0$ by Problem 4.31

(b) For imperfect gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$\text{or } PV = RT - \frac{a}{V} + bP + \frac{ab}{V^2}$$

$$P\left(\frac{\partial V}{\partial T}\right)_P = R + \frac{a}{V^2}\left(\frac{\partial V}{\partial T}\right)_P - \frac{2ab}{V^3}\left(\frac{\partial V}{\partial T}\right)_P$$

Re-arranging

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P - \frac{a}{V^2} + \frac{2ab}{V^3}} = \frac{R}{\frac{RT}{V-b} - \frac{2a}{V^2}\left(1 - \frac{b}{V}\right)}$$

Multiplying both numerator and denominator of RHS by $(V - b)/R$

$$T\left(\frac{\partial V}{\partial T}\right)_P = (V - b)\left[1 - \frac{2a}{RTV^3}(V - b)^2\right]^{-1}$$

$$= (V - b)\left[1 + \frac{2a}{RTV^3}(V - b)^2\right]$$

$$= (V - b) + \frac{2a}{RTV^3}(V - b)^3$$

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{2a}{RT} - b \qquad (\because b \ll V)$$

Using this in the expression for Joule–Thompson effect (Problem 4.31),

$$\Delta T = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)\Delta P$$

4.35 The equation of state for an imperfect gas is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

It can be shown that

$$\Delta T = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)\Delta p$$

If $T < 2a/bR$, $\Delta T/\Delta p$ is positive and there will be cooling.

If $T > 2a/bR$, $\Delta T/\Delta p$ will be negative and the gas is heated on undergoing Joule–Kelvin expansion.

If $T = 2a/bR$, $\Delta T/\Delta p = 0$, there is neither heating nor cooling.

The temperature given by $T_i = \frac{2a}{bR}$ is called the temperature of inversion since on passing through this temperature the Joule–Kelvin effect changes its sign. Figure 4.3 shows the required curve.

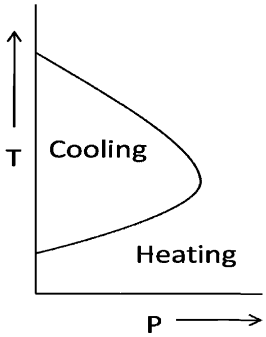

Fig. 4.3 Joule-Thompson effect

4.36 By definition

$$E_T = -V\left(\frac{\partial P}{\partial V}\right)_T ; E_S = -V\left(\frac{\partial P}{\partial V}\right)_S$$

$$\frac{E_S}{E_T} = \frac{(\partial P/\partial V)_S}{(\partial P/\partial V)_T} = \frac{(\partial P/\partial V)_S \left(\dfrac{\partial T}{\partial V}\right)_S}{(\partial P/\partial S)_T \left(\dfrac{\partial S}{\partial V}\right)_T}$$

$$= \frac{(\partial T/\partial V)_S \left(\dfrac{\partial S}{\partial P}\right)_T}{(\partial T/\partial P)_S \left(\dfrac{\partial S}{\partial V}\right)_T} = \frac{(\partial P/\partial S)_V(\partial V/\partial T)_P}{(\partial V/\partial S)_P(\partial P/\partial T)_V}$$

from the relations given in Problems 4.21 and 4.22

$$\therefore \frac{E_S}{E_T} = \frac{(\partial S/\partial T)_P}{(\partial S/\partial T)_V} = \frac{(\partial Q/\partial T)_P}{(\partial Q/\partial T)_V} = \frac{C_P}{C_V} = \gamma$$

4.37 $$\frac{(\partial V/\partial T)_S}{(\partial V/\partial T)_P} = \frac{1}{(\partial T/\partial V)_S(\partial V/\partial T)_P} = \frac{1}{-\left(\dfrac{\partial P}{\partial S}\right)_V \left(\dfrac{\partial V}{\partial T}\right)_P}$$

where we have used Eq. (23) of Problem 4.22.
Writing

$$\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_V = \frac{(\partial P/\partial T)_V}{(\partial S/\partial T)_V}$$

$$\frac{(\partial V/\partial T)_S}{(\partial V/\partial T)_P} = \frac{(\partial S/\partial T)_V}{(\partial P/\partial T)_V(\partial V/\partial T)_P} = \frac{(\partial S/\partial T)_V}{-(C_P - C_V)/T}$$

(by Eq. (4.1) of Problem 4.27

$$\frac{T(\partial S/\partial T)_V}{-(C_P - C_V)} = \frac{C_V}{-(C_P - C_V)} = \frac{1}{1-\gamma}$$

4.38 $$\frac{(\partial P/\partial T)_S}{(\partial P/\partial T)_V} = \frac{1}{(\partial T/\partial P)_S(\partial P/\partial T)_V} = \frac{1}{\left(\dfrac{\partial V}{\partial S}\right)_P \left(\dfrac{\partial P}{\partial T}\right)_V}$$

$$= \frac{1}{\left(\dfrac{\partial V}{\partial T}\right)_P \left(\dfrac{\partial T}{\partial S}\right)_P \left(\dfrac{\partial P}{\partial T}\right)_V} = \frac{(\partial S/\partial T)_P}{\left(\dfrac{\partial V}{\partial T}\right)_P (\partial P/\partial T)_V}$$

$$= \frac{T(\partial S/\partial T)_P}{(C_P - C_V)} = \frac{C_P}{(C_P - C_V)} = \frac{\gamma}{\gamma - 1}$$

where we have used Eq. (4.24) of Problem 4.22 and the relation

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

4.39 By Maxwell's first equation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{1}$$

$$\mathrm{d}S = \frac{\mathrm{d}U + P\mathrm{d}V}{T} \tag{2}$$

using (2) in (1)

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right) - P$$

For perfect gases,

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

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

Thus, temperature remaining constant, the internal energy of an ideal gas is independent of the volume.

4.40 $$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L}{T(\nu_2 - \nu_1)}$$

$$\mathrm{d}T = \frac{T}{L}(\nu_2 - \nu_1)\mathrm{d}P$$

$$= \frac{373(1677 - 1)(2 \times 10^6)}{546 \times 4.2 \times 10^7} = 55.1^\circ\mathrm{C}$$

4.41 $$\nu_1 = 1\ \mathrm{cm}^3;\ \nu_2 = \frac{1}{0.091} = 10.981\ \mathrm{cm}^3$$

$$\mathrm{d}P = \frac{L\mathrm{d}T}{T(\nu_2 - \nu_1)} = \frac{80 \times 4.2 \times 10^7 \times 1}{(-1 + 273)(10.981 - 1.0)}$$

$$= 1.238 \times \frac{10^6\mathrm{dynes}}{\mathrm{cm}^2} = 1.24\ \mathrm{atm}$$

$$P_2 = P_1 + \mathrm{d}P = 1.0 + 1.24 = 2.24\ \mathrm{atm}$$

4.42 $$\nu_1 = \frac{1}{\rho_1} = \frac{1}{1.145} = 0.873\ \mathrm{cm}^3/\mathrm{g}$$

$$\nu_2 = \frac{1}{\rho_2} = \frac{1}{0.981} = 1.019\ \mathrm{cm}^3/\mathrm{g}$$

$$\mathrm{d}T = \frac{T(\nu_2 - \nu_1)\mathrm{d}P}{L}$$

$$= \frac{(80 + 273)(1.019 - 0.873)(1.0 \times 10^6)}{35.5 \times 4.2 \times 10^7}$$

$$= 0.0346^\circ\mathrm{C}$$

4.43 (a) Use the relation

$$dU = Tds - PdV \tag{1}$$

Here,

$dV = 0(\because V = \text{constant})$ and

$$U = aVT^4 \tag{2}$$

$$dU = 4aVT^3 dT = Tds$$

$$\left(\frac{ds}{dT}\right)_V = 4aVT^2$$

Integrating $S = \frac{4}{3}aT^3V$

(b) $F = U - TS = aVT^4 - \dfrac{4}{3}aT^4V = -\dfrac{1}{3}aVT^4$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{1}{3}aT^4 = \frac{1}{3}u$$

4.44 According to Dulong-Petit's law the molar specific heats of all substances, with a few exceptions like carbon, have values close to 6 cal/mol°C^{-1}. The specific heat of Cu is $\frac{387}{\text{kgK}^{-1}} = \frac{0.387\text{J}}{\text{gK}^{-1}} = 0.0926\text{cal/gK}^{-1}$. Therefore, the atomic mass of Cu $= \frac{6}{0.0926} = 64.79$ amu.

4.3.3 Statistical Distributions

4.45 Probability for the rotational state to be found with quantum number J is given by the Boltzmann's law.

$P(E) \propto (2J + 1)\exp[-J(J + 1)\hbar^2/2I_0kT$

where I_0 is the moment of inertia of the molecule, k is Boltzmann's constant, and T the Kelvin temperature. The two lowest states have $J = 0$ and $J = 1$

$I_0 = M(r/2)^2 + M(r/2)^2 = \dfrac{1}{2}Mr^2$, where $M = 938\ \text{MeV/c}^2$

$2I_0 = Mr^2 = 938 \times (1.05 \times 10^{-10})^2/c^2$

$\hbar c = 197.3\,\text{MeV} - 10^{-15}\text{m}$

$$kT = 1.38 \times 10^{-23} \times \frac{50}{1.6 \times 10^{-13}} = 43.125 \times 10^{-10}$$

$$\frac{\hbar^2}{2I_0kT} = \frac{\hbar^2c^2}{Mc^2r^2kT} = \frac{(197.3)^2 \times 10^{-30}}{938 \times (1.05 \times 10^{-10})^2 \times 43.125 \times 10^{-10}} = 0.8728$$

For $J = 1$, $\dfrac{J(J+1)\hbar^2}{2kT} = 1 \times (1 + 1) \times 0.8728 = 1.7457$

For $J = 0$, $P(E_0) \propto 1.0$

For $J = 1$, $P(E_1) \propto (2 \times 1 + 1)\exp(-1.7457) = 0.52$

$\therefore P(E_0) : P(E_1) :: 1 : 0.52$

4.46 For stationary waves, in the x-direction

$k_x a = n_x \pi$

or $n_x = k_x a/\pi$

$\mathrm{d}n_x = (a/\pi)\mathrm{d}k_x$

Similar expressions are obtained for y and z directions.

$$\mathrm{d}n = \mathrm{d}n_x \mathrm{d}n_y \mathrm{d}n_z$$
$$= (a/\pi)^3 \mathrm{d}^3 k$$

However only the first octant of number space is physically meaningful. Therefore

$\mathrm{d}n = (1/8)(a/\pi)^3 \mathrm{d}^3 k$

Taking into account the two possible polarizations

$$\mathrm{d}n = \frac{2V}{(2\pi)^3}\mathrm{d}^3 k = \frac{2V}{8\pi^3}.4\pi k^2 \mathrm{d}k$$

But $k = \dfrac{\omega}{c}$; $\mathrm{d}k = \mathrm{d}\omega/c$

$$\therefore dn = \frac{V\omega^2 d\omega}{\pi^2 c^3}$$

4.47 $n! = n(n-1)(n-2)\ldots(4)(3)(2)$

Take the natural logarithm of n!

$$\ln n! = \ln 2 + \ln 3 + \ln 4 + \cdots + \ln(n-2) + \ln(n-1) + \ln n$$
$$= \Sigma_{n=1}^{n} \ln n$$
$$= \int_1^n \ln n \, dn$$
$$= n \ \ln n - n + 1$$
$$\approx n \ \ln n - n$$

where we have neglected 1 for $n \gg 1$

4.48 $p(E) = (2J+1)e^{-J(J+1)\hbar^2/2ikT}$

The maximum value of $p(E)$ is found by setting $\mathrm{d}p(E)/\mathrm{d}J = 0$

$$\left[2 - \frac{(2J+1)^2\hbar^2}{2I_0 kT}\right] e^{-J(J+1)\hbar^2/2I_0 kT} = 0$$

Since the exponential factor will be zero only for $J = \infty$,

$$\left[2 - \frac{(2J+1)^2\hbar^2}{2I_0 kT}\right] = 0$$

Solving for J, we get

$$J_{\max} = \frac{\sqrt{I_0 kT}}{\hbar} - \frac{1}{2}$$

4.49 $p(E_J) = (2j+1)e^{\frac{-J(J+1)\hbar^2}{2I_0kT}}$

The factor $\dfrac{\hbar^2}{2I_0k} = \dfrac{(1.055\times10^{-34})^2}{2\times4.64\times10^{-48}\times1.38\times10^{-23}\text{ J}} = 86.9$

$p(E_0) = 1$

$p(E_1) = 3e^{-2\times86.9/400} = 1.942$

$p(E_2) = 5e^{-6\times86.9/400} = 1.358$

$p(E_3) = 7e^{-12\times86.9/400} = 0.516$

4.50 $$p(E_2) = 5e^{-6\times86.9/T} = 5e^{-521.4/T} \tag{1}$$

$p(E_3) = 7e^{-12\times86.9/T} = 7e^{-1042.8/T}$

Equating $p(E_2)$ and $p(E_3)$ and solving for T, we find $T = 1{,}549$ K

4.51 For Boltzmann statistics $p(E) \propto e^{-E/kT}$ Therefore,

$\dfrac{p(E_n)}{p(E_1)} = e^{-(E_n-E_1)/kT}$

In hydrogen atom, if the ground state energy $E_1 = 0$, then $E_2 = 10.2$, $E_3 = 12.09$ and $E_4 = 12.75$ eV

The factor $kT = 8.625\times10^{-5}\times6{,}000 = 0.5175$

$P(E_2)/P(E_1) = e^{-10.2/0.5175} = 2.75\times10^{-9}$

$P(E_3)/P(E_1) = e^{-12.09/0.5175} = 1.4\times10^{-10}$

$P(E_4)/P(E_1) = e^{-12.75/0.5175} = 1.99\times10^{-11}$

Thus $P(E_1) : P(E_2) : P(E_3) :: 1 : 2.8\times10^{-9} : 1.4\times10^{-10} : 2.0\times10^{-11}$

This then means that the hydrogen atoms in the chromospheres are predominantly in the ground state.

4.52 $p(E) = \dfrac{1}{e^{(E-E_F)/kT}+1}$

For $E - E_F = kT$, $p(E) = \dfrac{1}{e+1} = 0.269$

For $E - E_F = 5kT$, $p(E) = \dfrac{1}{e^5+1} = 6.69\times10^{-3}$

For $E - E_F = 10kT$, $p(E) = \dfrac{1}{e^{10}+1} = 4.54\times10^{-5}$

4.53 For the conduction electrons, the number of states per unit volume with energy in the range E and $E+\mathrm{d}E$, can be written as $n(E)\mathrm{d}E$ where $n(E)$ is the density of states. Now, for a free electron gas

$n(E) = \dfrac{8\sqrt{2}\pi m^{3/2}}{h^3}E^{1/2}$

Let $P(E)$ be the probability function which gives the probability of the state at the energy E to be occupied. At $T = 0$ all states below a certain energy are filled ($P = 1$) and all states above that energy are vacant ($P = 0$). The highest occupied state under the given conditions is called the Fermi energy.
The product of the density $n(E)$ of available states and the probability $P(E)$ that those states are occupied, gives the density of occupied states $n_0(E)$; that is

$$n_0(E) = n(E)P(E)$$

The total number of occupied states per unit volume is given by

$$\begin{aligned} n &= \int_0^{E_\mathrm{F}} n_0(E)\mathrm{d}E \\ &= \frac{8\sqrt{2}\pi m^{3/2}}{h^3} \int_0^{E_\mathrm{F}} E^{1/2}\mathrm{d}(E) \\ &= \frac{8\sqrt{2}\pi m^{3/2}}{h^3} \cdot \frac{2}{3} E_F^{3/2} \\ \text{or} \quad E_F &= \frac{h^2}{8m}\left(\frac{3n}{\pi}\right)^{2/3} \end{aligned}$$

4.54 $P_+ = \dfrac{1}{e^{(E-E_F)/kT}+1} = \dfrac{1}{e^{\Delta/kT}+1} \approx \dfrac{1}{2+\Delta/kT} = \dfrac{1}{2}(1-\Delta/2kT)$

$$P- = \frac{1}{2}(1+\Delta/2kT)$$

$$\therefore \frac{P_+ + P_-}{2} = 1/2 = P_\mathrm{F}$$

4.55 (a) For n states, the number of ways is $N = n^2$. Therefore, for $n = 6$ states $N = 36$

(b) For n states the number of ways is $N = n^2-(n-1) or n^2-n+1$. Therefore, for $n = 6$, $N = 31$

(c) For n states, $N = n^2 - n + 1 - n \; or \; n^2 - 2n + 1$. Therefore for $n = 6$, $N = 25$

4.56 If the gas is in equilibrium, the number of particles in a vibrational state is

$$N_\nu = N_0 \exp\left(-\frac{h\nu}{kT}\right) = N_0 \exp\left(-\frac{\theta}{T}\right).$$

The ratios, $N_0/N_1 = 4.7619$, $N_1/N_2 = 4.8837$, $N_2/N_3 = 4.7778$, are seen to be constant at 4.8078. Thus the ratio $N_\nu/N_{\nu+1}$ is constant equal to 4.81, showing the gas to be in equilibrium at a temperature
$T = 3,350/(\ln 4.81) \approx 2,130$ K

4.57 $\Delta S = k \ln(\Delta W)$
But $\Delta S = \Delta Q/T$

or $\Delta Q = T\Delta S = kT \ln \Delta W$
$= (1.38 \times 10^{-23})(300) \ln 10^8$
$= 7.626 \times 10^{-20}\text{J} = 0.477$ eV

4.58 The Gaussian (normal) distribution is

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}$$

where μ is the mean and σ is the standard deviation. The probability is found from

(a) $P(\mu - \sigma < x < \mu + \sigma) = \int_{\mu-\sigma}^{\mu+\sigma} f(x)\mathrm{d}x$

Letting $z = \frac{x-\mu}{\sigma}$

$$P(-1 < z < 1) = \int_{-1}^{1} \phi(z)\mathrm{d}z$$

$= 2\int_0^1 \phi(z)\mathrm{d}z$ (from symmetry)
$= 2 \times 0.3413 = 0.6826$ (from tables)
or 68.26%(shown shaded under the curve, Fig 4.4)

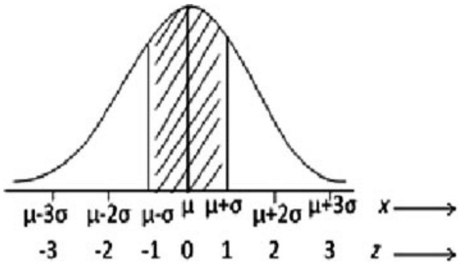

Fig. 4.4

(b) Similarly

$P(\mu - 2\sigma) < x < \mu + 2\sigma) = 0.9544$ or 95.44%

(c) $P(\mu - 3\sigma) < x < (\mu + 3\sigma) = 0.9973$ or 99.73%

4.59 $$P(n, T) = \frac{e^{-\frac{\left(n+\frac{1}{2}\right)\hbar\omega}{kT}}}{\Sigma_{n=0}^{\infty} e^{-\frac{\left(n+\frac{1}{2}\right)\hbar\omega}{kT}}}$$

$$= \frac{e^{-\left(n+\frac{1}{2}\right)\hbar\omega/kT}}{e^{-\frac{1}{2}\hbar\omega/kT}\Sigma_{n=1}^{\infty} e^{n\hbar\omega/kT}}$$

$$= \frac{e^{-n\hbar\omega/kT}}{\dfrac{e^{-\hbar\omega/kT}}{1 - e^{-\hbar\omega/kT}}} = \frac{e^{-n\hbar\omega/kT}}{\frac{1}{e^{\hbar\omega/kT}-1}}$$

$$= e^{-n\hbar\omega/kT}\left(e^{\hbar\omega/kT} - 1\right)$$

Substitute $n = 10$, $\dfrac{\hbar\omega}{k} = \dfrac{8.625 \times 10^{-5}}{(1.38 \times 10^{-23}/1.6 \times 10^{-19})} = 1.0$

$P(10, 300) = 3.2 \times 10^{-3}$

In the limit $T \to 0$, the state $n = 0$ alone is populated so that $n = 10$ state is unpopulated.

In the limit $T \to \infty$, probability for $n = 10$ again goes to zero, as higher states which are numerous, are likely to be populated.

4.60 Consider a collection of N molecules of a large number of energy states, E_1, E_2, E_3 etc such that there are N_1 molecules in state E_1, N_2 in E_2 and so on. The nature of energy is immaterial. The number of ways in which N molecules can be accommodated in various states is given by

$$W = \frac{N!}{N_1!N_2!\ldots} \tag{1}$$

The underlying idea is that the state of the system would be state if W is a maximum.

Taking logs on both sides and applying Stirling's approximation $\ln W = N \ln N - N - \Sigma N_i \ln N_i + \Sigma N_i$

$$= N \ln N - \Sigma N_i \ln N_i \tag{2}$$

because $\Sigma N_i = N$ (3)

$$\Sigma N_i E_i = E \tag{4}$$

If the system is in a state of maximum thermodynamic probability, the variation of W with respect to change in N_i is zero, that is

$$\Sigma \delta N_i = 0 \tag{5}$$

$$\Sigma E_i \delta N_i = 0 \tag{6}$$

$$\Sigma(1 + \ln N_i)\delta N_i = 0 \tag{7}$$

We now use the Lagrange method of undetermined multipliers. Multiplying (5) by α and (6) by β and adding to (7), we get

$$\Sigma\{(1 + \ln N_i) + \alpha + \beta E_i\}\delta N_i = 0 \tag{8}$$

Therefore

$$\ln N_i + 1 + \alpha + \beta E_i = 0 \tag{9}$$

or $N_i = Ce^{-\beta E_i}$ (10)

Where C = constant which can be determined as follows.

$$\Sigma N_i = N = C\Sigma e^{-\beta E_i} \tag{11}$$

$$\text{or } C = \frac{N}{\Sigma e^{-\beta E_i}} \tag{12}$$

Equation (10) then becomes

$$N_i = \frac{Ne^{-\beta E_i}}{\Sigma e^{-\beta E_i}} \tag{13}$$

The denominator in (13)

$$Z = \Sigma e^{-\beta E_i} \tag{14}$$

Is known as the partition function. It can be shown that the quantity

$$\beta = \frac{1}{kT} \tag{15}$$

where k is the Boltzmann constant and T is the absolute temperature.

$$\alpha = \frac{N}{Z} \tag{16}$$

4.3.4 Blackbody Radiation

4.61 Electric power = power radiated

$$W = \sigma T^4 A$$

$$A = 2\pi rl = 2\pi \times 10^{-3} \times 1.0 = 6.283 \times 10^{-3}\text{m}^2$$

$$T = \left[\frac{W}{\sigma A}\right]^{1/4} = \left[\frac{1{,}000}{5.67 \times 10^{-8} \times 6.283 \times 10^{-3}}\right]^{1/4} = 1{,}294\,K$$

4.62 The Solar constant S is the heat energy received by 1 m^2 of earth's surface per second. If R is the radius of the sun and r the earth-sun distance, then the total intensity of radiation emitted from the sun will be σT^4 W m^{-2} and from the sun's surface $\sigma T^4.4\pi R^2$. The radiation received per second per m^2 of earth's surface will be

$$S = \sigma T^4.\frac{4\pi R^2}{4\pi r^2}$$

Solving,

$$\sigma T^4 = S.\frac{r^2}{R^2} = 1{,}400\left(\frac{1.5 \times 10^8}{7 \times 10^5}\right)^2 = 6.43 \times 10^7\,\text{W m}^{-2}$$

$$T = \left(\frac{6.43 \times 10^7}{\sigma}\right)^{1/4} = \left(\frac{6.43 \times 10^7}{5.67 \times 10^{-8}}\right)^{1/4} = 5{,}800\,\text{K}$$

4.63 Using the analogy between radiation (photon gas) and gas molecules, the photons move in a cavity at random in all directions, rebounding elastically from the walls of the cavity. The pressure exerted by an ideal photon gas is

$$p = \frac{1}{3}\rho < v^2 >$$

where ρ is the mass density. In the case of photon gas, the speed of all photons is identical being equal to c. Furthermore, from Einstein's relation

$$u = \rho c^2$$

where u is the energy density. Replacing $< v^2 >$ by c^2

$$p_{\text{rad}} = \frac{1}{3}\rho c^2 = \frac{u}{3}$$

4.64 Let T and T_0 be the Kelvin temperatures of the body and the surroundings. Then, by Stefan–Boltzmann law, the rate of loss of heat per unit area of the body is

$$\begin{aligned}\frac{\mathrm{d}Q}{\mathrm{d}t} &= \sigma(T^4 - T_0^4)\\ &= \sigma(T - T_0)(T + T_0)(T^2 + T_0^2)\end{aligned}$$

If $(T - T_0)$ be small, $(T \approx T_0)$, and

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \sigma(T - T_0) \times 4T_0^3$$

Since T_0 is constant,

$$\frac{\mathrm{d}T}{\mathrm{d}t} \propto (T - T_0); \qquad \text{(Newton's law of cooling).}$$

4.65 The energy density u and pressure p of radiation are related by

$$p = \frac{u}{3}$$

Furthermore, $u = 4\sigma T^4/c$

Eliminating u,

$$T = \left(\frac{3cp}{4\sigma}\right)^{1/4} = \left(\frac{3 \times 3 \times 10^8 \times 4 \times 10^8 \times 1.013 \times 10^5}{4 \times 5.67 \times 10^{-8}}\right)^{1/4} = 2 \times 10^7\,\text{K}$$

4.66 (a) Power,

$$\begin{aligned}P &= \sigma A T^4 = 4\pi R^2 \sigma T^4\\ &= 4\pi(7 \times 10^8)^2(5.67 \times 10^{-8})(5{,}700)^4\\ &= 3.68 \times 10^{26}\,\text{W}\end{aligned}$$

Mass lost per second, $m = P/c^2 = \dfrac{3.68 \times 10^{26}}{(3 \times 10^8)^2} = 4.1 \times 10^9\text{kg/s}$

(b) Time taken for the mass of sun (M) to decrease by 1% is

$$\begin{aligned}t &= \frac{M}{100} \times \frac{1}{m} = \frac{2 \times 10^{30}}{100} \times \frac{1}{4.1 \times 10^9} = 4.88 \times 10^{18}\,\text{s}\\ &= \frac{4.88 \times 10^{18}}{3.15 \times 10^7} = 1.55 \times 10^{11}\ \text{years}\end{aligned}$$

4.67 Power radiated, $P = \sigma A T^4 = 4\pi R^2 \sigma T^4$

$$\frac{P_2}{P_1} = \frac{R_2^2}{R_1^2}.\frac{T_2^4}{T_1^4} = \frac{(4R_1)^2}{R_1^2}.\frac{(2T_1)^4}{T_1^4} = 256$$

Furthermore, $\dfrac{P_2}{P_1} = \dfrac{\mathrm{d}Q_2/\mathrm{d}t}{\mathrm{d}Q_1/\mathrm{d}t} = \dfrac{m_2 s(\mathrm{d}T/\mathrm{d}t)_2}{m_1 s(\mathrm{d}T/\mathrm{d}t)_1}$

where s is the specific heat
But $m_2 \propto R_2^3$ and $m_1 \propto R_1^3$

$$\therefore \frac{(\mathrm{d}T/\mathrm{d}t)_2}{(\mathrm{d}T/\mathrm{d}t)_1} = \frac{P_2}{P_1}.\frac{R_1^3}{R_2^3} = \frac{256}{4^3} = 4$$

4.68 (a) $\lambda_m.T = b$

$$T = \frac{b}{\lambda_m} = \frac{2.897 \times 10^{-3}}{1 \times 10^{-6}} = 2{,}897\,\mathrm{K}$$

$$\frac{P_2}{P_1} = \frac{T_2^4}{T_1^4} = 2$$

New temperature, $T_2 = T_1 \times 2^{1/4} = 2{,}897 \times 1.189 = 3{,}445\mathrm{K}$

(b) The wavelength at which the radiation has maximum intensity

$$\lambda_m = \frac{2.897 \times 10^{-3}}{3445} = 0.84 \times 10^{-6} m = 0.84\,\mu\mathrm{m}$$

4.69 The mean value $\overline{\in}$ is determined from;

$$\overline{\in} = \frac{\Sigma_{n=0}^{\infty} n \in e^{-\beta n \in}}{\Sigma_{n=0}^{\infty} e^{-\beta n \in}} = -\frac{\mathrm{d}}{\mathrm{d}\beta} \ln \sum_{n=0}^{\infty} e^{-\beta n \in}$$

$$= -\frac{\mathrm{d}}{\mathrm{d}\beta} \ln\left(1 + e^{-\beta\in} + e^{-2\beta\in} + \cdots\right)$$

$$= -\frac{\mathrm{d}}{\mathrm{d}\beta} \ln \frac{1}{1 - e^{-\beta\in}}$$

where we have used the formula for the sum of terms of an infinite geometric series.

$$\overline{\in} = \frac{\in e^{-\beta\in}}{1 - e^{-\beta\in}} = \frac{\in}{e^{\beta\in} - 1} \quad (\beta = 1/kT)$$

4.70 (a) $$u_\lambda \mathrm{d}\lambda = \frac{8\pi hc}{\lambda^5}.\frac{1}{e^{hc/\lambda kT} - 1}\mathrm{d}\lambda \quad \text{(Planck's formula)} \qquad (1)$$

For long wavelengths (low frequencies) and high temperatures the ratio $\frac{hc}{\lambda kT} \ll 1$ so that we can expand the exponential in (1) and retain only the first two terms

$$u_\lambda \mathrm{d}\lambda = \frac{8\pi hc}{\lambda^5[(1 + hc/\lambda kT + \ldots) - 1]} = \frac{8\pi kT}{\lambda^4}\mathrm{d}\lambda$$

writing $\lambda = \frac{c}{\upsilon}$; $\mathrm{d}\lambda = -\frac{c}{\upsilon^2}\mathrm{d}\nu$

$$u_\nu = \frac{8\pi\nu^2}{c^3}kT \qquad \text{(Rayleigh-Jeans law)}$$

(b) If $h\nu/kT \gg 1$ i.e $hc/\lambda kT \gg 1$ then we can ignore 1 in the denominator in comparison with the exponential term in Planck's formula
$u_\lambda \mathrm{d}\lambda = c_1 e^{-c_2/\lambda kT}\mathrm{d}\lambda$ (Wien's distribution law)
where the constants, $c_1 = 8\pi hc$ and $c_2 = hc$

4.71 $u_\lambda \mathrm{d}\lambda = \frac{8\pi hc}{\lambda^5}\cdot\frac{1}{e^{hc/\lambda kT}-1}\mathrm{d}\lambda$ (Planck's formula)

The wavelength λ_m corresponding to the maximum of the distribution curve is obtained from the condition

$$\left(\frac{\mathrm{d}u_\lambda}{\mathrm{d}\lambda}\right)_{\lambda=\lambda_m} = 0$$

Differentiating and writing $hc/kT\lambda_m = \beta$, gives

$$e^{-\beta} + \frac{\beta}{5} - 1 = 0$$

This is a transcental equation and has the solution

$\beta = 4.9651,$ so that

$$\lambda_m T = \frac{hc}{4.9651k} = b = \text{constant.}$$

Thus, the constant

$$b = \frac{6.626068 \times 10^{-34} \times 2.99792 \times 10^8}{4.9651 \times 1.38065 \times 10^{-23}} = 2.8978 \times 10^{-3}\ \text{m-K}$$

a value which is in excellent agreement with the experiment.

4.72 By definition

$$u = \int u_\nu \mathrm{d}\nu = aT^4 \qquad (1)$$

Inserting Planck's formula in (1)

$$u = aT^4 = \frac{8\pi h}{c^3}\int_0^\infty \frac{\nu^3 \mathrm{d}\nu}{e^{h\nu/kT}-1} = \frac{8\pi k^4 T^4}{h^3c^3}\int_0^\infty \frac{x^3 \mathrm{d}x}{e^x - 1}$$

where $x = h\nu/kT$

$$a = \frac{8\pi k^4}{h^3c^3}\int_0^\infty x^3(e^{-x} + e^{-2x} + \ldots e^{-rx} + \ldots)$$

Now, $\int_0^\infty x^3 e^{-rx}\mathrm{d}x = \frac{6}{r^4}$, and $\Sigma_{r=1}^{\infty}\frac{1}{r^4} = \frac{\pi^2}{90}$

$$a = \frac{48\pi k^4}{h^3c^3}\cdot\frac{\pi^4}{90} = \frac{8}{15}\frac{\pi^5 k^4}{h^3c^3}$$

$$\therefore \sigma = \frac{ac}{4} = \frac{2}{15}\frac{\pi^5 k^4}{h^3c^2}$$

$$= \frac{2}{15}\frac{(3.14159)^5(1.38065)^4 \times 10^{-92}}{(6.626068 \times 10^{-34})^3(2.99792 \times 10^8)^2}$$

$$= 5.67 \times 10^{-8}\text{W-m}^{-2}\text{-K}^{-4}$$

a value which is in excellent agreement with the experiment.

4.73 Number of modes per m^3 in the frequency interval $d\nu$ is

$$N = \frac{8\pi\nu^2 d\nu}{c^3}$$

But,

$$\nu = \frac{c}{\lambda}; d\nu = -\frac{d\lambda}{\lambda^2}; \lambda = \frac{4{,}990 + 5{,}010}{2} = 5{,}000\ A^0$$

$$d\lambda = 5{,}010 - 4{,}990 = 20\ A^0$$

$$\therefore N = \frac{8\pi d\lambda}{\lambda^4} = \frac{8\pi \times 20 \times 10^{-10}}{(5 \times 10^{-7})^4} = 8.038 \times 10^{17}/\text{m}^3$$

4.74 (a) $$P = AE_\lambda d\lambda = \frac{8\pi hcAd\lambda}{\lambda^5(e^{hc/\lambda kT} - 1)} \quad (2)$$

Mean wavelength $\lambda = 0.55\ \mu\text{m} = 5.5 \times 10^{-7}\text{m}$. (1)

$$d\lambda = (0.7 - 0.4)\ \mu\text{m} = 3 \times 10^{-7}\text{m}$$

$$A = \pi r^2 = \pi(2.5 \times 10^{-3})^2 = 1.96 \times 10^{-5}\text{m}^2$$

$$\frac{hc}{\lambda kT} = \frac{(6.63 \times 10^{-34})(3 \times 10^8)}{(5.5 \times 10^{-7})(1.38 \times 10^{-23})(4{,}000)} = 6.55$$

Using the above values in (2) we find

$$P = AE_\lambda d\lambda = 0.84 \times 10^{-6}\text{W} = 0.84\ \mu\text{W}.$$

(b) $$h\bar{\nu} = \frac{hc}{\bar{\lambda}} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{5.5 \times 10^{-7}} = 3.616 \times 10^{-19}$$

Number of photons emitted per second

$$n = \frac{P}{h\bar{\nu}} = 0.84 \times 10^{-6}/3.616 \times 10^{-19} = 2.32 \times 10^{12}/\text{s}$$

4.75 $$u_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda kT} - 1}d\lambda \quad (1)$$

Put $\lambda = c/\nu$ (2)

and $d\lambda = -\left(\frac{c}{\nu^2}\right)d\nu$ (3)

in the RHS of (1) and simplify

$$u_\nu d\nu = \frac{8\pi h\nu^3}{c^3(e^{h\nu/kT} - 1)}d\nu \quad (4)$$

The negative sign in (3) is omitted because as λ increases v decreases.

4.76 Power radiated from the sun = $\sigma \times$ (surface area) $\times T_s^4$

$$P_s = \sigma 4\pi R_s^2 T_s^4$$

Power received by the earth,

$$P_E = \frac{\pi R_e^2}{4\pi r^2}.P_s$$

The factor πR_e^2 represents the effective (projected) area of the earth on which the sun's radiation is incident at a distance r from the sun. The factor $4\pi r^2$ is the surface area of a sphere scooped with the centre on the sun. Thus $\pi R_e^2/4\pi r^2$ is the fraction of the radiation intercepted by the earth's surface area.

Now power radiated by earth,

$$P_E = \sigma 4\pi R_E^2 T_E^4$$

For radiation equilibrium, power radiated by the earth=power received by the earth.

$$\sigma 4\pi R_E^2 T_E^4 = \sigma 4\pi R_s^2 T_s^4 . \frac{\pi R_E^2}{4\pi r^2}$$

or $T_E = T_s \left(\frac{R_s}{2r}\right)^{1/2} = 5{,}800 \left[\frac{7 \times 10^8}{2 \times 1.5 \times 10^{11}}\right]^{1/2}$

$= 280$ K $= 7$°C

Note that the calculations are approximate in that the earth and sun are not black bodies and that the contribution of heat from the interior of the earth has not been taken into account.

4.77 Power radiated by the sun, $P_s = \sigma 4\pi R_s^2 T_s^4$

Power received by 1 m^2 of earth's surface,

$$S = \frac{\sigma 4\pi R_s^2 T_s^4}{4\pi r^2}$$

$$= \frac{(5.7 \times 10^{-8})(7 \times 10^8)^2 (5{,}800)^4}{(1.5 \times 10^{11})^2}$$

$= 1{,}400$ W/m^2

4.78 $P = 4\pi r^2 \sigma T^4$

$= 4\pi (0.3)^2 (5.67 \times 10^{-8})(10^7)^4$

$= 6.4 \times 10^{20}$ W