Problems **and** Solutions on Thermodynamics **and**

CONTENTS

PART I THERMODYNAMICS

1. THERMODYNAMIC STATES AND THE FIRST LAW (1001-1030)

1001

Describe briefly the basic principle of the following instruments for making temperature measurements and state in one sentence the special usefulness of each instrument: constant-volume gas thermometer, thermocouple, thermistor.

(***Wisconsin)***

Solution:

Constant-volume gas thermometer: It is made according to the principle that the pressure of a gas changes with its temperature while its volume is kept constant. It can approximately be used as an ideal gas thermometer.

Thermocouple thermometer: It is made according to the principle that thermoelectric motive force changes with temperature. The relation between the thermoelectric motive force and the temperature is

$8 = a + bt + ct2 + dt3$,

where E is the electric motive force, *t* is the difference of temperatures of the two junctions, ***a,b,c*** and *d* are constants. The range of measurement of the thermocouple is very wide, from **-2OOOC** to **16OOOC.** It is used as a practical standard thermometer in the range from **630.74'C** to **1064.43"C.**

Thermister thermometer: We measure temperature by measuring the resistance of a metal. The precision of a thermister made of pure platinum is very good, and its range of measurement is very wide, so it is usually used as a standard thermometer in the range from **13.81K** to **903.89K.**

1002

Describe briefly three different instruments that can be used for the accurate measurement of temperature and state roughly the temperature range in which they are useful and one important advantage of each instrument. Include at least one instrument that is capable of measuring temperatures down to **1K.**

(*Wisconsin)*

Solution:

1. Magnetic thermometer: Its principle is Curie's law $X = C/T$, where X is the susceptibility of the paramagnetic substance used, T is its absolute temperature and C is a constant. Its advantage **is** that it can measure temperatures below 1K.

2. Optical pyrometer: It is based on the principle that we can find the temperature of a hot body by measuring the energy radiated from it, using the formula of radiation. While taking measurements, it does not come into direct contact with the measured body. Therefore, it is usually used to measure the temperatures of celestial bodies.

3. Vapor pressure thermometer: It is a kind of thermometer used to measure low temperatures. Its principle is as follows. There exists a definite relation between the saturation vapor pressure of a chemically pure material and its boiling point. If this relation is known, we can determine temperature by measuring vapor pressure. It can measure temperatures greater than **14K,** and is the thermometer usually used to measure low temperatures.

1003

A bimetallic strip **of** total thickness z is straight at temperature T. What is the radius of curvature of the strip, R, when it **is** heated to temperature $T+AT$? The coefficients of linear expansion of the two metals are $a1$ and $a2$, respectively, with $a2 > a1$. You may assume that each metal has thickness **212,** and you may assume that $x << R$.

(Wisconsin)

Solution:

We assume that the initial length is 10. After heating, the lengths of the mid-lines of the **two** metallic strips are respectively

Fig. **1.1.**

Assuming that the radius **of** curvature is R, the subtending angle **of** the strip is 8, and the change **of** thickness is negligible, we have

z z 11 + 12 210

12 - 11 = -8 = - - = -l2 + (a1 + a2)ATI .

2 2 2R 4R (3)

From (1) and **(2)** we obtain

(3) and (4) then give

1004

An ideal gas is originally confined to a volume Vl in an insulated container **of** volume $Vl +V2$. The remainder **of** the container is evacuated. The partition is then removed and the gas expands to fill the entire container. If the initial temperature **of** the gas was T, what is the final temperature? Justify your answer.

(**Was cons in)**

insulated container *C*

Fig. **1.2.**

Solution:

This is a process of adiabatic free expansion of an ideal gas. The internal energy does not change; thus the temperature does not change, that is, the final temperature is still *T*.

1005

An insulated chamber is divided into two halves of volumes. The left half contains an ideal gas at temperature *TO* and the right half is evacuated. A small hole is opened between the two halves, allowing the gas to flow through, and the system comes to equilibrium. No heat is exchanged with the walls. Find the final temperature of the system.

(Columbia)

Solution:

After a hole has been opened, the gas **flows** continuously to the right side and reaches equilibrium finally. During the process, internal energy of the system *E* is unchanged. Since *E* depends on the temperature *T* only for an ideal gas, the equilibrium temperature is still *To.*

Fig. 1.3.

1006

Define heat capacity *C,* and calculate from the first principle the numerical value (in caloriesj'C) for a copper penny in your pocket, using your best physical knowledge or estimate of the needed parameters.

***(UC,* Berkeley)**

Solution:

penny is about **32** g, i.e., 0.5 mol. Thus ***C,*** = 0.5 x ***3R*** = **13** J/K.

C, , = *(dQ/dT),*. The atomic number of copper is **64** and a copper

1007

Specific heat of granite may be: 0.02,0.2,20,2000 cal/g.K.

(Columbia)

Solution:

The main component of granite is CaC03; its molecular weight is 100. The specific heat is C = 3R/100 = 0.25 cal/g. K. Thus the best answer is 0.2 cal/g.K.

1008

The figure below shows an apparatus for the determination of C,/C,, for a gas, according to the method of Clement and Desormes. A bottle G, of reasonable capacity (say a few litres), is fitted with a tap H, and a manometer M. The difference in pressure between the inside and the outside can thus be determined by observation of the difference h in heights of the two columns in the manometer. The bottle is filled with the gas to be investigated, at a very slight excess pressure over the outside atmospheric pressure. The bottle is left in peace (with the tap closed) until the temperature of the gas in the bottle is the same as the outside temperature in the room. Let the reading of the manometer be *hi.* The tap H is then opened for a very short time, just sufficient for the internal pressure to become equal to the atmospheric pressure (in which case the manometer reads h = 0). With the tap closed the bottle is left in peace for a while, until the inside temperature has become equal to the outside temperature. Let the final reading of the manometer be h. From the values of *h;* and *h,* it is possible to find **Cp/Cv.** (a) Derive an expression for **C,/Cv** in terms of *h;* and *h,* in the above experiment. (b) Suppose that the gas in question is oxygen. What is your theoretical prediction for **C,/Cv** at ***2OoC,*** within the framework of statistical mechanics?

***(UC,* Berkeley)**

h

Fig. 1.4.

Solution:

(a) The equation of state of ideal gas is ***pV*** = **nkT.** Since the initial

and final ***T,V*** of the gas in the bottle are the same, we have ***p f / p ; = n f / n ; .***
Meanwhile, nf/n; = ***V/V',*** where ***V'*** is the volume when the initial gas in the bottle expands adiabatically to pressure ***PO***. Therefore

-= (E) 7 1 *VV'* 1 "=(a)+ ***Pi*** ,

Since *h;/ho* << 1 and ***hf/ho*** << 1, we have **7** = *h;/(h;* ***- h f) .***
(b) Oxygen consists of diatomic molecules. When *t* = **2OoC,** only the translational and rotational motions of the molecules contribute to the specific heat. Therefore

1009

(a) Starting with the first law of thermodynamics and the definitions of **cp** and **c,,** show that

c p - c , = ***[P + (a****a**v**U) T 1*** (%)

P

where **cp** and **c, are** the specific heat capacities per mole at constant pressure and volume, respectively, and *U* and ***V*** are energy and volume of one mole.

(b) Use the above results plus the expression

p + (%) , = T (%) V

to find **cp - c, for** a Van der Waals gas
Use that result to show that as ***V*** --+ *oo* at constant ***p ,*** you obtain the ideal gas result for **cp - c,.**

(SUNY, ***Buflulo)***

Solution:

(a) From *H* = *U* **+** ***pV,*** we obtain

(%) p = (%) , + p (%) P *

Let *U* = *U[TV, (T ,**p)] .*** The above expression becomes

Hence

P

(b) For the Van der Waals gas, we have

R

RT 2a(V *- b)*

v3

Hence ,

R

cp *- c"* =

1 - ***2a(*** **1** - ***b/V)2/VRT*** '

When ***V*** *-+ oo,* ***cp - c, + R,*** which is just the result for an ideal gas.

1010

One mole of gas obeys Van der Waals equation of state. If its molar internal energy is given by **u** = ***cT - a/V*** (in which ***V*** is the molar volume, ***a*** is one of the constants in the equation of state, and ***c*** is a constant), calculate the molar heat capacities ***C,*** and ***C,.***

Solution:

(**was** ***co*** nsin)

c,=(%) ***= c ,***

%= (g) p + p (%) p = **(%) v+** [(3 , + P 1

V

x(%) = ***c + (& + p) (E) .***

From the Van der Waals equation

(p + a/Vz)(V - b) = RT ,

we obtain

Therefore

R

RTV3

a 2ab 2 a (-~ b)2 ·

c , = c +

p - ,+V, V 1-

1011

A solid object has a density p, mass M, and coefficient of linear expansion a. Show that at pressure p the heat capacities C, and C,, are related bY

C, - C,, = 3aMp/p .

(Wisconsin)

Soh tion:

From the first law of thermodynamics dQ = dU + pdV and (%),- (g),, (for solid), we obtain

c , - c ''=(g) , - (g)= p $dVT .

u

From the definition 1 dV of coefficient of linear expansion a = asolid/3 = - - 3V dT'

we obtain M

- = 3aV = 3a- . dV

dT P

Substituting this in (*), we find

M

P

C, - C,, = 3a-p .

1012

One mole of a monatomic perfect gas initially at temperature To expands from volume Vo to 2VOl (a) at constant temperature, (b) at constant pressure.

Calculate the work of expansion and the heat absorbed by the gas in each case.

(Wisconsin)

Solution:

(a) At constant temperature To, the **work** is

2vo

W = L B pdV = RTo lo d V / V = RTo In2 .

As the change of the internal energy is zero, the heat absorbed by the gas is

Q = W = RTo l n 2 .

(b) At constant pressure p, the **work** is

The increase of the internal energy is

3 3 3
2 2 2
AU = C,AT = -RAT = - p A V = -pVd

3 -RTo **.** *2*

Thus the heat absorbed by the gas is

5
2
Q=AU+W=-RTo.

101s

For a diatomic ideal gas near room temperature, what fraction. of the heat supplied is available for external work if the gas is expanded at constant pressure? At constant temperature?

(Wisconsin)

Solution:

In the process of expansion at constant pressure *p ,* assuming that the volume increases from *V1* to *V2* and the temperature changes from *TI* to *T2,* we have

pV1 = nRT1 { *pV2 = nRT2* **.**

In this process, the work done by the system on the outside world is *W* = *p(V2 - V1)* = *nRAT* and the increase of the internal energy of the system is

AU = *C,AT* **.**

Therefore

W **2**
Q AU+W C,+nR **7**
-- -
_ -- *W - nR*

In the process of expansion at constant temperature, the internal energy does not change. Hence

W / Q = 1 .

1014

A compressor designed to compress air is used instead to compress helium. It is found that the compressor overheats. Explain this effect, assuming the compression is approximately adiabatic and the starting pressure is the same for both gases.

(wis ***cons in)***

Solution:

The state equation of ideal gas is

pV = *nRT.*

The equation of adiabatic process is

P (v6)7 = P o ,

where *7 = cP/c,,po* and *p* are starting and final pressures, respectively, and

*VO*a nd ***V*** are volumes. Because *VO*> *V* and **7He** > *7 A i r (7 =~ 7/5~;7* ir* = **5/3) ,** we get

PHe > **PAir** and *THe* > *TAir* ·

1015

Calculate the temperature after adiabatic compression of a gas to 10.0 atmospheres pressure from initial conditions of 1 atmosphere and 300K (a) for air, (b) for helium (assume the gases are ideal).

Soh tion:

(wis ***co*** nsin)

The adiabatic process of an ideal gas follows the law

TB = (pB/pA)(7-1)/7 TA = 10(7-1)/7 x 300 K **.**

(a) For air, **7 = Cp/C,,** = 1 . 4 , thus TB = 5.8 x 10'K.

(b) For helium, **7 = Cp/Cu** = 5/3 **,** thus TB = 7.5 x **102K .**

1016

(a) For a mole of ideal gas at *t* = OOC, calculate the work *W* done (in Joules) in an isothermal expansion from VO to lOV0 in volume.

(b) For an ideal gas initially at *ti* = *O"C,* find the final temperature *tf* (in "C) when the volume is expanded to lOV0 reversibly and adiabatically.

*(UC, **Berkeley)***

Solution:

pdV = -*dV* = RTln 10 = 5.2 x 103J

(b) Combining the equation of adiabatic process pV7 = const and the equation of state pV = RT, we get TV7-l = const. Thus

If the ideal gas molecule is monatomic, **7 = 5/3,** we get tf = 59K or -214°C.

1017

(a) How much heat **is** required to raise the temperature of 1000 grams

(b) How much has the internal energy of the nitrogen increased?

(c) How much external work was done?

of nitrogen from -20°C to 100°C at constant pressure?

(d) How much heat is required if the volume is kept constant?

Take the specific heat at constant volume **c,** = **5** cal/mole "C and **R** = **2** cal/mole.'C.

(*Wisconsin)*

Solution:

(a) We consider nitrogen to be an ideal gas. The heat required is

1000

28

Q = **n(c, + R)AT** = *-(5* **+** 2) x 120 = 30 x 103cal

(b) The increase of the internal energy is

100

28

AU = **nc,AT** = - x **5** x **120**

= 2 1 x 1 0 ~ **.** ~ ~ 1

(c) The external work done is

W = Q - **AU** = **8.6** x lo3 cal **.**

(d) If it is a process of constant volume, the required heat is

Q = **nc,AT** = **21** x 103cal **.**

1018

10 litres of gas at atmospheric pressure is compressed isothermally to a volume of 1 litre and then allowed to expand adiabatically to 10 litres.

(a) Sketch the processes on a pVdiagram for a monatomic gas.

(b) Make a similar sketch for a diatomic gas.

(c) Is a net work done on or by the system?

(d) Is it greater or less for the diatomic gas?

(was ***co*** *nsin)*

Solution:

We are given that VA = lOl,V, = **l l , V c** = **101** and pA = 1 atm..

A -+ *B* is an isothermal process, thus

pV = const. or ~ A V A= ~ B V B**,**

hence
VA
VB

p~ = ---PA = 10 atm **.**

(The curve ***AB*** of the two kinds of gas are the same).

B -+ C is an adiabatic process, thus

pV7 = const, or p ~ V 2= pcV2 **,** hence

(a) For the monatomic gas, we have

7 = 5/3,pc = **lOe2I3** = 0.215 atm **.**

(b) For the diatomic gas, we have

7 = 7/5,pc = **10-2'5** = 0.398 atm.

The two processes are shown in the figures 1.5. (The curve *BC* of the monatomic gas (a) is lower than that of the diatomic gas (b)).

(c) In each case, as the curve ***AB*** for compression is higher than the curve *BC* for expansion, net work is done on the system. **As pc** (monatomic gas) < pc (diatomic gas) the work on the monatomic gas is greater than that on the diatomic gas.

1 ***p*** **(atm** 1
10-
8-
6 -
l **-**
2 -
A
C,
0 2 / 6 8 1Oy(
p **(atm)**
L)

1019

An ideal gas is contained in a large jar of volume ***Vo.*** Fitted to the jar is a glass tube of cross-sectional area ***A*** in which a metal ball of mass *M* fits snugly. The equilibrium pressure in the jar is slightly higher than atmospheric pressure ***po*** because of the weight of the ball. If the ball is displaced slightly from equilibrium it will execute simple harmonic motion (neglecting friction). If the states of the gas represent a quasistatic adiabatic process and 7 is the ratio of specific heats, find a relation between the oscillation frequency *f* and the variables of the problem.

(UC, **Berkeley)**

Fig. 1.6.

Solution:

have

Assume the pressure in the jar is ***p*.** As the process is adiabatic, we

pV7 = const **,**

giving

dp dV
- +-y- = ***0*.**
P V

This can be written as *F* = ***Adp*** = ***-kz,*** where *F* is the force on the ball,

3: = ***dV/A*** and ***k*** = ***-yA2p/V.*** Noting that ***p*** = ***po*** + ***mg/A,*** we obtain

1020

The speed of longitudinal waves of small amplitude in an ideal.gas is

where *p* is the ambient gas pressure and ***p*** is the corresponding gas density. Obtain expressions for

(a) The speed of sound in a gas for which the compressions and rarefactions are isothermal.
(b) The speed of sound in a gas for which the compressions and rarefactions are adiabatic.

(Wisconsin)

Solution:

The isothermal process of an ideal gas follows pV = const; the adiabatic process of an ideal gas follows $pV7$ = const. We shall use pVt = const for a general process, its differential equation being

$d p$ dV
- + t - = O .
P V

Thus **(2)** = -tvP .

With **p** = M / V, we have

RT

Therefore

(a) The isothermal process: t = 1, thus c = $d\ m$.

(b) The adiabatic process: t = 7, thus c = $d\ m$.

1021

Two systems with heat capacities C1 and Cz, respectively, interact thermally and come to a common temperature **Tf.** If the initial temperature of system 1 was TI, what was the initial temperature of system **2?** You may assume that the total energy of the combined systems remains constant.

(*wis* **co** nsin)

Solution:

We assume that the initial temperature of system **2** is $T2$. According to the conservation of energy, we know the heat released from system 1 is equal to that absorbed by the other system, i.e.,

The solution is

C1
c2

$T2$ = -(Tf - **TI**) + Tf.

1022

A large solenoid coil for a physics experiment is made of a single layer of conductor of cross section 4cm x 2cm with a cooling water hole **2** cm x Icm in the conductor. The coil, which consists of 100 turns, has a diameter of **3** meters, and a length of 4 meters (the insulation thickness **is** negligible). At the two ends of the coil are circular steel plates to make the field uniform and to return the magnetic flux through a steel cylindrical structure external to the coil, as shown in the diagram. A magnetic field of 0.25 Tesla is desired. The conductor is made of aluminium.

(a) What power (in kilowatts) must be supplied to provide the desired field, and what must be the voltage of the power supply?

(b) What rate of water flow (litres/second) must be supplied to keep the temperature rise **of** the water at **40"C?** Neglect all heat losses from the coil except through the water.

(c) What is the outward pressure exerted on the coil by the magnetic forces?

(d) If the coil is energized by connecting it to the design voltage calculated in (a), how much time is required to go from zero current to 99% of the design current? Neglect power supply inductance and resistance. The resistivity of aluminium is **3** x lo-* ohm-meters. Assume that the steel is far below saturation.

(CUSPEA)

r----------- cooling - 7

I

I coil in detail I

r- - ------I

I-----

Fig. 1.7.

Solution:

where *N* is the number of turns, *L* is the length of the solenoid coil. The current is therefore

(a) The magnetic field is *B* = *poNI/L,*

I = - -*B*- -*L*- - **0.25** x **4 = 7960A .**

p o ~**4T** x **10-7** x **100**

The total resistance of the coil is *R* = ***pL/A.*** Therefore, the resistance, the voltage and the power are respectively

(3 x **10-8)(100** x **2~** x **1.5)**

R= = **0.0471i-l**

(4 x **2 - 2** x **1)** x **10-4**

V = *RI* = **375V**

P = *V I* = **2.99** x **lo3 kw** ,

(b) The rate of flow of the cooling water is *W.* Then *pWCAT* = P,

where ***p*** is the density, C is the specific heat and *AT* is the temperature rise of the water. Hence

2.99 x **103** x **103**

P = **17.8 *11s***

pCAT

W=-=

1 x **4190** x **40**

(c) The magnetic pressure is

(0.25)'

= **2.49** x **lo4 N/m2 .** *B2*

2po **z(4Tx 10-7)**

***p* = - =**

(d) The time constant of the circuit is

T = *LIR,* with *L*= ***N@/I,***

where *L* is the inductance, *R* is the resistance, ***N*** is the number of turns, *I* is the current and **Q** is the magnetic flux. Thus we have

L = 100 x 0.25~x (1.5)'/7960 = 0.0222 **H**

and

7 = 0.0222/0.0471 = 0.471 s .

The variation of the current before steady state is reached is given by

I (t) = **Imax[I** - exp(-t/.r)] **.**

When **I(t)/Imax** = 99%,

t = 71n 100 = 4.67 *M* 2.17 s

102s

Consider a black sphere of radius *R* at temperature **T** which radiates to distant black surroundings at T = OK.

(a) Surround the sphere with a nearby heat shield in the form of a black shell whose temperature is determined by radiative equilibrium. What is the temperature of the shell and what is the effect of the shell on the total power radiated to the surroundings?

(b) How is the total power radiated affected by additional heat shields?

(UC, Berkeley)

(a) At radiative equilibrium, $J - J_1 = J_1$ or $J_1 = 512.$ Therefore

(Note that this is a crude model of a star surrounded by a dust cloud.)

Solution:

$Tf = T4/2$, or $TI =$

Fig. 1.8.

(b) The heat shield reduces the total power radiated to half of the initial value. This is because the shield radiates a part of the energy it absorbs back to the black sphere.

1024

In vacuum insulated cryogenic vessels (Dewars), the major source of heat transferred to the inner container is by radiation through the vacuum jacket. **A** technique for reducing this is to place "heat shields" in the vacuum space between the inner and outer containers. Idealize this situation by considering two infinite sheets with emissivity = 1 separated by a vacuum space. The temperatures of the sheets are TI and Tz $(TZ > TI)$. Calculate the energy flux (at equilibrium) between them. Consider a third sheet (the heat shield) placed between the two which has a reflectivity of *R.* Find the equilibrium temperature of this sheet. Calculate the energy **flux** from sheet **2** to sheet 1 when this heat shield is in place.

For Tz = room temperature, TI = liquid He temperature (**4.2** K) find the temperature of a heat shield that has a reflectivity of 95%. Compare the energy flux with and without this heat shield.

$(o = 0.55 \times$ lo-' watts/m2K)

(UC, **Berkeley)**

Fig. 1.9.

Solution:

When there is no "heat shield", the energy flux is

When Uheat shield" is added, we have

$J' = Ez - RE, - (1 - R)E3$,

$J' = (1 - R)E3 + RE1 - El$.

These equations imply $E3 = (El + E2)/2$, or $T3 = [(T; + Tf)/2]'I4$. Hence

$J^* = (1 - R)(E2 - E1)/2 = (1 - R) J/2$.

With $Tl = 4.2$ K, $T2 = 300$K and $R = 0.95$, we have

$T3 = 252$ K and $J^*/J = 0.025$.

1025

Two parallel plates in vacuum, separated by a distance which is small compared with their linear dimensions, are at temperatures TI and $T2$ respectively

$(TI > T2)$.

(a) If the plates are non-transparent to radiation and have emission powers e l and $e2$ respectively, show that the net energy W transferred per unit area per second is

$El - E2$

Ei $E2$ $W =$

-+--1

where El and $E2$ are the emission powers of black bodies at temperatures

TI and ***Tz*** respectively.

(b) Hence, what is W if ***TI*** is ***300*** K and ***T2*** is **4.2** K, and the plates are black bodies?

(c) What will *W* be if n identical black body plates are interspersed between the two plates in (b)?

(o = 5.67 x 10-8W/m2K4).

*(SVNY, **Buflulo)***

Solution:

reflection) of the two plates respectively. We have

(a) Let fl and *f2* be the total emission powers (thermal radiation plus

The solution is

Hence

Ei - ***E2***

-***Ei***+ - -***E***1***2***

W =*f 1 - f 2 =*

el *e2*

(b) For **black bodies,** *W* = ***El*** - ***E2*** = *u(Tf* **-** *T;)* = *460* **W/m2.**

(c) Assume that the n interspersed plates are black bodies at temperatures

t1, t2, . . . , *t,.* **When equilibrium is reached, we have**

T: - t: = t: **-** *Ti* , for **n = 1** ,

with solution

with solution

Then in the general we have

Tf - tt = t; **-** *tf =* **. . .** = *t*4, **- *Ti*** ,

with solution

d W = o (T ~- T i)= -(Tt **-** *T i)* **.**

n+1

1026

A spherical black body of radius r at absolute temperature T is surrounded by a thin spherical and concentric shell of radius R, black on both sides. Show that the factor by which this radiation shield reduces the rate of cooling of the body (consider space between spheres evacuated, with no thermal conduction losses) is given by the following expression:

aR2/(R2 **+** br2), and find the numerical coefficients *a* and 6.

Solution:

black body before being surrounded by the spherical shell is

(SUNY, Buflulo)

Let the surrounding temperature be ***To.*** The rate of energy loss of the

Q = 4ar2u(T4 - ***Ti)*** **.**

The energy loss per unit time by the black body after being surrounded by the shell is

Q' = 4rr2u(T4 - T:), where TI is temperature of the sheli **.**

The energy loss per unit time by the shell is

Q'' = 4aR2a(T; - ***TO)*** **.**

Since **Q''** = Q', we obtain

Tf = (r2T4 -t R2T;)/(R2 **+** r2)

Hence *Q'/Q* = R2/(R2 **+** r2), i.e., a = **1** and b = 1.

1027

The solar constant (radiant flux at the surface of the earth) is about 0.1 W/cm2. Find the temperature of the sun assuming that it is a black body.

Solution:

(MITI

The radiant flux density of the sun is

J = uT4 , where ***u*** = **5.7** x lo-' W/m2K4. Hence ~ T ~ (r s / r=s 0~.1) ,~

where the radius of the sun ***rs*** = 7.0 x 105km, the distance between the earth and the sun rSE = 1.5 x 108km. Thus

1028

(a) Estimate the temperature of the sun's surface given that the sun subtends an angle **0** as seen from the earth and the earth's surface temperature is ***To.*** (Assume the earth's surface temperature is uniform, and that the earth reflects a fraction, E, of the solar radiation incident upon it). Use your result to obtain a rough estimate of the sun's surface temperature by putting in 'reasonable" values for all parameters.

(b) Within an unheated glass house on the earth's surface the temperature is generally greater than ***To.*** Why? What can you say about the maximum possible interior temperature in principle?

(Columbia)

Solution:

(a) The earth radiates heat while it is absorbing heat from the solar radiation. Assume that the sun can be taken as a black body. Because of reflection, the earth is a grey body of emissivity 1 - E. The equilibrium condition is

where *Js* and *JE* are the radiated energy flux densities on the surfaces of the sun and the earth respectively, *Rs, R E* and TS-E are the radius of the sun, the radius of the earth and the distance between the earth and the sun respectively. Obviously *Rs/rs-E* = tan(8/2). From the Stefan-Boltzman law, we have

for the sun, *Js* = aTt ;

for the earth *JE* = (1 - E)UT;.

Therefore

7 x 106 km

Ts = T E / F w300Kx (2 x

w *6000* K

(b) Let *T* be temperature of the glass house and *t* be the transmission coefficient of glass. Then

(1 - *t)T4* + *tT:* = ***tT4*** ,

giving

Since *t* < 1, we have *t* > ***2t*** - 1, so that

T > *To*

1029

Consider an idealized sun and earth, both black bodies, in otherwise empty flat space. The sun is at a temperature of *Ts* = 6000 K and heat transfer by oceans and atmosphere on the earth is so effective as to keep the earth's surface temperature uniform. The radius of the earth is *RE* = **6** x lo8 cm, the radius of the sun is *Rs* = 7 x lolo cm, and the earth-sun distance is d = 1.5 x 1013 cm.

(a) Find the temperature of the earth.

(b) Find the radiation force on the earth.

(c) Compare these results with those for an interplanetary Uchondrulen in the form of a spherical, perfectly conducting black-body with a radius of R = O.lcm, moving in a circular orbit around the sun with a radius equal to the earth-sun distance d.

(Princeton)

Solution:

approximately

(a) The radiation received per second by the earth from the sun is

The radiation per second from the earth itself is

Neglecting the earth's own heat sources, energy conservation leads to the relation QE = qSE, so that

i.e.,

(b) The angles subtended by the earth in respect of the sun and by the sun in respect of the earth are very small, so the radiation force is

(c) AS *RE* + *R,T* = *TE* = 17°C

F = *(R/RE)2FE*= 1.7 *x 10-l'* N .

1030

Making reasonable assumptions, estimate the surface temperature of Neptune. Neglect any possible internal sources of heat. What assumptions have you made about the planet's surface and/or atmosphere?

Astronomical data which may be helpful: radius of sun=7 *x lo5* km; radius of Neptune = *2 . 2 ~ 1 0*km~ ; mean sun-earth distance = *1 . 5 ~ 1 0 8*k m; mean sun-Neptune distance = *4 . 5* ~lo 9 km; *TS* = 6000 K; rate at which sun's radiation reaches earth = *1.4* kW/m2; Stefan-Boltzman constant = **5.7** x W/m2K4.

(wasco nsin)

Solution:

We assume that the surface of Neptune and the thermodynamics of its atmosphere are similar to those of the earth. The radiation flux on the earth's surface is

JE = *4.lrR:uT;/4.lrRiE*

The equilibrium condition on Neptune's surface gives

Hence

REE JEIRgN = 4aTi ,

and we have

(1.5 x lo8)'

(5.7 x 10912 4 x 5.7 x 10-8

= 5 2 K .

2. THE SECOND LAW AND ENTROPY (1031-1072)

1031

A steam turbine is operated with an intake temperature of 4O0OC, and an exhaust temperature of 150OC. What is the maximum amount of work the turbine can do for a given heat input Q? Under what conditions is the maximum achieved?

(*wis* ***co*** *nsin)*

Solution:

From the Clausius formula

we find the external work to be

Substituting Q1 = Q,T1 = 673 K and *Tz* = 423 K in the above we have

W, = (1 - *2)* Q = 0.379 .

As the equal sign in the Clausius formula is valid if and only if the cycle is reversible, when and only when the steam turbine is a reversible engine can it achieve maximum work.

1032

What is a Carnot cycle? Illustrate on a pV diagram and an ST diagram. Derive the efficiency of an engine using the Carnot cycle.

(was **cons** in)

Solution:

adiabatic lines (as shown in Fig. 1.10 (a)).

A Carnot cycle is a cycle composed of two isothermal lines and two

A

L

V

s t

Fig. 1.10.

Now we calculate the efficiency of the Carnot engine. First, we assume the cycle is reversible and the gas **is** 1 mole of an ideal gas. **As** ***A*** -+ ***B*** is a process of isothermal expansion, the heat absorbed by the gas from the heat source **is**

Qi = RTi 1n(vB/vA) **.**

As *C* -+ ***D*** **is** a process of isothermal compression, the heat released by the gas is

9 2 = ***RT2*** ln(Vc/VD) **.**

The system comes back to the initial state through the cycle ***ABCDA.*** In these processes, the relations between the quantities of state are

Thus we find

VE VC

VA VD ·

-

Therefore the efficiency of the engine is

If the engine (or the cycle) is not reversible, its efficiency is

q' < *q* = 1 - *Tz/Tl* .

1033

A Carnot engine has a cycle pictured below.

and

V

Fig. 1.11.

(a) What thermodynamic processes are involved at boundaries ***AD BC;AB*** and ***CD?***

(b) Where is work put in and where is it extracted?

(c) If the above is a steam engine with Z , = , **450** K, operating at room temperature, calculate the efficiency.

Solution:

processes.

the processes ***AB*** and ***BC.***

(Wisconsin)

(a) ***DA*** and ***BC*** are adiabatic processes, ***AB*** and ***CD*** are isothermal

(b) Work is put in during the processes ***GD*** and ***DA;*** it is extracted in

(c) The efficiency is

1034

A Carnot engine has a cycle as shown in Fig. 1.12. If *W* and *W'* represent work done by 1 mole of monatomic and diatomic gas, respectively, calculate *W'IW.*

(Columbia)

Thermodynamics

y & ı *TO* ı 3

Solution:

For the Carnot engine using monatomic gas, we have

W = R(T1 - T2) ln(V2/Vi) **,**

VO **6C** *Vo*

Fig. **1.12**

where Tl = 4TC, and Tz = *TO* are the temperatures of the respective heat sources, V, = V,, and V2 is the volume at state **2.** We also have V3 = **64** VO.

With *W'* = R(T1 - T2) In (g) for the diatomic gas engine, we obtain

Then, using the adiabatic equations 4ToV2-l = TOV;-~,

4T v'7'--1 = T V7'-l

0 2 0 3 **,**

we obtain

W'

W **3 + (1 - 7) - '** *

_ **-**- 3 **+** (**1** - y y

For a monatomic gas 7 = **5/3;** for a diatomic gas, 7' = **7/5.** Thus

W' 1

w 3 - _ - -

1035

Two identical bodies have internal energy *U* = NCT, with a constant C. The values of *N* and *C* are the same for each body. The initial temperatures of the bodies are TI and T2, and they are used as a source of work by connecting them to a Carnot heat engine and bringing them to a common final temperature Tf.

(a) What is the final temperature ***Tf?***

(b) What is the work delivered?

(GUSPEA)

(a) The internal energy is ***U = NCT.*** Thus ***dQ1 = NCdT1*** and ***dQ2*** =

Solution :

dQi *dQ2*

Tl T2

NCdT2. For a Carnot engine, we have - = **--.** Hence

Tf ***dT1*** ***Tfd T2*** In-***T***=***r*** - ln- , ***Tf***

Thus **Li** = ***K'*** ***Tl T2***

Therefore ***Tf*** = *m.*

(b) Conservation of energy gives

$W = (Ul - U) - (U - U2) = U, + u2 - 2u$

$= NC(Ti + T2 - 2Tf)$.

1036

Water powered machine. A self-contained machine only inputs two equal steady streams of hot and cold water at temperatures ***TI*** and ***T2.*** Its only output is a single high-speed jet of water. The heat capacity per unit mass of water, ***C,*** may be assumed to be independent of temperature. The machine is in a steady state and the kinetic energy in the incoming streams is negligible.

(a) What is the speed `of` the jet in terms of ***T1,TZ*** and ***T,*** where ***T*** is

(b) What is the maximum possible speed of the jet?

the temperature of water in the jet?

Fig. 1.13.

Solution:

(a) The heat intake per unit mass of water is

AQ [C(Tl - T) - C(T - T2)]/2 .

As the machine is in a steady state, **v2/2** = AQ, giving

u = **JC(T1 + T2 - 2T) .**

(b) Since the entropy increase is always positive, i.e.,

1037

In the water behind a high power dam (110 m high) the temperature difference between surface and bottom may be 10°C. Compare the possible energy extraction from the thermal energy of **a** gram of water with that generated by allowing the water to flow over the dam through turbines in the conventional way.

(***Col urn bia)***

Solution:

The efficiency of a perfect engine is

The energy extracted from one gram of water is then

where Q is the heat extracted from one gram of water, **Cu** is the apecific heat of one gram of water. Thus

If ***Thigh*** can be taken as the room temperature, then

W = **1** x **102/300** = **0.3** cal **.**

The energy generated by allowing the water to flow over the dam is

W' = mgh = **1** x **980** x **100** x 10'

= **lo7** erg = **0.24** cal **.**

We can see that under ideal conditions *W'* < *W.* However, the efficiency of an actual engine is much less than that of a perfect engine. Therefore, the method by which we generate energy from the water height difference is still more efficient.

1038

Consider an engine working in a reversible cycle and using an ideal gas with constant heat capacity **cp as** the working substance. The cycle consists of two processes at constant pressure, joined by two adiabatics.

adiabatics

c

Fig. *V* 1.14.

(a) Find the efficiency of this engine in terms of **pl, p2.**

(b) Which temperature of ***T, , Tb, T, , Td*** is highest, and which is lowest?

(c) Show that a Carnot engine with the same gas working between the highest and lowest temperatures has greater effficiency than this engine.

(***Col*** **urn** ***baa)***

Solution:

source of higher temperature is

(a) In the cycle, the energy the working substance absorbs from the

The energy it gives to the source of lower temperature is Qgi = c,(Tc - Td).

Thus

From the equation of state pV = nRT and the adibatic equations

P2Vd' = PlVJ , p2v: = p1v; ,

we have

(b) From the state equation, we know Tb > T,,Tc > Td; from the adiabatic equation, we know Tb > Tc, T, > Td; thus

1039

A building at absolute temperature T is heated by means of a heat pump which uses a river at absolute temperature To as a source of heat. The heat pump has an ideal performance and consumes power *W.* The building loses heat at a rate cr(T - To), where Q is a constant.

(a) Show that the equilibrium temperature T, of the building is given

by

Te =To +2wa [1+ (1+9)']

(b) Suppose that the heat pump is replaced by a simple heater which also consumes a constant power *W* and which converts this into heat with 100% efficiency. Show explicitly why this is less desirable than a heat pump.

(Columbia)

Solution:

(a) The rate of heat from the pump is

At equilibrium, *T* = *T,* and *Q* = *Q,* = *a(Te - To).* Thus

(b) In this case, the equilibrium condition is

W = *Q (T-~ T o)* .

Thus

W

Ti=To+-<Te.

Q

Therefore it is less desirable than a heat pump.

1040

A room at temperature *T2* loses heat to the outside at temperature ***T1*** at a rate *A(Tz - Tl).* It is warmed by a heat pump operated as a Carnot cycle between *TI* and *Tz.* The power supplied by the heat pump is *dW/dT.*

(a) What is the maximum rate *dQm/dt* at which the heat pump can deliver heat to the room? What is the gain *dQm/dW?* Evaluate the gain for *tl* = 2"C, *t2* = 27°C.

(b) Derive an expression for the equilibrium temperature of the room,

(UC, Berkeley)

Tz, in terms of *TI,* A and *dW/dt.*

Solution:

(a) From *dQm . (TZ - T1)/T2 = dW,* we get

With *TI* = **275K,** *T2* = **300K,** we have *dQm/dW* = 12.

(b) When equilibrium is reached, one has

T2 dW

A(T2 - Ti) = - - T2 -TI ***dt*** '

giving

1041

A building at a temperature *T* (in K) is heated by an ideal heat pump which uses the atmosphere at *To(K)* as heat source. The pump consumes power *W* and the building loses heat at a rate *a(T - To).* What is the equilibrium temperature of the building?

(MIT)

Solution:

Let *Te* be the equilibrium temperature. Heat is given out by the pump at the rate *Q1* = W/r], where r] = 1 - *To/Te.* At equilibrium *Q1* = *a(T, - TO)s,o* that

W = -***a****(Te - To)'* **,**

Te

from which we get

Te=T0+"./ToF+(E) 2 **.**

2a

1042

Let *M* represent a certain mass of coal which we assume will deliver 100 joules of heat when burned - whether in a house, delivered to the radiators **or** in a power plant, delivered at 1000°C. Assume the plant is ideal (no waste in turbines or generators) discharging its heat at **30°C** to a river. How much heat will M, burned at the plant to generate electricity, provide **for** the house when the electricity is:

(a) delivered to residential resistance-heating radiators?

(b) delivered to a residential heat pump (again assumed ideal) boosting heat from a reservoir at 0°C into a hot-air system at ***3OoC?***

(**Wisconsin)**

Solution:

When *M* is burned in the power plant, the work it provides is

= **76.2J .**

This is delivered in the form of electric energy.

(a) When it is delivered to residential resistance-heating radiators, it

(b) When the electricity is delivered to a residential heat pump, heat **flows** from a source of lower temperature to a system at higher temperature, the working efficiency being

will transform completely into heat: ***Q'*** **=** ***W*** **= 76.2J.**

m

&=- **"** **= 273/30 = 9.1**

Tl - T2

Hence the heat provided for the house is

Q' = (1 **+** *E)W* = **770** J **.**

1043

An air conditioner is a device used to cool the inside of a home. It is, in essence, a refrigerator in which mechanical work **4** done and heat removed from the (cooler) inside and rejected to the (warmer) outside.

A home air conditioner operating on a reversible Carnot cycle between the inside, absolute temperature ***T2,*** and the outside, absolute temperature ***TI*** **>** ***T2,*** consumes *P* joules/sec from the power lines when operating continuously.

(a) In one second, the air conditioner absorbs ***9 2*** joules from the house and rejects ***Q1*** joules outdoors. Develop a formula for the efficiency ratio ***Q2/P*** in terms of ***TI*** and ***T2.***

(b) Heat leakage into the house follows Newton's law ***Q*** **=** ***A(T1 - T2).*** Develop a formula for ***T2*** in terms of ***TI,*** *P,* and ***A*** for continuous operation of the **air** conditioner under constant outside temperature ***TI*** and uniform (in space) inside temperature ***T2.***

(c) The air conditioner is controlled by the usual on-off thermostat and it is observed that when the thermostat set at **2OoC** and an outside

temperature at ***30°,*** it operates ***30%*** of the time. Find the highest outside temperature, in ***"C,*** for which it can maintain ***20°C*** inside (use ***-273°C*** for absolute zero).

(d) In the winter, the cycle is reversed and the device becomes a heat pump which absorbs heat from outside and rejects heat into the house. Find the lowest outside temperature in ***"C*** for which it can maintain ***20°C*** inside.

(***CUSPEA)***

(a I **(b l**

Fig. **1.15.**

Solution:

(a) From the first and second thermodynamic laws, we have

***Qi* = *P* + *Qzr Qz/Tz* = *Qi,JTi* .**

Hence

__Q2 -_- T2

P ***TI* - *T2* .**

(b) At equilibrium, heat leakage into the house is equal to the heat transfered out from the house, i.e., ***Q2 = A(T1 - T2).*** We obtain, using the result in (a).

Hence /

In view of the fact ***T2 < TI,*** the solution is

T 2 = T2 1 A+ l [E - / m) .

(c) When the air conditioner works **30%** of the time, we know from (b)
When it operates continuously, we have

100 100

p = pSon. **30 239 = A . - . - w 1.13774 .**

With **T2 = 20°C = 293K,** we get

Tl = T2 + = 293 +

= 293 + 18.26 K **= 38.26"C .**

Id) When the cycle is reversed in winter, we have **9 2** = *P* **+ Q1** and

-*Qz* =' **-**Q. i At equilibrium, **Qz = A(T2 - Ti))** so that

T2 Tl

Thus **Ti = T2 -** *K* **-T2 = 293 - (1.14 x 293)'/2 = 275K = 2°C.**

1044

Calculate the change of entropy involved in heating a gram-atomic weight of silver at constant volume from *0"* to **30°C.** The value of ***C,*** over this temperature may be taken **as** a constant equal to **5.85** cal/deg.mole.

(*wis* ***ca*** *nsin)*

Solution:

The change of entropy is

7'2 **30 + 273**

273 as -= **nC,** In - = 5.851n = **n 6 cg T** **Ti**

= 0.61 cal/K **.**

1045

A body of constant heat capacity *C,* and a temperature ***Ti*** is put into contact with a reservoir at temperature ***Tf.*** Equilibrium between the body and the reservoir is established at constant pressure. Determine the total entropy change and prove that it is positive for either sign of (Tf - Ti)/Tf. You may regard 1% - Ti\/Tf < 1.

Solution:

Ti = Tf). The change of entropy of the body is

(wis **co** *nsin)*

We assume Ti # ***fi*** (because the change of entropy must be zero when

The change of entropy of the heat source is

Therefore the total entropy change is

When z > *0* and z # 1, the function f (z) = ***x*** - 1 - Ins > 0. Therefore

1046

One kg of H_2O at 0°C is brought in contact with a heat reservoir at

(a) what is the change in entropy of the water?

(b) what is the change in entropy of the universe?

(c) how could you heat the water to 100°C so the change in entropy of

100OC. When the water has reached 100°C,

the universe is zero?

(was ***co*** nsin)

Solution:

The process is irreversible. In order to calculate the change of entropy of the water and of the whole system, we must construct a reversible process which has the same initial and final states as the process in this problem.

(a) We assume the process is a reversible process of constant pressure. The change in entropy of the water is

r373

We substitute m = lkg, and C H ,=~ 4 .18 J /g into it, and find

ASH,, = 1305 J/K **.**

(b) The change in entropy of the heat source is

Ash, = -IQI/T = -1000 x **4.18** x 100/373

= -11121 J/K **.**

Therefore the change of entropy of the whole system is

(c) We can imagine infinitely many heat sources which have infinitesimal temperature difference between two adjacent sources from O°C to 100°C. The water comes in contact with the infinitely many heat sources in turn in the order of increasing temperature. This process which allows the temperature of the water to increase from 0°C to 100°C is reversible; therefore **AS** = 0.

1047

Compute the difference in entropy between 1 gram of nitrogen **gas** at a temperature of 20°C and under a pressure of **1** atm, and 1 gram of liquid nitrogen at a temperature -196"C, which is the boiling point of nitrogen, under the same pressure of 1 atm. The latent heat of vaporization of nitrogen is 47.6 cal/gm. Regard nitrogen **as** an ideal **gas** with molecular weight **28,** and with a temperature-independent molar specific heat at constant pressure equal to 7.0 cal/mol.K.

(UC, **Berkeley)**

Solution:

The number of moles of l g nitrogen is

n = 1/28 = 3.57 x lO-'rnol.

The entropy difference of an ideal gas at 20°C and at -196°C is

AS' = nCpln(T,/T2) = 0.33 cal/K **,**

and the entropy change at phase transition is

AS" = *nL/Tz* = 0.64 cal/K **.**

Therefore **AS** = **AS' + AS''** = 0.97 cal/K.

1048

A Carnot engine is made to operate as a refrigerator. Explain in detail, with the aid of (a) a pressure-volume diagram, (b) an enthalpy-entropy diagram, all the processes which occur during a complete cycle or operation. This refrigerator freezes water at 0°C and heat from the working substance is discharged into a tank containing water maintained at 20°C. Determine the minimum amount of work required to freeze **3** kg of water.

(SVNY, Buflalo)

V S

[a) (b)

Fig. 1.16.

Solution:

(a) **As** shown in Fig. l.l6(a),

1-2: adiabatic compression,

2-3: isothermal compression,

3-4: adiabatic expansion,

4-1: isothermal expansion.

(b) As shown in Fig. l.l6(b):

1-2: Adiabatic compression. The entropy is conserved.

2-3: Isothermal compression. If the working matter is an ideal gas, the

3-4: Adiabatic expansion. The entropy is conserved.

4-1: Isothermal expansion. The enthalpy is conserved.

The refrigeration efficiency is

enthalpy is conserved.

Hence

TI - ***T2***

T2

W = *9 2 ~.*

Q2 = *ML* is the latent heat for *M* = **3** kg of water at ***T*** = 0°C to become ice. As

L = **3.35 x lo5** J/kg **,**

we find *W* = **73.4** x **lo3** J.

1049

n = 0.081 kmol of He gas initially at **27°C** and pressure = **2** x **105N/m2** is taken over the path *A* -+ *B* --t C. For He

C, = **3R/2 ,** *C,* = **5R/2 .**

Assume the ideal gas law.

from *A* -+ *B?*

(a) How much work does the gas do in expanding at constant pressure

(b) What is the change in thermal or internal energy of the helium

(c) How much heat **is** absorbed in going from *A* -+ *B?*

(d) **If** *B* -+ *C* **is** adiabatic, what is the entropy change and what is the

from *A* → *B?*
final pressure?
Solution:
(was *co* nsin)

(a) For *A B,* the external work is

W = *PA(VB - VA)* = 1.0 **x lo5** J .

(b) For *A* → *B,* the increase of the internal energy is

AU = &',,AT = *C,,PA(VB - VA)/R* = *3W/2* = **1.5** x 1o5 J .

*:-A

21 x ' l0o55[■ I

C
I I I
I I I I I I
0 1.0 1.5 2.0
v(m3)

Fig. 1.17.

(c) By the first law of thermodynamics, the heat absorbed during *A* +
B is *W* + *AU* = **2.5** x 1o5 3.

(d) For *B* + C, the adiabatic process of an monatomic ideal gas satisfies the equation

pV7 = const. , where 7 = *C,/C,* = **5/3** .

Thus *p~v;* = *pcv,'* and ***p c*** = *(vB/vc)7pB*= **1.24** *x* 1o5 **N/rn2.**

In the process of reversible adiabatic expansion, the change in entropy is AS = 0. This is shown by the calculation in detail as follows:

TC VC
TB VB
TcV2-l
= nC, In = O .
~Bv2-l

AS = nC,, In - + **nR** In -

1050

A mole of an ideal gas undergoes a reversible isothermal expansion

from volume **V1** to **2V1.**

(a) What is the change in entropy of the gas?
(b) What is the change in entropy of the universe?

Suppose the same expansion takes place as a free expansion:

(a) What is the change in entropy of the gas?
(b) What is the change in the entropy of the universe?

(wis *co* nsin)

Solution:

the system is

(a) In the process of isothermal expansion, the external work done by
pdV = R T - -- R T I n 2 .

Because the internal energy does not change in this process, the work is supplied by the heat absorbed from the external world. Thus the increase of entropy of the gas is

(b) The change in entropy of the heat source **AS2** = **-ASl,** thus the total change in entropy of the universe is

If it is a free expansion, the internal energy of the system is constant. **As** its final state is the same **as** for the isothermal process, the change in entropy of the system is also the same. In this case, the state of the heat source does not change, neither does its entropy. Therefore the change in entropy of the universe is **AS** = Rln2.

1051

N atoms of a perfect gas are contained in **a** cylinder with insulating walls, closed at one end by a piston. The initial volume is **V1** and the initial temperature 2'1.

(a) Find the change in temperature, pressure and entropy that would occur if the volume were suddenly increased to V2 by withdrawing the piston.

(b) How rapidly must the piston be withdrawn for the above expressions to be valid?

(MITI

[Ejl. -

Fig. 1.18.

Solution:

(a) The gas does no work when the piston is withdrawn rapidly. Also, the walls are thermally insulating, so that the internal energy of the gas does not change, i.e., dU = 0. Since the internal energy of an ideal gas is only dependent upon temperature *T,* the change in temperature is 0, i.e., *Tz* = *TI.* As for the pressure, *p 2/p 1* = Vl/V2. The increase in entropy is

(b) The speed at which the piston is withdrawn must be far greater than the mean speed of the gas molecules, i.e., u >> *0 = (8 k T l/~ m) ~/~.*

1052

A cylinder contains a perfect gas in thermodynamic equilibrium at **p,** V, *T, U* (internal energy) and *S* (entropy). The cylinder **is** surrounded by a very large heat reservoir at the same temperature *T.* The cylinder walls and piston can be either perfect thermal conductors or perfect thermal insulators. The piston is moved to produce a small volume change *AV. "Slow" or "fast" means that during the volume change the speed of the piston is very much less than, or very much greater than, molecular speeds at temperature T. For each of the five processes below show (on your answer sheet) whether the changes (after the reestablishment of equilibrium) in the other quantities have been positive, negative, or zero.

+ ***AV***

-AV

T

Fig. 1.19

I I I 1 *A T* 1 AU 1 AS

1. **(+AV)** (slow) (conduct)
2. **(+AV)** (slow) (insulate)
3. **(+AV)** (fast) (insulate)
4. **(+AV)** (fast) (conduct)
5. **(-AV)** [fast) (conduct)

(wis co *ns* ***in)***

Solution:

(1) For isothernial expansion, **AT** = 0, **AU** = *0,* and

A S = *R*-A V > *0,* **Ap** = --*P*A V < 0 . *V* **V**

(2) For adiabatic expansion, **AQ** = 0. Because the process proceeds very slowly it can be taken as a reversible process of quasistatic states, then **AS** = *0.* The adiabatic process satisfies pV7 = const. While V increases, ***p*** decreases, i.e., **Ap** < 0; and the internal energy of the system decreases because it does work externally, thus **AU** < 0, or **AT < 0.**

(3) The process is equivalent to adiabatic free expansion of an ideal gas, thus **AS** > 0, **AU** = *0,* **AT** = *0,* **Ap** < 0.

(4) The result is as the same as that of isothermal free expansion, thus **AT** = *0,* **AU** = 0, **AS** > *0,* **Ap** < *0.*

(5) The result is the same as that of isothermal free compression, thus
The above are summarized in the table below

AT = 0, **AU** = 0, **Ap** > 0, AS < 0.

1053

A thermally insulated box is separated into two compartments (volumes *Vl* and *Vi)* by a membrane. One of the compartments contains an ideal gas at temperature T; the other is empty (vacuum). The membrane is suddenly removed, and the gas fills up the two comparments and reaches equilibrium.

(a) What is the final temperature of the gas?

(b) Show that the gas expansion process is irreversible.

(MIT)

insulated walls ml . ... ,. . ·.. ..*. .. . . . : .: . ..:: .. .: .;. :

Fig. 1.20.

Solution:

(a) Freely expanding gas does no external work and does not absorb heat. So the internal energy does not change, i.e., *dW* = 0. The internal energy of an ideal gas is only a function of temperature; as the temperature does not change in the process, ***Tf*** = T.

(b) Assuming a quasi-static process of isothermal expansion, we can calculate the change in entropy resulting from the free expansion. In the

process, we have dS = pdV/T,pV = NkT. Hence,

S, - S = P Vl +v2 > (). / dS = -dV = Nkln ___

Vl

Thus the freely expanding process of the gas is irreversible.

1054

A thermally conducting, uniform and homogeneous bar of length ***L,*** cross section ***A,*** density ***p*** and specific heat at constant pressure ***cp*** is brought to a nonuniform temperature distribution by contact at one end with a hot reservoir at a temperature TH and at the other end with a cold reservoir at a temperature T,. The bar is removed from the reservoirs, thermally insulated and kept at constant pressure. Show that the change in entropy of the bar is

where *C,,* = ***cppAL,***

(SVNY, ***Buflulo)***

Solution:

As the temperature gradient in the bar is (T'-T,)/L, the temperature at the cross section at a distance x from the end at T, can be expressed by

T, = T, + (TH - T,)x/L. **As** the bar is adiabatically removed, we have

Tf = (TH + T,)/2 **.**

from which we obtain

But **cp** = T(aS/aT),

rL ***Jo***

Tf =

L

AS =***cppA*** dx

where ***C,,*** = ***c,pAL.***

1055

A mixture of 0.1 mole of helium **(71 = C,/Cv = 5/3)** with **0.2** mole of nitrogen **(72 = 7/5),** considered an ideal mixture of two ideal gases, is initially at **300K** and occupies 4 litres. Show that the changes of temperature and pressure of the system which occur when the gas is compressed slowly and adiabatically can be described in terms of some intermediate value of **7.** Calculate the magnitude of these changes when the volume is reduced by 1%.

*(UC, **Berkeley)***

Solution:

The entropy change for an ideal gas is

AS = nC, ln(Tf/z) + **nR** ln(Vf/x) **,**

where **n** is the mole number, i and f indicate initial and final states respectively. **As** the process is adiabatic the total entropy change in the nitrogen gas and helium gas must be zero, that is, **AS,** + **AS2** = 0. The expression for **AS** then gives

where

Together with the equation of state for ideal gas, it gives

where

nlCpl+ n2Cp2

nlCvl+ n2G2

7 =

Helium is monatomic, **so** that **C,, = 3R/2,** ***C,,*** **= 5R/2;** nitrogen is diatomic, so that **C,, = 5R/2, C,, = 712.** Consequently, **7** = 1.46.

When Vf = **0.99x,** we have

Tf = **1.006Ti = 302** K **,**

pf = 1.016pi = l.O16nRT/V = **2.0** x lo5 **N/m2**

1056

Consider two ways to mix two perfect gases. In the first, an adiabatically isolated container is divided into two chambers with a pure gas ***A*** in the left hand side and a pure gas *B* in the right. The mixing is accomplished by opening a hole in the dividing wall.

Cross section: [-z;zzJ

Fig. 1.21(a).

In the second case the chamber is divided by two rigid, perfectly selective membranes, the membrane on the left is perfectly permeable to gas *A* but impermeable to gas *B*. The membrane on the right is just the reverse. The two membranes are connected by rods to the outside and the whole chamber is connected to a heat reservoir at temperature *T*. The gases can be mixed in this case by pulling left hand membrane to the left and the right hand one to the right.

A permeable *B* permeable

Cross sect ion: B

Fig. 1.21(b).

(a) Find the change in entropy of the container and its contents for second process.

(b) Find the change in entropy of the container and contents for the first process.

(c) What is the change in entropy of the heat reservoir in part (a)?

(CUSPEA)

Solution:

(a) Because the process is reversible, we have

where we have made use of the equation of state $pV = nRT$.

(b) Because energy is conserved and the internal energy of an ideal gas is related only to its temperature, the temperatures of the initial and final states are the same. The initial and final states of the gas in this case are identical with those in case (a). **As** entropy is a function of state, **AS** is equal to that obtained in (a).

(c) **Asheat** source = **-AS,** where **AS** is that given in (a).

1057

Consider a cylinder with a frictionless piston composed of a semipermeable membrane permeable to water only. Let the piston separate a volume V of *N* moles of pure water from a volume ***V'*** of a dilute salt (NaC1) solution. There are ***N'*** moles of water and *n* moles of the salt in the solution. The system is in contact with a heat reservoir at temperature *T*.

(a) Evaluate an expression for entropy of mixing in the salt solution.

(b) If the piston moves so that the amount of water in the salt solution

(c) Derive an expression for the pressure *A* across the semipermeable

***(Prince** ton)*

(a) The entropy of mixing, i.e., the increase of entropy during mixing doubles, how much work is done?

membrane as a function of the volume of the salt solution.

Solution:

isothermally and isobarically is

$$N' n \ \mathrm{AS} = -N'R \ \mathrm{In} \ N' + n - nR \ \mathrm{In} - N' + n .$$

(b) The osmotic pressure of a dilute solution is

AV' = *nRT* (Van't Hoff's law) **.**

When the amount of water in the salt solution doubles, the **work** done is

W = 12"'*ndV* = 1 **: '** -n*dV*y = **nRTln2.**

v'

(c) *A* = *nRT/V'.* The osmotic pressure, i.e., the pressure difference across the membrane, is the net and effective pressure on the membrane.

1058

(a) In the big-bang theory of the universe, the radiation energy initially confined in a small region adiabatically expands in a spherically symmetric manner. The radiation cools down as it expands. Derive a relation between the temperature *T* and the radius *R* of the spherical volume of radiation, based purely on thermodynamic considerations.

(b) Find the total entropy of a photon gas as a function of its temperature *T,* volume *V ,* and the constants ***k, h,c.***

*(SUNY, **Bufulo)***

Solution:

(a) The expansion can be treated as a quasi-static process. We then have *dU* = *TdS* - *pdV.* Making use **of** the adiabatic condition *dS* = 0 and the expression for radiation pressure **p** = *U/3V,* we obtain *dU/U* = *-dV/3V;* hence ***U*** cx *V-'f3.* The black body radiation energy density is *u* = *U/V* = *aT4, a* being a constant. The above give *T4* o(*V-4/3* cx *RP4, so* that *To(R-l,* i.e., *RT* = constant.

(b) *dS* = *-dU* + -**P***d V* = *-Vd u* + -**4**-*d***u***V* = *d*

T T T 3T

4

we obtain *S* = *,aT3V.* By dimensional analysis we find *a* - ***k 4 / (h ~) 3***In.

fact, *a* = -- so that *S* = 4-T2 -*k4 T 3V.*

n2 k'

15 *(h ~') ~* 45 ***(hc)3***

1059

(a) A system, maintained at constant volume, is brought in contact with a thermal reservoir at temperature *Tf.* If the initial temperature of the system **is** *X* **,** calculate *AS,* change in the total entropy of the system + reservoir. You may assume that ***c,,*** the specific heat of the system, is independent of temperature.

(b) Assume now that the change in system temperature is brought about through successive contacts with *N* reservoirs at temperature + *AT,* + *2AT,. . . ,* ***fi*** - *AT,* ***fi,*** where *NAT* = ***fi*** - *X* **.** Show that in the limit *N* -+ *oo, AT* -+ *0* with *NAT* = *Tf* - *X* fixed, the change in entropy of the system + reservoir is zero.

(c) Comment on the difTerence between (a) and (b) in the light of the second law of thermodymmics.

(SUNY, Bufulo)

Solution:

(a) The change in entropy of the system is

Tf Mc,dX **Tf**

Ti

- Mc, In - **.**

The change in entropy of the heat source is

The total change in entropy is

AS = AS, +**AS,** = Mc,

N-1

AS= lim *C* AS, ,

AT-0

AN+w n=O

where

-

Tj + **nAT** + **(n** + **1)AT**

is the change in entropy of the **(n** + 1)th contact. Thus

(c) The function f(z) = z - Ins - 1 > 0 **if** z > 0 and z # 1. Thus in (a) **AS** = Mc,f(Ti/Tf) > 0, that is, the entropy is increased. We know the process is irreversible from the second law of thermodynamics. In (b) **AS** = 0, the process is reversible.

1060

A material is brought from temperature 3 to temperature **Tf** by placing it in contact with a series of ***N*** reservoirs at temperatures ***Ti*** + **AT,** ***Ti*** +

2AT,. . . , ***Ti*** + NAT = Tf. Assuming that the heat capacity of the material, C, is temperature independent, calculate the entropy change of the total system, material plus reservoirs. What is the entropy change in the limit

N + 00 for fixed Tf - Z ?

(*wis* ***co nsin)***

Solution:

reservoir at temperature ***Ti*** + ***(t*** + 1)AT.

equilibrium, the change of entropy of the material is

Consider the material at temperature ***Ti*** + tAT in contact with the

When they come to thermal

T i + (t + 1)AT CdT *T* + *(t* + 1)AT

~- - Cln T z + t A T ·

AS1 = *1* Ti+tAT

The change in entropy of the heat reservoir is

CAT

z + (t + 1) A T '

AS2 = -

The total change in entropy is

- AT *)* **. *Ti*** + ***(t*** + 1)AT

Therefore, after the material of initial temperature ***Ti*** has had contacts with

the series of reservoirs, the total change of entropy of the whole system is
N-1 **N-1**
A S = C A S t = C (ln' *11* -

2?, + *(t* + 1)AT *t =o* t = o

When N -+ 00, *or* AT -t 0, the above sum can be written as an integration, so that

1061

The specific heat of water is taken as 1 cal/g.K, independent of temperature, where 1 calorie = 4.18 joules.

(a) Define the specific heat of a substance at constant pressure in terms of such quantities as Q (heat), S (entropy), and T (temperature).

(b) One kg of water at 0°C is brought into sudden contact with a large heat reservoir at 100°C. When the water has reached 1OO"C, what has been the change in entropy of the water? Of the reservoir? Of the entire system consisting of both water and the heat reservoir?

(c) If the water had been heated from 0°C to 100°C by first bringing it into contact with a reservoir at 50°C and then another reservoir at 1OO"C, what would be the change in entropy of the entire system?

(d) Show how the water might be heated from 0°C to 100°C with
(UC, **Berkeley)**
negligible change in entropy of the entire system.

Solution: (a)cp=(g),=~(g). P

(b) The change in the entropy of the water is
and the change in entropy of the reservoir is
AS, = T2 - **Ti** *-cP-* = -0.268 *T2*

cal/g,K **.**

Thus **AS** = 0.044 cal/g.K.

(c) In this process, the change in entropy of the water is still AS': = 0.312 cal/g,K, while that of the reservoir **is**
AS; = - 1 x (50 - 1) - 1 X (100 - 50)

273 + 50 273 + 100
= -0.289 cal/g.K

So that **AS'** = **AS:** + AS; = 0.023 cal/g.K **.**

(d) Divide the range of temperature 0°C - 100°C into *N* equal parts, with *N* >> 1.

At every temperature point, there exists a large heat rcservoir. Let the water come into contact with them successively from low temperature to high temperature, to make the process of thermal contact quasi-static. Then *AS* = 0 at every step and consequently for the entire process.

1062

Two finite, identical, solid bodies of constant total heat capacity per body, C, are used as heat sources to drive heat engine. Their initial temperatures are *TI* and *T2* respectively. Find the maximum work obtainable from the system.

Soh t ion :

As energy is conserved, the work obtainable is *W* = *C(T1* + *T2* - **2 q) ,** where *Tf* is the final temperature of the system. From the second law of thermodynamics, we have

(MIT)
Tf Tr
Tl TZ

AS = Cln - + Cln - > 0 , so that *Tf* > *m.*

Hence *W,,,* = *C(T1* + *T2* - **2 m) .**

1063

A rigid box containing one mole of air at temperature *2'0* (in K) is initially in thermal contact with an "infinite' heat-capacity reservoir" at the same temperature *TO.* The box is removed from the reservoir and **a** cyclic engine is used to take some heat from the reservoir and put some into the air in the box. What is the minimum amount of work from *To* to *TI?* Express *W* in terms **of** *TO, TI* and the gas constant *R,* and state units. Ignore vibrational degrees-of-freedom in the air molecules and the heat capacity of the container. Would inclusion of vibrational degrees-offreedom increase or reduce the value of *W?*

(***Columbia)***

Solution:

"infinite heat-capacity reservoir" **,** we get

As AQ + *W* = *C,(T1 - To),* where *AQ* is the heat absorbed from the

0 **I** *AS* = *ASsourc*+*e* **Asair** = *-AQ/To* + ***C,,*** ln(Tl/To) **.**

Hence

W *2* Cu(Tl - ***To)*** - **CUT,** ln(Tl/To) = Wmin **.**

With the inclusion of vibrational degrees-of-freedom, Wmin increases **as** C, increases.

1064

A reversible heat engine operates between two reservoirs, *Ti* and *T2* ***(T2*** > Tl). Ti can be considered to have infinite mass, i.e., Ti remains constant. However the warmer reservoir at Tz consists of a finite amount of gas at constant volume ***(p*** moles with a specific heat capacity ***C,) .*** After the heat engine has operated for some long period of time, the temperature *Tz* is lowered to *TI.*

(a) What is the heat extracted from the warmer reservoir during this period?

(b) What is the change of entropy of the warmer reservoir during this period?

(c) How much work did the engine do during this period?

(Columbia)

Solution:

(a) ***Qab*** = *pC,(T,* - Ti).

dQ G U d T Tl
T ***T*** *Tz*

(b) Because *dS* = - = ___ **,** AS=pC, ln- .

dW Tl ***(c)*** **- = 1 - -** *dQ T ' dQ* = ***-pC,dT,*** therefore the **work** done by the engine is

W=/dW=-/TT1 **(1- *~) p C u d T =p C , (T 2 - 4)) L C , T l l ~*** *(2)* .

1065

Large heat reservoirs are available at 900 K (H) and 300 K (C).

(a) 100 cal of heat are removed from the reservoir *H* and added to C.
(b) A reversible heat engine operates between *H* and C. For each
What is the entropy change of the universe?

100 cal of heat removed from *H,* what work is done and what heat is added
to *C?*
(c) What is the entropy change of the universe in the process of part
(b) above?
(d) **A** real heat engine is operated as a heat pump removing heat from
C and adding heat to *H.* What can be said about the entropy change in
the universe produced by the heat pump?

(Wisconsin)

Solution:

(a) The change of entropy of the universe is
2
(b) The external work done by the engine for each 100 cal of heat is
200
3
xlOO=-cal.
The heat absorbed by *C* is
100
Q2=Q1 -*W* = **-3** c a l .
(c) The change in entropy of the universe is
(d) The change of entropy is
AS = - - +92- , Qi
TC TH
where Q2 is the heat released by the reservoir of lower temperature, Q1 is
the heat absorbed by the reservoir of higher temperature. **As** - - - *5*
O,AS>O.
Qz Qi
TC *TH*

1066

Consider an arbitrary heat engine which operates between two reservoirs,
each of which has the same finite temperature-independent heat capacity
c. The reservoirs have initial temperatures *TI* and *T2,* where *T2* > *TI,*
and the engine operates until both reservoirs have the same final temperature
T3.

(a) Give the argument which shows that *T3* > ***m.***
(b) What is the maximum amount of work obtainable from the engine?
(UC, **Berkeley)**

Solution:

(a) The increase in entropy of the total system is

Thus *T:* 2 *T1T2,* or *T3* 2 ***a.***
(b) The maximum amount of work can be obtained using a reversible
heat engine, for which **AS** = 0.

Wmax = *C(TI*+ *T2* - **2T31nin)** = *c(T1* + *T2* - ***2 m)*** = ~ *(f i -* **.**

1067

(a) What is the efficiency for a reversible engine operating around
the indicated cycle, where *T* **is** temperature in K and *S* is the entropy in
joules/K?
T

~30O0 -O --~ -; -- - -- -- -- - - - - r L ~ s

Fig. **1.22.**

(b) **A** mass *M* of a liquid at a temperature *TI* is mixed with an equal mass of the same liquid at a temperature *T2.* The system is thermally insulated. **If** *cp* is the specific heat of the liquid, find the total entropy change. Show that the result is always positive.

***(UC,* Berkeley)**

Solution :

(a) In the cycle, the heat absorbed by the engine is

400 + *300*

2

Q = (1000 - *500)* = **1.75 *x* lo5** J ,

and the work it does is

400 - 300

2

W = (1000 - 500) = 2.5 x **lo4** J

Thus the efficiency is ***q*** = *W/Q* = **14.3%.**

fore

(b) Obviously the equilibrium temperature is *T3* = (TI +*T2)/2.* Thereand

thus

Since *(TI* + T2)2 *2 4TlT2,* we have AS *2* 0.

1068

(a) One mole of an ideal gas is carried from temperature *TI* and molar volume *V1* to *T2,VZ.* Show that the change in entropy is

T2 v2

Ti *Vl*

A S = C , l n - + R l n - .

(b) An ideal gas is expanded adiabatically from *(p l , Vl)* to *(p2,* V2). Then it is compressed isobarically to *(p2,* V1). Finally the pressure is

increased to *p1* at constant volume *Vl.* Show that the efficiency of the cycle is

r] = 1 - 7(V2/vl - l) / (P l / P 2 - 1) ;

where *7* = *C,/C,,.*

(Columbia)

Solution:

1 1

T T (a) From *dS* = *-(dU* + *pdV)* = *-(C,dT* + *pdV)* and

pV = *RT* ,

we obtain

T2 v2

Tl Vl

A S = C , l n - + R l n - .

(b) The cycle is shown in the Fig. **1.23.**

A

adiabatic

p2

Vl

Fig. **1.23.**

The work the system does in the cycle **is**

Because *AB* is adiabatic and an ideal gas has the equations $pV = nkT$ and

$C, = C, + R,$ we get

During the *CA* part of the cycle the gas absorbs heat

$$Q = \int_{CA} TdS = CvdT = CV(Tl - Tz)$$

Hence, the efficiency of the engine is

1069

(1) Suppose you are given the following relation among the entropy S, volume V, internal energy U, and number of particles N of a thermodynamic system: $S = A[NVU]\ 1/3$w, here A is a constant. Derive a relation among:

(a) U, N, V and $T;$

(b) the pressure p, $N, V,$ and T.

(c) What is the specific heat at constant volume c,?

(2) Now assume two identical bodies each consists solely of a material obeying the equation of state found in part (1). N and V are the same for both, and they are initially at temperatures TI and $T2$, respectively. They are to be used as a source of work by bringing them to a common final temperature Tf. This process is accomplished by the withdrawal of heat from the hotter body and the insertion of some fraction of this heat in the colder body, the remainder appearing as work.

(a) What is the range of possible final temperatures?

(b) What Tf corresponds to the maximum delivered **work,** and what is

You may consider both reversible and irreversible processes in answer-

(Prince *ton)*

this maximum amount of **work?**

ing these questions.

Solution:

(1)

$U=- s3$

$A3NV$

(2) When no work is delivered, Tf will be maximum. Then

2

$$3\ 91 = \int^{Tf}_{T} c,dT = XfidT = -A(Tfi2 - ,$$

2

3

$$Q\ 2 = \int^{T(}_{T} c,dT = -A(TfI2 - Ti12)\ .$$

Since $91 + 92 = 0$, we have

The minimum of T corresponds to a reversible process; for which the change in entropy of the system is zero. As

$$AS1 = c,dT/T = 2A(T;I2 - T;I2)\ ,$$

$$AS2 = 12\quad c,dT/T = 2A(T;12 - T i f 2)\ .$$

r Tf

and *AS1* + *AS,* = *0,* **we have**

Hence

-

W,,, corresponds to Tfn,in,i .e., the reversible heat engine has the maximum delivered work

1070

One kilogram of water is heated by an electrical resistor from 20°C to 99°C at constant (atmospheric) pressure. Estimate:

(a) The change in internal energy of the water.

(b) The entropy change of the water.

(c) The factor by which the number of accessible quantum states of

(d) The maximum mechanical work achievable by using this water as

(UC, **Berkely)**

the water is increased.

heat reservoir to run an engine whose heat sink is at 20°C.

Solution:

(a) The change in internal energy of the water is

AU = ***McAT*** = 1000 x 1 x 79 = 7.9 x lo4 cal.

(b) The change in entropy is

AS = S ***-MdTc*** = *Mc* In ***-T2*** = **239** cal/K,

T Tl

(c) Rom Boltzmann's relation S = Iclnr2, we get

nl

-n2 = exp *(y)* = exp(7 x ***1025).***

(d) The maximum mechanical work available is

= 9 x lo3 **cal .**

1071

One mole of the paramagnetic substance whose TS diagram is shown below is to be used as the working substance in a Carnot refrigerator operating between a sample at **0.2** K and a reservoir at 1K:

(a) Show a possible Carnot cycle on the TS diagram and describe in detail how the cycle is performed.

(b) For your cycle, how much heat will be removed from the sample per cycle?

(c) How much work will be performed on the paramagnetic substance

(Columbia)

per cycle?

Fig. 1.24.

Solution:

(a) The Carnot cycle is shown in the Fig. 1.24;

A -+ *B,* adiabatically decrease the magnetic field;

B 4 ***C,*** isothermally decrease the magnetic field;

C -+ D, adiabatically increase the magnetic field;

D + *A,* isothermally increase the magnetic field;

(b) Qabs= *z owAS~- - . c= 0.2* x (1.5 - 0.5)R

= 1.7 x lo7 ergs/mol.

(c) Qrel= ***T h i g h A S*** ~ +=~ 1 x (1.5 - 0.5)R

= 8.3 x lo7 ergs/mol.

The work done is

W = Qrel - Qabs = 6.6 x lo7 ergs/mol.

1072

A capacitor with a capacity that is temperature sensitive is carried through the following cycle:

(1) The capacitor is kept in a constant temperature bath with a temperature ***TI*** while it is slowly charged (without any ohmic dissipation) to charge *q* and potential ***V1.*** An amount of heat Q1 flows into the capacitor during this charging.

(2) The capacitor is now removed from the bath while charging con-

(3) The capacitor is kept at a temperature ***T2*** and is slowly discharged.

(4) It is removed from the bath which kept it at temperature ***T2*** and discharged completely until it is returned to its initial uncharged state at temperature ***T1.***

(a) Find the net amount of work done in charging and discharging the capacitor.

(b) How much heat flows out of the capacitor in step **(3)?**

(c) For fixed capacitor charge *q* find ***dV/dT.***

tinues until a potential ***V2*** and temperature ***T2*** are reached.

Hint: Consider ***V2*** = ***V1*** + ***dV***

(Columbia)

Solution:

(a) The whole cycle can be taken as a reversible Carnot cycle.

(1) and **(3)** are isothermal processes; **(2)** and **(4)** are adiabatic pro-

In the whole cycle, the work done by the outside world is

cesses.

Fig. ***1.25.***

(c) We construct the V(Vo1tage)-q(charge) diagram for the cycle as shown in the Fig. **1.25.** We have

W = Vdq.

Assume V2 = V, + *d V,* where dV is an infinitesimal voltage change, and let the capacitance of the capacitor be *C(T).* We then have

£

0 -+ *A* : V = *q/C(T1)* , ***B*** -+ C : V = q/C(T2)

Obviously the adiabatic line *B* -+ *C* crosses point 0. Thus if dV is.a small quantity, V3 is also **a** small quantity. Then in the first-order approximation,

Therefore

On the other hand, we know from (a)

Qi Q

Tl T W = *-(T2* - *Ti)* = *-dT.*

Thus

or

Finally we have

(%)q = [" dT . '1, C(T) = 9& (&)

or

where $Q(T,q)$ is the heat that the capacitor absorbs when it **is** charged from 0 to q while in contact with a heat source of constant temperature T.

3. THERMODYNAMIC FUNCTIONS AND EQUILIBRIUM CONDITIONS (1073-1105)

1073

For each of the following thermodynamic conditions, describe a system, *or* class of systems (the components *or* range of components, temperatures, etc.), which satisfies the condition. Confine yourself to classical, single

component, chemical systems of constant mass. U is the internal energy and S is the entropy of the system.

(*wis* **co** nsin)

Solution:

(a) The classical ideal gas.

This requires $a < 0$, i.e., the system has a negative coefficient of expansion at const ant pressure.

= 0. This requires C, = 00. The system has two

T

P CP

coexistent phases.

(d) (g)T = (g) = 0. This requires ,d = ; - (g)V = 0.

v

It is a system whose coefficient of pressure at constaht volume is zero.

(e) All systems of a single component and constant mass satisfy this Maxwell relation.

1074

Consider an ideal gas whose entropy is given by " I n

U

n

u+5Rln-++Rln- ,

where n = number **of** moles, R = universal gas constant, U = internal energy, V = volume, and u = constant.

(a) Calculate **cp** and **cv**, the specific heats at constant pressure and volume.

(b) An old and drafty house is initially in equilibrium with its surroundings at **32°F.** Three hours after turning on the furnace, the house is at a cozy **70°F.** Assuming that the air in the house is described by the above equation, show how the energy density (energy/volume) of the air inside the house compares at the two temperatures.

(***Columbia)***

Solution:

(a) The temperature T is determined by the following equation:

1 = -n5 R - ,1 or U = - 5n R T .

T=(%)" **2** *u* **2**

Therefore, the specific heat at constant volume is

c v = (g) = **-5**n R .

v 2

The specific heat at constant pressure is

v

cp = c, -l- nR = :nR. **2**

U 5 n

(b) - = ***-R*** (p) T .

v 2

Using the equation of state of ideal gas pV = nRT, we have

_u - 5 v ***- iiP***

Because the pressure of the atmosphere does not change at the two temperatures in the problem, neither does the energy density.

1075

A perfect gas may be defined as one whose equation **of** state is ***pV*** = ***NkT*** and whose internal energy is only a function **of** temperature. For a perfect gas **show** that

(a) **cp** = **c,** + ***k,*** where **cp** and c, are the heat capacities (per molecule)

(b) The quantity **pV7** is constant during an adiabatic expansion. **(As**at constant pressure and constant volume respectively.

sume that **7** = cp/c, is constant.)

(MITI

Solution:

Let *C,* and *C,* be the principal molar specific heats.

(a) From *pV* = *NkT* and *TdS* = *dU* + *pdV,* we find

C, - C, = T (%),- *T* (g)V *= p* (g) = *Nk* .

P

Hence *C,* - *C,* = *k.*

pV = *NkT,* we have

(b) For an adiabatic process, *TdS* = 0 and hence *C,dT* = *-pdV.From*

pdV + *Vdp* = *NkdT* = *(C, - C,)dT* ,

giving *7pdV* + *Vdp* = *0,* i.e.,

pV7 = const.

1076

The difference between the speficif heat at constant pressure and the specific heat at constant volume **is** nearly equal for all simple gases. What is the approximate numerical value of cp - c,? What is the physical reason for the difference between cp and c,? Calculate the difference for an ideal gas.

Solution:

(*wis cons* **in)**

c, - c, = 1*m* [. (g), - *T*(3V]

where *m* is the mass of the gas. From the functional relationship we can find

(%),= (%) V (z)(T%) ,

Utilizing Maxwell's relation (g)T = (g)V, the above formula becomes

VTa2 (*I

P m

where *a* is the coefficient of thermal expansion, and *K* is the coefficient of compression. For an ideal gas, *a* = - and *K* = -, thus cp - *c,* = nR/m = *RIM. (M* is the molecular weight of the gas).

The formula (*) relates the difference of two specific heats to the equation of state. For some materials, the specific heat at constant volume or constant pressure is not easily measured in experiments; it can be determined with formula (*) by measuring *K* and *a.* For a simple gas, its values of *a* and *K* are near to those of an ideal gas. Thus, the difference between the two specific heats **is** approximately *RIM.* The reason that **cp > *c,* is** that the gas expanding at constant pressure has to do work so that more heat is absorbed for this purpose.

1 1

T P

1077

A paramagnetic system in an uniform magnetic field H is thermally insulated from the surroundings. It has an induced magnetization *M* = aH/T and a heat capacity ***CH*** = *b / p* at constant H, where *a* and *b* are constants and T is the temperature. How will the temperature of the system change when *H* is quasi-statically reduced to zero? In order to have the final temperature change by a factor of **2** from the initial temperature, how strong should be the initial *H?*

(UC, **Berkeley)**

Solution:

From the relation dU = TdS + HdM, we have (g)S = (g) ,

M

so that

a(T, *S)*

8 (H , M) = -l*

Therefore

and *T* = exp(aH2/2b)Tf. This shows that the temperature of the system will decrease as H is reduced to zero.

If Tf = **z/2,** then Hi =

1078

The thermodynamics of a classical paramagnetic system are expressed by the variables: magnetization *M,* magnetic field *B,* and absolute temperature *T.*

The equation of state is

M = *CB/T,* where C = Curie constant .

The system's internal energy is

The increment of **work** done by the system upon the external environment is $dW = MdB$.

(a) Write an expression for the heat input, dQ, to the system in terms of thermodynamic variables M and B:

$dQ = (\ )dM + (\ )dB$.

(b) Find an expression for the differential of the system entropy:

$dS = (\ )dM + (\ )dB$.

(c) Derive an expression for the entropy: S =

(*wis* **co nsin)**

Solution:

(a) $dQ = dU + dW = -d(MB) + MdB = -BdM.$

M2

2 c

(c) *S*=*SO*--.

(Note: the internal energy and the work done in the problem have been given new definitions).

1079

The state equation of a new matter is

$p = AT3/V$,

where ***p*** , V and T are the pressure, volume and temperature, respectively, ***A*** is a constant. The internal energy of the matter is

$U = BT''$ ln(V/Vo) + $f(T)$,

where B, n and Vo are all constants, $f(T)$ only depends on the temperature. Find B and n.

(C *USPEA)*

Solution:

From the first law of thermodynamics, we have

d U + p d V = 1 *dU* [-(-),+$]dV+-(-) 1 aU d T .

T T dV T aT dS =

We substitute in the above the expressions

sure ***p*** and get

BTn-' + ***AT2*** dV ['IF)

V

dS =

for internal energy U and pres-

From the condition of complete differential, we have

giving

2AT - *BTn-'* = 0 .

Therefore $n = 3$, $B = 2A$.

1080

The following measurements can be made on an elastic band:

(a) The change in temperature when the elastic band is stretched. (In case you have not tried this, hold the attached band with both hands, test the temperature by touching the band to your lips, stretch the band and

check the temperature, relax the band and check the temperature once more).

(b) One end of the band is fixed, the other attached to weight *W,* and

(c) With the weight at rest *OQ* is added, and the equilibrium length *L*

Derive the equation by which you can predict the result of the last

(Princeton)

the frequency *u* of small vibrations is measured.

is observed to change by 6L.

measurement from the results of the first two.

Solution:

When heat *6Q* is added with the weight at rest, i.e., with the stress kept unchanged, we have 6s = *6Q/T.* Therefore,

The elastic coefficient of the band is *k* = *W (~ K Y) ~ / ~ .*

As L - Lo = *W/k,* we get

(%) *dLo W dk* = ***dT*** - **kz dT** ,

Thus

where

1081

The tension *F* in an ideal elastic cylinder is given by the equation of state

where *a* is a constant, *Lo* is the length at zero tension, and *L(T)* is a function of temperature *T* only.

(a) The cylinder is stretched reversibly and isothermally from *L* = *Lo* to *L* = *2Lo.* Find the heat transferred to the cylinder, Q, in terms of *a, TI LO* and *ao,* the thermal expansion coefficient at zero tension, being

a o= -1 *d~Lo(T)*

Lo(T) dT ·

(b) When the length is changed adiabatically, the temperature of the cylinder changes. Derive an expression for the elastocaloric coefficient, *(d T / a L) s* where *S* is the entropy, in terms of *a ,* ***T,*** *L , LO,a o,* and *Ct ,* the heat capacity at constant length.

(c) Determine whether *CL* is a function of T alone, *CL(T)*o, r whether it must also depend on the length, *CL(TL,) ,* for this system.

Solution:

(MITI

Let @ be the free energy. From *d@* = *-SdT* + *FdL,* we get

Thus

and

-aTLo

Fig. **1.26.**

(a) Q = *T [S (T , 2 L o)- SO]= -aTLo (1*+ *$Tao).*

a2s = *TaLaT*

L; L

= *-aT*{ + - + *T (2 g* + g) [-- *a01* }, Z *0 L2 Lo*

Thus *CL* = *CL (T, L).*

1082

Information: If **a** rubber band is stretched adiabatically, its temperature increases.

(a) If the rubber band is stretched isothermally, does its entropy in-

(b) If the rubber band is stretched adiabatically, does the internal

crease, decrease, or stay the same?

energy increase, decrease, **or** stay the same?

Solution:

done on it is

(wis ***co*** **nsin)**

(a) We assume that when the rubber band is stretched by *dx* the work

dW = *kxdx* **,**

where *k,* the elastic coefficient, is greater than 0. From the formula *dF* =

-*SdT* + *kxdx,* we can obtain the Maxwell relation: ***(g)T*** = - *(k g) z = 0*

Hence the entropy of the rubber band stays the same while it is stretched

isothermally. (EjS =

(b) According to the formula *dU* = *TdS* + *kxdx,* we have

kx > *0,* that is, its internal energy increases while it is stretched adiabatically.

1083

The tension of a rubber band in equilibrium is given by

where *t* = tension, *T* = absolute temperature, z = length of the band, *lo*

= length of the band when *t* = 0, *A* = constant.

When z is the constant length *lo,* the thermal capacity *cx(z,T)* is

observed to be a constant *K.*

(a) Find as functions of *T* and *x:* ,,

8E

(1) (a ,) where *E* = internal energy, **(2)**

T

E(z, T), (5) S(z,T), where S = entropy.

(b) The band is stretched adiabatically from z = *lo* to z = 1.510. Its

(CUSPEA)

initial temperature was *TO.* What is its final temperature?

Solution:

Then as

(a) From the theory of thermodynamics, we know *dE* = *TdS* + *tdz.*

cx=T(%) x **,**

we have

Generally, *E* = *E(z, T),* and we have

(g) *T dz.*

i.e., *dE* = *c,dT* +

On the other hand,

dS = -**1***(dE- tdx)* = -*cdx T*+ *T T*

we obtain

a2E a2E a2s - a2s

axaT aTaxl axaT aTax

From __ -- -

a2E

aTax

Thus *(aE/a+* = *t* - *T(at/aT),.*

Substituting the expression for *t,* we have *(aE/az)T* = 0. It follows that *(ac,/az),* = 0. Integrating, we get

E(z, T) = E(T) = 6 *dE* + *E(To) =* [*g d T* + *E(To)*

= Lr *KdT* + *E(To) = K(T* - *To)* + *E(To)* .

From

*d S= %dT+T*1 *[(aE,) , - t] d z*

T

we find after integration

S(z, *2')* = K In *T* - A - + - + const.

(;l: :)

(b) For an adiabatic process *dS* = 0 *so* that

After integration we have

= 0.292AZo ,

Hence ***fi*** = *TO* exp(0.292Alo/K).

1084

Consider a gas which undergoes an adiabatic expansion (throttling process) from a region of constant pressure p; and initial volume Vi to a region with constant pressure pf and final volume Vf (initial volume 0). Fig. 1.27.

(a) By considering the work done by the gas in the process, show that the initial and final enthalpies of the gas are equal.

(b) What can be said about the intermediate states of the system?

(c) Show for small pressure differences **Ap** = pf - pi that the temperature difference between the two regions is given by ***AT*** = ***- (Ta*** **- l)Ap,**

V

cv

where ***a*** = - (av) and **cp** = (g) v d T p **P**

(d) Using the above result, discuss the possibility of using the process to cool either an ideal gas, or a more realistic gas for which p = RT/(V- *b)* . Explain your result.

(SUNY, Buffalo)

Solution:

which is equal to a reduction of the internal energy:

(a) The work done by the gas in the throttling process is pfVf - pix,

ui - Uf = pfvf - piVi .

Thus *Ui* + pi& = Uf + pfVf, i.e., *Hi* = Hf.

(b) Because the process is quasi-static, the final and initial states can be any two intermediate states. Thus the conclusion is still valid for intermediate states.

(c) From dH = TdS + Vdp = 0 and

d S = (g) p d T + ($) T d p = $ d T -c (g) d p ,

P

we obtain

Thus for a small pressure difference Ap, we have approximately
(d) For an ideal gas, we have pV = NRT and *a* = 1/T. Hence

AT = V(TQ - l)Ap/c, = 0 .

As AT = 0 this process cannot be used to cool ideal gases. For a realistic gas for which **p** = RT/(V - *b),a* = R/Vp and V(aT - 1) = -b. Hence
AT = -bAp/c,. As Ap < 0 for a throttling process, AT > 0, such a gas cannot be cooled by this process either.

1085

(a) Using the equation of state pV = NRT and the specific heat per mole *C,* = 3R/2 for a monatomic ideal gas, find its Helmholtz free energy *F* as a function of number of moles N, V, and T.

(b) Consider a cylinder separated into two parts by an adiabatic, impermeable piston. Compartments a and b each contains one mole of a monatomic ideal gas, and their initial volumes are Vai = 10 litres and Vbi = 1 litre, respectively. The cylinder, whose walls allow heat transfer only, is immersed in a large bath at 0°C. The piston is now moved reversibly so that the final volumes are Vat = ***6*** and Vbf = ***5*** litres. How much work is delivered by (or to) the system?

(Princeton)

(a) For an ideal gas, we have dU = NC,dT and *U* = NC,T + *Uo,*

Solution:

where ***Uo*** is the internal energy of the system when T = 0. As

d S = -NCud T + ;dV , T

S =3-N R l n T + N R l n V + S h ,
2

where SA is a constant. Assuming the entropy of the system is *SO* when *T* = *TO,* V = Vo1 we have

S =3-NR- T V In-+NRln-+So
2 *To* VO

where FO = *UO* - T O S O .

(b) The process described is isothermal. When dT = 0,dF = -pdV.
The work delivered by the system is

1086

A Van der Waal's gas has the equation of state
(a) Discuss the physical origin of the parameters a and *b.* Why is the correction to *p* inversely proportional to V2?
(b) The gas undergoes an isothermal expansion from volume Vl to
(c) From the information given can you calculate the change in internal
volume V2. Calculate the change in the Helmholtz free energy.
energy? Discuss your answer.

(wisco *nsifl)*

Solution:

(a) On the basis of the equation of state of an ideal gas, we introduce the constant *b* when considering the volume of a real gas to allow for the finite volumes of the molecules and we introduce the constant a to allow for the mutual attraction between molecules of the gas. Now we discuss why the pressure correction term is inversely proportional to V2.

Each of the molecules of the gas has a certain interaction region. For the molecules near the center of the volume, the forces on them are isotropic because of the uniform distribution of molecules around them. For the molecules near the walls (the distances from which are smaller than the interaction distance of molecules), they will have a net attractive force directing inwards because the distribution of molecules there is not uniform. Thus the pressure on the wall must have a correction ***Ap.*** If ***Ak*** denotes the decrease of a molecule's momentum perpendicular to the wall due to the net inward attractive force, these ***Ap*** = (The number of molecules colliding with unit area of the wall in unit time) **~ *2 A k*A. s *k*** is obviously proportional to the attractive force, the force is proportional to the number of molecules in unit volume, **n,** i.e., ***Ak*** *o(n*, and the number of molecules colliding with unit area of the wall in unit time is proportional to n too, we have

Ap *o(* **n2** *o(* ***1/V2* .**

(b) The equation of state can be written as

kT *a*

p = *-V- - - b V 2 '*

In the isothermal process, the change of the Helmholtz free energy is

a

pdV = -k: *kT* - -***dV***

V - b V2

V2 - b

= -kTln (m)+ *a* ($ -4) .

(c) We can calculate the change of internal energy in the terms of *T* and ***V:***

For the isothermal process, we have

d U = (g) ***d V .***

T

The theory of thermodynamics gives

(g)T= *T* (g) *v* -Pa

Use of the equation of state then gives

a

dU = -dV . V2

Integrating, we find

`1087`

A 100-ohm resistor is held at a constant temperature of 300 K. **A** current of 10 amperes is passed through the resistor for 300 sec.

(a) What is the change in the entropy of the resistor?

(b) What is the change in the entropy of the universe?

(c) What is the change in the internal energy of the universe?

(d) What is the change in the Helmholtz free-energy of the universe?

(***Wisconsin)***

Solution:

(a) **As** the temperature of the resistor is constant, its state does not change. The entropy is a function of state. Hence the change in the entropy of the resistor is zero: **AS1** = 0.

(b) The heat that flows from the resistor to the external world (a heat source of constant temperature) is

PRt = 3 x 1oG J

The increase of entropy of the heat source is **AS, = 3** x 1OG/3OO = 1o4 J/K.

Thus the total change of entropy is **AS = AS1** + **AS2** = **lo4** J/K.

(c) The increase of the internal energy of the universe is

AU=3x1O6 J

(d) The increase of the free energy of the universe is

AF = AU - TAS = 0 .

1088

Blackbody radiation.

(a) Derive the Maxwell relation

(b) From his electromagnetic theory Maxwell found that the pressure *p* from an isotropic radiation field is equal to - the energy density *u(T)* :

where *V* is the volume of the cavity. Using the first

and second laws of thermodynamics together with the result obtained in part (a) show that *u* obeys the equation

1

3

1

3 3v

p = *-u(T)* = -

1 du 1

3 *dT* **3**

u = **−*T*−** - *-U*

(c) Solve this equation and obtain Stefan's law relating ***u*** and T.

(was **co** nsin)

Solution:

(a) From the equation of thermodynamics *dF* = *-SdT-pdV,* we know

= - *s* , (%) = - *p* . (%) V *T*

we get

Noting *a 2F d 2F* .-

avaT aTav'

(b) The total energy of the radiation field is *U(T,V)* = *u(T)V.* Substituting it into the second law of thermodynamics:

(!g)T = *T* *(g)T* *-P=T* ($) *V* - *P* 7

T du 1

3 *dT 3*

we find *u* = -- - ***-u.***

du

(c) The above formula can be rewritten as *T-* = *4u,* whose solution

dT

is *u* = *aT4,* where *a* is the constant of integration. This is the famous Stefan's law of radiation for a black body.

1089

A magnetic system of spins is at thermodynamic equilibrium at temperature *T.* Let ***p*** be the magnetic moment of each spin; and let *M* be the mean magnetization per spin, so ***-p*** < *M* < ***p.*** The free energy per spin, for specified magnetization *M,* is *F (M)* .

(1) Compute the magnetization *M* **as** a function of external magnetic field strength *B,* given that

where X is a constant.

(2) Suppose, instead, that someone gives you

F (M) = **Al(M/P)4** - **(M/d2I** *9*

you should respond that this is unacceptable - this expression violates a fundamental convexity principle **of** thermodynamics. (a) State the principle. (b) Check it against the above expression. ***(c)*** Discuss, by at least one example, what would go wrong with thermodynamics if the principle is not satisfied.

(Princeton)

Solution:

(1) From *dF* = *-SdT* + *HdM,* we have

Hence

M

' 7

-M- *5* - -1.

LC **2**

1

F a ,

Thermodynamics **89**

(2) (a) The convexity principle of free energy says that free energy is a concave function of T while it is a convex function of *M,* and if exists then *(:;*-*)T=.*

(-Z> ,

(b) Supposing *F(M)* = X [(f) 4 - (f)'], we have

2X ***6M2***

(s)T= *&-l)*

(s)T = *l / X T* < *0* ,

M a2F

When l - l < 8 , (S<) 0, i.e ., *F* is not convex.

c1 T

(c) If the convexity principle is untenable, for example if

that is, (g) < 0, then the entropy of the equilibrium state is a minimum and the equilibrium state will be unstable.

T

1090

A certain system is found to have a Gibbs free energy given by

G(p **,7 ')** = R T I & (I [n -

where *a* and *R* are constants. Find the specific heat at constant pressure,

Solution:

The entropy is given by

5

S=-(g)= i R - R l n **[** (RG5j2] '

P

The specific heat a.t constant pressure is

1091

Consider a substance held under a pressure **p** and at a temperature *T.*

Show that *(a* (heat emitted)/ap)T = *T(aV/aT),.*

Solution:

(was ***co*** ns in)

FYom Maxwell's relation

we find

-

a(heat emitted)

1092

A given type of fuel cell produces electrical energy *W* by the interaction of **0 2** fed into one electrode and **H2** to the other. These gases are fed in at 1 atmosphere pressure and **298** K, and react isothermally and isobarically to form water. Assuming that the reaction occurs reversibly and that the internal resistance of the cell is negligible, calculate the e.m.f. of the cell.

Given: one Faraday = **96,500** coulombs/g mole.

hydrogen, and water are respectively **17,200, 8,100** and **-269,300.**

hydrogen, and water are respectively **201, 128** and **66.7.**

Enthalpies in joules/g.mole at **1** atmospheric and **298** K for oxygen,

Entropies in joules/mole.K at 1 atmosphere and **298** K for oxygen,

(Wisconsin)

Solution:

The chemical equation is

1

2 H2 + *- 0 2* = **H2O .**

In the reversible process at constant temperature and pressure, the decrease of Gibbs function of the system is equal to the difference between the total external work and the work the system does because of the change of volume. Thus

-Ag = EAq ,

or

- z (A h i - TASi) = EAq .

If 1 mole of water forms, there must have been electric charges of 2F flowing in the circuit, i.e., *Ag* = 2F. Thus the e.m.f. is

1

As given **,** *So* = 201 J/mol.K, SH = 128 J/mol K **,**

SW = 66.7 J/mol.K, *izo* = -17200 J/mol

hH = 8100 J/mol, *hw* = -269300 J/mol , and *T* = 298 K**,**

We have *E* = 1.23 V.

1093

It is found for a simple magnetic system that if the temperature T is held constant and the magnetic field *H* is changed to *H* + *A H ,* the entropy *S* changes by an amount *AS,*

where *C* is a constant characteristic of the system. From this information determine how the magnetization *M* depends on the temperature and sketch a plot of *M* versus *T* for small *H.*

(wis co *ns* ***in)***

Solution:

We are given that (g) =-- *CH*

T 2 '

From *dG* = *-SdT* - *MdH,* we have

, *C H* that is *M* = -. *CH*

T Thus (z) = --

H *T2*

The diagram of *M* vs *T* is shown in Fig. 1.28.

T

Fig. 1.28.

1094

A certain magnetic salt is found to obey Curie's law, and to have a heat capacity per unit volume (at constant magnetic field) inversely proportional **t.0** the square of the absolute temperature, i.e., *X* = *b / T , c H* = *aV/T2,* where *or* = *b* + *aH2, a* and *b* being constants, and *X* is the susceptibility. **A** sample of this salt at temperature ***Tj*** is placed in a magnetic field of strength *H.* The sample is adiabatically demagnetised by slowly reducing the strength of the field to zero. What is the final temperature, *T,* of the salt?

(Columbia)

Solution:

This process can be taken as reversible adiabatic. Then

d S = *(g) , d T* + *(g) T d H* = *O .*

fiom *CH* = *T* (g) and *dG* = *-SdT* - *poMVdH,* we can write

H (gJT =*poV* (%) ***H*** ·

(g) = *p oVH dX* (S) = *p0VH-* . Therefore,

dT

As *M* = ***xH,*** we have

for the above adiabatic process, we have

H

dH ***H***

The final temperature is obtained by integration to be

1095

Explain the principles of cooling by adiabatic demagnetization. What factors limit the temperature obtained with this method?

(wis ***co*** *ns* in)

Solution:

The fundamental equation of the thermodynamics of a magnetic medium is *dU* = *TdS* + *HdM.* The Gibbs function is *G* = *U* - *TS* - *HM,*

giving $dG = -SdT - MdH$. From the condition of complete differential
and

and the definition of specific heat, $CH = T$ (%) we obtain

If we assume the magnetic medium satisfies Curie's law

CV

T

M=---H,

and substitute it into the above formula, we have

We can see that if the magnetic field is decreased adiabaticaily, the temperature of the magnetic medium will decrease also. This is the principle of cooling by adiabatic demagnetization.

Adiabatic demagnetization can produce temperatures as low as 1 K to
K,
the interactions between the paramagnetic ions cannot be neglected. The interactions are equivalent to a magnetic field. It thus limits the lowest temperature obtainable with this method.
K; but when the temperature is of the order of magnitude of

1096

A flask of conical shape (see figure) contains raw milk. The pressure is measured inside the flask at the bottom. After a sufficiently long time, the cream rises to the top and the milk settles to the bottom. [You may assume that the total volume of liquid remains the same.] Does the pressure increase, decrease, or remain the same? Explain.

Soh tion:

Let the volume of the cream be *VI,* its thickness be *HI,* and its density be *p1;* and let the volume of the milk be *Vz,* the thickness be *Hz* and the density be *p2* PO stands for the density of raw milk.

(M W

milk

pressure

gauge

1097

Assume the atmosphere to be an ideal gas of constant specific heat ratio *7* = **Cp/Cv.** Also assume the acceleration due to gravity, g, to be constant over the range of the atmosphere. Let ***z*** = 0 at sea level, ***To,po,*** *PO* be the absolute temperature, pressure, and density of the gas at ***z*** = 0.

(a) Assuming that the thermodynamic variables of the gas **are** related

in the same way they would be for an adiabatic process, find ***p (z)*** and ***p (z) .***

(b) Show that for this case no atmosphere exists above a **zmaX** given

by **zmax -** *2* (*7*,) wh ere ***R*** is the universal gas constant per gram.

Solution:

7 - 1

(SUNY, ***Buflulo)***

(a) When equilibrium is reached, we have

By using the adiabatic relation ***pp-7 = pOpO7,*** we obtain,

p 7 - 2 (~) d p (=~)- -dSzP ; .

7PO

With the help of the equation of state ***p = pRT,*** we find

and

7/(7-1)

p (2) = p o [1 - -- ***7;1;;0]***

(b) In the region where no atmosphere exists, ***p(z,,,)*** = 0. Thus

z, = -7 . **-*m o* .**

7 - 1 9

1098

Consider simple models for the earth's atmosphere. Neglect winds, convection, etc, and neglect variation in gravity.

(a) Assume that the atmosphere is isothermal (at 0°C). Calculate an expression for the distribution of molecules with height. Estimate roughly the height below which half the molecules lie.

(b) Assume that the atmosphere is perfectly adiabatic. Show that the temperature then decreases linearly with height. Estimate this rate of temperature decrease (the so-called adiabatic lapse rate) for the earth.

(GUSPEA)

Solution:

(a) The molecular number density at height *h* is denoted by *n(h).* From the condition of mechanical equilibrium *dp* = *-nmgdh* and the equation of state *p* = *nkT,* we find

-1*d p* mg = --*dh* .

P kT

Thus *n(h)* = *no* exp(-mgh/kT). Let Jf *n(h)dh/JT n(h)dh* = -, then

1

2

The average molecular weight of the atmosphere is 30. We have

8.31 x lo7 x 273

30 x 980

H = x In2 *M* 8 x 1o5 cm = 8 km .

1 mg

P kT (b) *-dp* = --*dh* is still correct and the adiabatic process follows

p('-7)/7T = const

where *7* = 5 **w** 7/2 (for diatomic molecules). Therefore *-dT* ~*7* -

cu T 7-1

-m_g *d h* . Integrating we get

kT

T - ***To*** = -(7 - l)mg(h - *ho)/7k* .

Furthermore,

dT --

-

mg *NN* -0.1 K/m .

dh 7 k

1099

The atmosphere is often in a convective steady state at constant entropy, not constant temperature. In such equilibrium *pV7* is independent of altitude, where 7 = ***Cp/Cu.*** Use the condition of hydrostatic equilibrium in a uniform gravitational field to find an expression for *dT/dz,* where *z* is the altitude.

(UC, Berkeley)

Solution:

In the atmosphere, when the gas moves, pressure equilibrium can be quickly established with the new surroundings, whereas the establishment

of temperature equilibrium is much slower. Thus, the process of formation of gas bulk can be regarded as adiabatic. Resulting from many times of mixing by convection, the temperature distribution of the atmosphere can be considered such that there is no temperature difference between the compressed or expanded gas bulk and its new surroundings. This is the so called "convective steady state at constant entropy". Fkom dp/dz = -nmg (where n is the molecular number density and *z* the altitude) and the equation of state of an ideal gas p = *nkT,* we get
Together with the equation of adiabatic process

Tr = const.p7-' ,
we find

_dT - ** *7 - 1* **mg
dz 7 **k -**

It can be seen that the temperature decreases linearly. The temperature drops **w** *l0C* when the height increases by 100 metres.

1100

The gas group that is slowly and adiabatically arising and unrestricted near the ground cannot continuously rise; neither can it fall (the atmosphere almost does not convect). If the height *z* is small, the pressure and temperature of the atmosphere are respectively ***p*** = *po(1 -* ***az)*** and *T* = *To(1 -* **pz),** where ***po*** and ***TO*** are respectively the pressure and temperature near the surface. Find ***a*** and *p* as functions of the temperature ***To,*** gravitational acceleration near the surface, g, and the molecular weight ***M.*** Suppose that air consists of **-Na** and *- 0 2 ,* and that *TO* is low enough so that the molecule oscillations cannot be excited, but is high enough so that the molecule rotation can be treated by the classical theory.
(CUSPEA)

4 1
5 5

Solution:
Near the ground, we have

d p / d z = *-ape* **.**

Dynamic considerations give *d p l d z* = *-pg.*
Thus *a* = *pog/po,* where ***po*** is the density of air near the ground. Treating air as an ideal gas, we have

PO = *RTo/Vo* = *RTopo/M* **,**

where *R* is the gas constant, *Vo* is the volume and *M* the molecular weight

(: 1 '28 + '32 = 29 . Thus we have *a* = *Mg/RT.*

The slow rising of the gas group can be taken as a quasi-static process. It has the same ***p*** and ***p*** as the atmosphere surrounding it. Thus the same is also true of the temperature *T.* In the adiabtic process,

F p l - 7 = const **,**
with

7 = **Cp/Cv** = ***(Cv*** **+** *R)/Cv* = **715 .**

Differentiating we have

_d T **-- 7- -- 1** *d p*
T **7 P**

On the ground, *d T / T* = *- p d z* and *d p / p* = *- a d z* . We substitute them into above formula and obtain

p* = -** 7 - 1 *a* = -**2a* .

1101

Suppose that the earth's atmosphere is an ideal gas with molecular weight ***p*** and that the gravitational field near the surface is uniform and produces an acceleration *g*.

(a) Show that the pressure *p* varies as

where **z** is the height above the surface, *T* is the temperature, and *R* is the gas constant.

(b) Suppose that the pressure decrease with height is due to adiabatic expansion. Show that

(c) Evaluate *dT/dz* for a pure **N2** atmosphere with **y = 1.4.**

(d) Suppose the atmosphere is isothermal with temperature T. Find

(e) Suppose that at sea level, *p* = *po* and *T* = *To.* Find *p (z)* for an

p(z) in terms of *T* and *PO,* the sea level pressure.

adiabatic atmosphere.

(Columbia)

Solution:

(a) Mechanical equilibrium gives *dp* = *-npgdz,* where n is the mole number of unit volume. Thus using the equation of state of an ideal gas p = *nRT,* we find

d p = *--pgPd Z* , *RT*

or

dP -- *--1- 19 d z*

P *RT* ·

(b) The adiabatic process satisfies *T7/(1-7)p*= const. Thus

(c) Comparing the result of (b) with that of (a), we deduce

dT

dz

For **NZ,** 7 = 1.4, we get *dT/dz* = **-4.7** K/km.

(d) From (a) we find

(e) From (a) and (b) we have

Thus *pg* 1--L

R To

p - l l 7 d p = *- -po* 7 dz ,

Integrating, we get

This is, of course, valid only if

1102

A fully ionized gas containing a single species of ion with charge Z / e (and atomic weight ***A* is** in equilibrium in a uniform gravitational field g. The gas is isothermal with temperature ***T*** and there is thermal equilibrium between the ions and the electrons. The gas has a low enough density that local interactions between the particles can be neglected.

(a) Show that to avoid charge separation there must be a uniform electric field *E* given by

where **mp** and

(b) Show

me are the proton and electron masses respectively.

that the above equation is also valid if the plasma is not

isothermal. (Hint: Treat each component ***i*** as an ideal gas subject to the equation of hydrostatic equilibrium

where ***p;*** is the partial pressure of the ith component, *n,* is its number density, and *F,,* is the total force per particle in the z direction.)

(c) The equation in (a) is also valid throughout the sun where **E** and `g` are now directed radially. Show that the charge on the sun is given approximately by

A GMm,

l + Z leJ ’ *Q*=--

where *M* is the mass of the sun.

(d) For the sun *M* = **2** x grams. If the composition of the sun were pure hydrogen, what would be Q in coulombs? Given this value of Q, is the approximation that there is no charge separation `a` good one?

Solution:

`(a)` Take an arbitrary point in the gravitational field as the zero potential point. The number density at this point is n and the height is taken opposite to the direction of `g`. Suppose there exists an uniform electric field **E** in the direction opposite to ***g.*** The electron and ion distributions as functions of height are respectively

(MITI

ne(h) = no, exp[-(m,gh + Elelh)/kT] ,

nI(h) = n,Iexp[-(Am,gh - EZlelh)/kT] .

To avoid charge separation, the following condition must be satisfied:

nI(h)/n,(h) = nO1/noe .

Am,g - *EZlel*= m,g + *Elel* ,

This gives

from which we get

(b) -dPI = nI(-Am,g + *ZlelE),*

dh

At equilibrium, the partial pressure for each type of particles (at the same height) should be the same. Thus

i.e.,

-Am,g + ZjelE = *-m,g* - lelE .

Am, - m,

(1 + *z)lel* Hence *E* = ′ .

Q r *GM* **r**

r2 r g = *r2* ***r*** (c) **AS E = --, ,** we have

GMAm,-me GM Am,

Q/r2 = - ***Mr2***

(I+ .Z)lel *r2* **(I+** *Z)lel* .

GMAm,

Hence Q =

(1 + Z) 14.

(d) For hydrogen, one has *A* = 1, Z = 1, giving

GMm,

QW- **1.5** x lo3 oc .

214

1103

Consider a thermally isolated system consisting of two volumes, V and ***2V*** of an ideal gas separated by a thermally conducting and movable partition.

Fig. 1.30

The temperatures and pressures are as shown. The partition is now allowed

to move without the gases mixing.
When equilibrium is established what is the change in the total internal energy? The total entropy?
What is the equilibrium temperature? Pressure?

(SUN Y, Buffalo)

Solution:

Let the molar numbers of the gas in the two sides be nl and n2 respectively. From the equations 6pV = nlRT and pV = nzRT, we obtain
nl = 6n2. **As** this is an isolated system of ideal gas, the final temperature is Tf = T since both the initial temperatures are equal to T. The final pressure **pf** is

pf = (nl + n2)RT/3V =
3

We calculate the change of the state function *S* by designing a quasi-static isothermal process. Then
Vl nl 18

Since Vl + VZ = 3V and -V2 = - = 6,Vl = 6V2 = -V. Hence n2 **7**

AS = n lRl n **9**- + n2Rln -3 PV *M* - 7 7 T

1104

A thermally insulated cylinder, closed at both ends, is fitted with a frictionless heat-conducting piston which divides the cylinder into two parts. Initially, the piston is clamped in the center, with 1 litre of air at 200 K and 2 atm pressure on one side and **1** litre of air at 300 K and 1 atm on the other side. The piston is released and the system reaches equilibrium in pressure and temperature, with the piston at a new position.
(a) Compute the final pressure and temperature.
(b) Compute the total increase in entropy.
Be sure to give all your reasoning.

(SUNY, Buflulo)

Solution:

(a) The particle numbers of the two parts do not change. Let these be *N1* and *N2,* the final pressure be *p ,* and the final temperature be *T.* Taking air **as** an ideal gas, we have

pivo = *NikT1* , *p2Vo* = *N2kT2* ,

where *p1* = *2* atm, *TI* = *200* K**,** *p 2* = **1** atm, *T2* = 300 K , *Vo* -**1 l .**

The piston does not consume internal energy of the gas as it is frictionless, so that the total internal energy of the gas is conserved in view of the cylinder being adiabatical. Thus

PNlkT1 + *PNzkT* = *p(Nl+ N2)kT* ,

where ***p*** is the degree of freedom of motion of an air molecule. Hence

P2 TI + *-NT22 1+-*
Nl = *p1 TI* = *225 K*
-N+2 1 **l**+-*P2*- ' **-T1-**
Nl PI T2
T =

By *V1+ V2* = *2V0,* we find
and hence

(Ni + ***N2)***
2VO **P=**

(b) Entropy is a state function independent of the process. To calculate the change of entropy by designing a quasi-static process, we denote the entropies of the two parts by S1 and *S2.* Then

AS = AS1 + *AS2* =

where nl and **n2** are the molar numbers of the particles in the two parts, ***c,*** is the molar specific heat at constant volume, and *R* is the gas constant. Thus

3

2

Taking *c,* = -*R* as the temperature of the system is not high, we have AS = 0.4 J/cal.

1105

A cylindrical container is initially separated by a clamped piston into two compartments of equal volume. The left compartment is filled with one mole of neon gas at a pressure of **4** atmospheres and the right with argon gas at one atmosphere. The gases may be considered as ideal. The who$ system is initially at temperature T = 300 K, and is thermally insulated from the outside world. The heat capacity of the cylinder-piston system is ***C*** (a constant).

piston /

argon

Fig. 1.31.

The piston is now unclamped and released to move freely without friction. Eventually, due to slight dissipation, it comes to rest in an equilibrium position. Calculate:

(a) The new temperature of the system (the piston is thermally conductive).

(b) The ratio of final neon to argon volumes.

(c) The total entropy change of the system.

(d) The additional entropy change which would be produced if the piston were removed.

(e) If, in the initial state, the gas in the left compartment were a mole of argon instead of a mole of neon, which, if any, of the answers to (a), (b) and (c) would be different?

(UC, Berkeley)

Solution:

(a) The internal energy of an ideal gas is a function dependent only on temperature, so the internal energy of the total system does not change. Neither does the temperature. The new equilibrium temperature is 300 K.

(b) The volume ratio is the ratio of molecular numbers, and is also the ratio of initial pressures. Thus

VN, : V A=~ 4~ : 1 = 1: n .

where n = **1/4** is the mole number of the argon gas.

(c) The increase of entropy of the system is

4 1

- R -

2 2

= R In *5* + - ln **4** = 2.0 J/K **.**

-1 4 -1

(d) The additional entropy change is

AS' = Rln(1 + n) + nRln

(e) If initially the gas on the left is a mole of argon, the answers to (a), (b) and (c) will not change. **As** for **(d),** we now have **AS'** = 0.

4. CHANGE OF PHASE AND PHASE EQUILIBRIUM

(1 106- 1147)

1106

Is the melting point of tungsten 350, 3500, 35,000, or 350,000°C?

(Columbia)

Solution:

The answer is 3500°C.

1107

Assuming that 1/20 eV is required to liberate a molecule from the surface of a certain liquid when T = 300 K, what is the heat of vaporization in ergs/mole?

[le V = 1 . 6 ~ 1 0 - 'e~rg]

(Wisconsin)

Solution:

The heat of vaporization is

1

20

Lvapor = - x 1.6 x x 6.023 x

= 4.8 x lo1' ergs/mol.

1108

Twenty grams of ice at 0°C are dropped into a beaker containing 120 grams of water initially at 70°C. Find the final temperature of the mixture neglecting the heat capacity of the beaker. Heat of fusion of ice is 80 cal/g.

(wis **c** *o nsin)*

Solution:

We assume the temperature of equilibrium to be T after mixing. Thus

We substitute **Ml** = 20 g, *M2* = 120 g, *To* = 70"C, Lfusion = 80 cal/g and **Cp,wate**=**r** 1 cal/g, and obtain the final temperature T = 48.57"C.

1109

The entropy **of** water at atmospheric pressure and 100°C is 0.31 cal/g.deg, and the entropy of steam at the same temperature and pressure is 1.76 cal/g.deg.

(a) What is the heat of vaporization at this temperature?

(b) The enthalpy *(H* = *U* + *PV)* of steam under these conditions is 640 cal/g. Calculate the enthalpy of water under these conditions.

(c) Calculate the Gibbs functions **(G** = *H* - **TS)** of water and steam

(d) Prove that the Gibbs function does not change in a reversible

(UC, **Berkeley)**

under these conditions.

isothermal isobaric process.

Solution:

(a) Heat of vaporization is

L = TAS = 540 cal/g.

(b) From **dH** = **TdS** + **Vdp,** we get

Hwater= Hstealn- **TAS** = 100 cal/g.

(c) Since **G** = *H* - **TS,**

Gwater = **Hwater - TSwater** = -16 cal/g 7

Geteam = **Hsteam - TSsteam** = -16 cal/g

(d) From **dG = -SdT** + **Vdp,** we see that in a reversible isothermal isobaric process, **G** does not change.

1110

Given 1.0 kg of water at 100°C and a very large block of ice at 0°C.

A reversible heat engine absorbs heat from the water and expels heat to the ice until work can no longer be extracted from the system. At the completion of the process:

(a) What is the temperature of the water?

(b) How much ice has been melted? (The heat of fusion of ice **is** 80 cal/g)

(c) How much work has been done by the engine?

(was ***co* win)**

Solution:

(a) Because the block of ice is very large, we can assume its temperature to be a constant. In the process the temperature of the water gradually decreases. When work can no longer be extracted from the system, the efficiency of the cycle is zero:

Therefore, the final temperature of the water is 0°C.

(b) The heat absorbed by the ice block is

9 2 = / [I - rl(t)]dQ= **mCv** L:I3 *Y d T* = 8.5 x *lo4* cal .

This heat can melt ice to the amount of

MI- *Q2* -- 8.5 *x lo4*

&ion 80

= *1.06* kg .

(c) The work done by the engine is

W = *Q1* - *Q2* = 1000 *x 100 x* 1 - 8.5 x lo4 = 1.5 x lo4 cal .

1111

What is the smallest possible time necessary to freeze **2 kg** of water at 0°C if a **50** watt motor is available and the outside air (hot reservoir) is at 27OC?

(***Wisconsin)***

Solution:

When **2** kg of water at 0°C becomes ice, the heat released is

9 2 = 1.44 x 2 x 103/18 = 1.6 x *lo2* kcal .

The highest efficiency of the motor is

Thus,

If we use the motor of *P* = 50 W, the smallest necessary time is

With TI = 300 K, Tz = **273** K, we find

= 1.3 x lo3 .

1112

Compute the theoretical minimum amount of mechanical work needed to freeze 1 kilogram of water, if the water and surroundings are initially at a tempera.ture ***To*** = **25°C.** The surroundings comprise the only large heat reservoir available.

(Lice = 80 cal/g, ***C,*** = 1 cal/g . *o*C) .

(UC, **Berkeley)**

Solution:

The minimum work can be divided into two parts *W1* and *Wz: W1* is used to lower the water temperature from ***25OC*** to O"C, and *W2* to transform water to ice. We find

W1 = - (To - T)MC,dT/T

ITo

= MCpTo ln(To/Tr) - MC,(To - Z)

= 1.1 x **lo3** cal **,**

W2 = (TO - Tf)LM/Tf = **7.3** x **lo3** cal **,**

W = *W1* + *W2* = 8.4 x lo4 cal = **3.5** x lo4 J .

111s

An ideal Carnot refrigerator (heat pump) freezes ice cubes at the rate
of 5 g/s starting with water at the freezing point. Energy is given **off** to
the room at 3OoC. If the fusion energy of ice is 320 joules/gram,
(a) At what rate is energy expelled to the room?
(b) At what rate in kilowatts must electrical energy be supplied?
(c) What **is** the coefficient of performance of this heat pump?
(wzs ***co*** *nsin)*

Solution:

(a) The rate that the refrigerator extracts heat from water is

9 2 **=** ***5*** x **320 = 1.6** x **lo3** J/s **.**

The rate that the energy is expelled to the room is

1 - -***T1Q 2*** **= (303/273)** x **1.6** x **lo3**

-T2

= **1.78** x **10** J/s .

(b) The necessary power supplied is

W = ***Q1-*** *Q 2* = 0.18 **kW .**

(c) The coefficient of performance is

273

& = - - - *T2* - = **9.1 .**

Ti - ***Tz*** **30**

1114

A Carnot cycle is operated with liquid-gas interface. The vapor pressure
is ***pv,*** temperature ***T,*** volume V. The cycle is operated according to
the following ***p*** - V diagram.
The cycle goes isothermally from **1** to **2,** evaporating *n* moles of liquid.
This is followed by reversible cooling from **2** to **3,** then there is an isothermal
contraction from **3** to **4,** recondensing *n* moles of liquid, and finally a
reversible heating from **4** to **1,** completes the cycle.

I I ***/*** 1 ***pv, T*** *, V Pv-AP* ***pp=p3*** --r **, ,**

b ' 1 / I 1 L

"I ***v2***

(a) (b)

Fig. **1.32.**

(a) Observe that *V2* - ***V1*** = *V, - Vt* where *V,* = volume of *n* moles of
gas, *Vt* = volume of **n** moles of liquid. Calculate the efficiency in terms of

Ap, V, - Ve, and L, = latent heat vaporization of a mole of liquid. Treat
Ap and AT as small.
(b) Recognizing that any two Carnot engines operating between T and
T - AT must have the same efficiency (why?) and that this efficiency is a

function of T and T alone, use the result of part (a) to obtain an expression for dp,/dT in terms of V, - Ve, n, L, and T.

(CUSPEA)

Solution:

(a) The temperature T in the process from 1 to **2** is constant. Because the total volume does not change, V2 - Vl = V, - Ve. The engine does work Ap(V2 - Vl) on the outside world in the cyclic process. The heat it absorbs is nL,. Therefore, the efficiency is

(b) The efficiency of a reversible Carnot engine working between *T* and T - A T i s

AT Ap(V, - Ve)

I]=-= T L, n ı

Thus -dPV = nL,

dT T(V, - Ve)

1115

Many results based on the second law of thermodynamics may be obtained without use of the concepts of entropy or such functions. The method is to consider a (reversible) Carnot cycle involving heat absorption *Q* at (T + *dT)* and release at T such that external work *(W* + *dW)* is done externally at (T + dT) and -*W* is done at T. Then *Q* = AU + *W,* where AU is the increase in the internal energy of the system. One must go around the cycle so positive net work *dW* is performed externally, where *dW/dT* = *Q/T.* In the following problems devise such a cycle and prove the indicated relations.

(a) **A** liquid or solid has vapor pressure p in equilibrium with its vapor. For **1** mole of vapor treated as a perfect gas, V (vapor) >> V (solid orJiquid), let ***1*** be the **1** mole heat of vaporization. Show that

dlnp/dT = l/RT2 **.**

(b) **A** liquid has surface energy density *u* and surface tension *r.*

dr

i) Show that ***u*** = *r* - *T*-.

dT

ii) If - < 0, and - > 0, will *T* increase or decrease for an

(Columbia)

Solution:

`(a)` Consider the following cycle: 1 mole of a liquid vaporizes at temperature *T* + *dT,* pressure *p* + *dp,* the vapor expands adiabatically to *T,p* and then condenses at *T, p* and finally it arrives adiabatically at its initial state. Thus we have *Q* = *1, dW* = *(p* + *dp)V* - *pV* = *Vdp,* where *V* is the molar volume of the vapor, and

dr d2r

adiabatic increase in area?

dT dT2

-Vd-P *4* -

dT T·

From the equation of state of an ideal gas *V* = *RT/p,* we have

d l n p - ***1***

dT RT2·

(b)(i) Consider the following cycle: **A** surface expands by one unit area at *T* + *dT,* and then expands adiabatically to *T,* it contracts at *T,* and comes back adiabatically to its initial state. For this cycle:

Q = u - r ,

dr

dT

dW = *-r(T* + *dT)* + *T (T)*= *--dT*

Thus

or

- **_-***d r -*

***_u -_r** dW*

dt dT T' --

dr

dT

u = r - T - .

(ii) From conservation of energy, we have

d(Au) = dQ + *r(T)dA* ,

where *A* is the surface area. **As** *dQ* = *0* in the adiabatic process,

(U - 7)dA + *Adu = 0* ,

or

From (i) we have *u*

-d u **=-T($) .**

d T

With *d r / d T* < 0 and *d 2 r / d p* > 0, the above equations give

Hence when the surface area increases adiabatically, its temperature increases also.

1116

The heat of melting of ice at **1** atmosphere pressure and *O°C* is **1.4363** kcal/mol. The density of ice under these conditions is **0.917** g/cm3 and the density of water is **0.9998** g/cm3. If **1** mole of ice is melted under these conditions, what will be

(a) the work done?

(b) the change in internal energy?

(c) the change in entropy?

(***wisco ns in)***

Solution:

(a) The work done is

= **1.013** x **lo5** x [(&)-(&)]

= **-0.1657 J** = **-0.034** cal **.**

(b) The heat absorbed by the **1** mole of ice is equal to its heat of fusion:

Q = **1.4363** x **lo3** cal **.**

Thus the change in internal energy is

AU = *Q* - *W* cJ **Q = 1.4363** x **lo3** cal

(c) The change in entropy is

A s = **-** = 1'4363 lo3 = 5.26 cal/K **.** *T* 273

1117

10 kg of water at 20°C is converted to ice at -10°C by being put in contact with a reservoir at -10°C. This process takes place at constant pressure and the heat capacities at constant pressure of water and ice are 4180 and 2090 J/kg deg respectively. The heat of fusion of ice is 3 . 3 4 ~lo 5 J/kg.

Calculate the change in entropy of the universe.

(was co nsin)

Solution:

The conversion of water at 2OoC to ice at -10°C consists of the following processes. Water at 20" C -% water at OOC -+ ice at OOC *5* ice at -lO°C, where a and c are processes giving out heat with decreases of entropy and b is the process of condensation of water giving `off` the latent heat with a decrease of entropy also. As the processes take place at constant pressure, the changes of entropy are

b

273

AS, = /,,, *F d T* = MC,ln (*g*) = -2955 J/K ,

IQI 10 x 3.34 x **105**

As2 = -- = - = -1.2234 x lo4 J /K ,

To 273

263

AS3 = 1:r *Mt* 273

2dT = MC,ln - = -757 J/K .

In the processes, the increase of entropy of the reservoir due to the absorbed heat is

10 x (4180 x 20 + 3.34 x lo5 + 2090 x 10)

263

AS, =

= 16673 J/K .

Thus, the total change `of` entropy of the whole system is

AS = AS, + AS2 + AS, + AS, = 727 J/K .

1118

Estimate the surface tension of a liquid whose heat of vaporization is

(Columbia)

10" ergs/g **(250** cal/g).

Solution:

The surface tension is the free energy of surface of unit area; therefore the surface tension is ***a*** = **Qrp,** where Q is the heat of vaporization, **r** is the thickness of the surface **(r** = lov8 cm) and ***p*** is the liquid density **(*p*** = 1 g/cm3). Thus

1119

Put letters from *a* to *h* on your answer sheet. After each put a T or an F to denote whether the correspondingly numbered statement which follows is true or false.

`(a)` The liquid phase can exist at absolute zero.

(b) The solid phase can exist at temperatures above the critical tem-

(c) Oxygen boils at a higher temperature than nitrogen.

(d) The maximum inversion temperature of He is less than **20** K.

(e) *7* of a gas is always greater than one.

(f) **A** compressor will get hotter when compressing a diatomic gas than perature.

wheacompressing a monatomic gas at the same rate.

(g) The coefficient of performance of a refrigerator can be greater than one.

(h) A slightly roughened ball is thrown from north to south. As one looks down from above, the ball is seen to be spinning counterclockwise. The ball is seen to curve toward east.

(wis c o ns in)

1120

One gram each of ice, water, and water vapor are in equilibrium together in a closed container. The pressure is 4.58 mm **of** Hg, the temperature is 0.01OC. Sixty calories of heat are added to the system. The total volume is kept constant. Calculate to within 2% the masses of ice, water, and water vapor now present in the container. Justify your answers. (Hint: For water at O.0loC, the latent heat of fusion is 80 cal/g, the latent heat of vaporization is 596 cal/g, and the latent heat of sublimation is 676 cal/g. Also note that the volume of the vapor is much larger than the volume of the water or the volume of the ice.)

Solution:

It is assumed that the original volume of water vapor is V, it volume is also V after heating, and the masses of ice, water, and water vapor are respectively x, y and z at the new equilibrium. We have

(**Wisconsin)**

-1+- -x

Pice Pwater

RT

PP

v,=-.

z V=-RT

PP

(3)

(4)

(5)

where p = 18 g/mole,p = 4.58 mmHg,T = 273.16 K, R = **8.2** x **1o8** m3 . atm/mol . K, **Pice** = Pwater = 1 g/cm3, Lsub = 676 cal/g, and Lvap = 596 cal/g. Solving the equations we find

x = 0.25 g , **y** = 1.75 g , z = 1.00 g .

That is, the heat of 60 cal is nearly all used to melt the ice.

1121

Define (a) critical point and (b) triple point in phase transformation. Helium boils at **4.2** K under the atmospheric pressure **p** = *760* mm of mercury. What will be the boilding temperature of helium if **p** is reduced to 1 mm of mercury?

(UC, **Berkely)**

Solution:

Critical point is the terminal point of the vaporization line. It satisfies equations

(a p) T = o , (3) = o . av av2

Triple point is the coexistence point for solid, liquid, and gas. When **p'** = 1 mmHg, the boilding temperature is **2.4** K.

1122

(a) State Van der Waals' equation of state for a real gas.

(b) Give a physical interpretation of the equation.

(c) Express the constants in terms of the critical data *Tc, Vc,* a nd ***p c .***

(**Wisconsin)**

Solution:

(a) Van der Waal's equation of state for a real gas is

(p + -3 (V - b) = n R T .

(b) On the basis of the state equation for an ideal gas, we account for the intrinsic volumes of real gas molecules by introducing a constant ***b,*** and for the attractive forces among the molecules by introducing a pressure correction *a JV2.*

(V - b) = nRT, we have

p = - - p

nRT a

so that

2nRT _ -6 a

(%)T = (V-b)3 v4 ·

dP d2P

dV av2 ***T***

At the critical point, we have *(-) T* = 0, (-)

a 8a

- 276

= 0, so that

V, = 36, p - - nRT - - .

- 27b2 '

namely, *a = 3pCV,2b, = Vc/3.*

1123

The Van der Waals equation of state for one mole of an imperfect gas reads

(p + - V "Z) (V - b) = R T .

[Note: part (d) of this problem can be done independently of part (a) to (c1.1

(a) Sketch several isotherms of the Van der Waals gas in the *p-V* plane *(V* along the horizontal axis, *p* along the vertical axis). Identify the critical point.

(b) Evaluate the dimensionless ratio *pV/RT* at the critical point.

(c) In a portion of the *p-V* plane below the critical point the liquid and gas phases can coexist. In this region the isotherms given by the Van der Waals equation are unphysical and must be modified. The physically correct isotherms in this region are lines of constant pressure, *po(T).* Maxwell proposed that *p o (T)* should be chosen so that the area under the modified isotherm should equal the area under the original Van der Waals isotherm. Draw a modified isotherm and explain the idea behind Maxwell's construction.

P

Fig. **1.33.**

(d) Show that the heat capacity at constant volume of a Van der Waals gas is **a** function of temperature alone (i.e., independent of *V) .*

(MIT)

Solution:

= 0, we get

(a) As shown in Fig. *1.33,* from *(dp/dV)T=T, = 0* and *(azp/dV2)r=r,*

3a (Vc - b)3

T - - - v,4

so

a 8a

27b2' ‘**-** *27bR*

Vc = 3 b , p , = - T - -

(b) *pcVciRTc* = ***318.***

(c) In Fig. *1.33,* the horizontal line *CD* is the modified isotherm. The area of *CAE* is equal to that of *EBD.* The idea is that the common points, i.e., C and D of the Van der Waals isotherm and the physical isotherm have the same Gibbs free energy. Because of G = *G(T,p),* the equality of *T's* and *p's* respectively will naturally cause the equality of G. In this way, That is,

LE V dp - L *C V dp = /DB Vdp -LB V dp,* or **A S ~ A E**= ASEBD

For a Van der Waals gas, the equation of state gives

so that

1124

Determine the ratio *(pV/RT)* at the critical point for a gas which obeys the equation of state (Dieterici's equation)

p(V - *b) = RTexp(-a/RTV)* **.**

Give the numerical answer accurately to two significant figures.

(UC, Berkeley)

Solution:

The critical point satisfies

From the equation of state, we get

a(V - b)

e RTV , [*RTV2*

($) T *= RT (V -* ***b)2***

a(V - b)

RTV2

Consequently, - 1 = o .

Using this result, we get

a a

4b

Thus, **-- 2** = 0. Then, *V* = ***26,*** *RT* = **-.** *RTV*

Substituting these back in the equation of state, we find *-PV* = **0.27.** *RT*

1125

Find the relation between the equilibrium radius ***r,*** the potential **4,** and the excess of ambient pressure over internal pressure *Ap* of a charged **soap** bubble, assuming that surface tension can be neglected.

(wi3 **c** *o f l 3* in)

Solution:

We assume that the air inside the bubble is in a-phase, the air outside the bubble is in P-phase, and the soap bubble itself is in 7-phase. We can solve this problem using the principle of minimum free energy. If the temperature is constant, we have

6F" *= - p a 6 V a , 6FP = - p P 6 V P l* and *6F7 = q (a 4 / d r) 6 r ,*

4

3

where *V"* = ***-m36***, *V " = 4.rrr26r,6VP = - 6 V " .*

The condition of minimum free energy demands

With **4** = ***q / r*,** we have *A p* = -Y

4 7 4·

1126

Consider a spherical soap bubble made from a soap film of constant surface tension, *a,* and filled with air (assumed to be a perfect gas). Denote the ambient external pressure by *po* and temperature by T.

(a) Find a relation between the equilibrium radius ***r*** of the soap bubble

(b) Solve the relation of part (a) for the radius *r* in the limit that the

and the mass of air inside it.

bubble is =large". Define precisely what is meant by "large".

W I T)

Solution:

(a) Let *d r* be an infinitesimal area of soap bubble surface, *p l* .and *po* be the pressures inside and outside the soap bubble, and *p1,p2* be their chemical potentials. We have *dU* = *T d S* - *pldV1* -*podV2* + *adr* + *p l d N 1* + *P2 dN2.*

From the condition of equilibrium: *dU* = *0,dS* = *Olpl* = *p2, dVl* = -*dV2* and *d(N1+N2)* = 0, we get *(p1-po)dVl* = *udr,* or *p l - p o* = *udr/dVl,*

dr 2

where - = - Hence **pi** -*po* = ***2u/r.***

dV1 ***r***

m

is the molecular weight of air, we have

Since *plV1* = -*RT,* where m is the mass of air inside the bubble, *M* *M*

4T *M*

3 *RT* **m= --r3** *(Po+* F) .

4rMpor3

3RT

(b) When *po* >> ***2u/r,*** Le., ***r*** >> *2a/po,* we have `rn` =

1127

Derive the vapor pressure equation (Clausius-Clapeyron equation):

(UC, ***B e r k e l e y)***

d p l d T =?

Solution:

Conservation of energy gives

where *V1* is the volume of the vapor, and *V2* is the volume of the liquid. In phase transition from liquid to vapor, chemical potential is invariant, i.e., *p1* = *p2, so* that one has the vapor pressure equation:

where L is the latent heat of vaporization.

Usually *V2* << *Vl,* and this equation can be simplified to

dv L

1128

(a) By equating the Gibbs free energy or chemical potential on the two sides of the liquid-vapor coexistence curve derive the Clausius-Clapeyron

, where *q* is the heat of vaporization per

particle and *VL* is t I , e volume per particle in the liquid and *VV* is the

equation: - -

volume per particle in the vapor.

Q dP

dT T Vv - VL)

(b) Assuming the vapor follows the ideal gas law and has a density

which is much less than that of the liquid, show that *p* **-** exp(-q/kT), when the heat of vaporization is independent of *T*.

(wis ***co*** *nsin)*

Solution:

(a) From the first law of thermodynamics

dp ₁ *-SdT* **+** *Vdp*

and **the** condition that the chemical potential of the liquid is equal to that of the vapor at equilibrium, we obtain

It follows that

_*d P* **--** *s v - SL*

dT Vv - VL ·

With *q* = *T(Sv - SL),* we have

which is the Clausius-Clapeyron equation.

(b) If the vapor is regarded as an ideal gas, we have

Because the density of vapor is much smaller than that of liquid, we can neglect *VL* in the Clausius-Clapeyron equation and write

The solution is *p* **-** exp(-q/kT).

1129

A gram of liquid and vapor with heat of vaporization *L* is carried around the very flat reversible cycle shown in Fig. **1.34.** Beginning at point ***A,*** a volume ***Vl*** of liquid in equilibrium with a negligible amount of its saturated vapor is raised in temperature by ***AT*** and in pressure by ***Ap*** so as to maintain the liquid state. Then heat is applied at constant pressure and the volume increases to ***Vz*** leaving a negligible amount of liquid. Then the pressure is lowered by ***Ap*** and the temperature decreased by ***AT*** so that essentially all the material remains in the vapor state. Finally, heat is removed, condensing essentially all the vapor back into the liquid state at point ***A.***

Consider such a Carnot cycle and write the change of boiling point with pressure, ***dTldp,*** for the liquid in terms of the heat of vaporization and other quantities.

(*wis* ***co nsin)***

I i II

V1 ***v2 V***

Fig. 1.34.

Solution:

In this cycle, the process at constant pressure is isothermal. We assume the net heat absorbed by the system is Q. Then its efficiency is r] = Q L.

For the reversible Carnot cycle, the efficiency is r] = **-,** giving Q = -L.

Q must be equal to the external work *W* of the system in the cycle, W = ***Ap(V2 - Vl),*** so that

AT A *d*

T T

Z L = *Ap(V2 -* ***vl)*** .

T

Therefore,

AT** - **T(Vz** - **Vl)

dT/dp= lim - -

Ap-0 *Ap L* *

1130

(a) Deduce from the 1st and 2nd laws of thermodynamics that, if a substance such as ***H 2 0*** expands by 0.091 cm3/g when it freezes, its freezing temperature must decrease with increasing pressure.

(b) In an ice-skating rink, skating becomes unpleasant (i.e., falling frequently) if the temperature is too cold ***so*** that the ice becomes too hard. Estimate the lowest temperature of the ice on a skating rink for which ice skating for a person of normal weight would be possible and enjoyable. (The latent heat of ice is 80 cal/g).

Solution:

(SUNY, ***Bufalo)***

Denote the liquid and solid phases by 1 and 2 respectively.

(a) The condition for coexistence of the two phases is

p2 = 1-11, so that ***dp2 = dp1*** ,

giving

Vidpi - ***SldT1 = Vzdpz*** - ***S2dT2*** .

As ***pa*** = ***p i*** = ***p*** and ***T2*** = ***TI*** = ***T*** on the coexistence line, we have

For regions whose temperatures are higher than those of phase transformation we have ***1-1-11*** < ***p2,*** and for the regions whose temperatures are lower than those of phase transformation we have ***p1*** > ***p2.*** This means that

i.e., for any temperature, ***S1*** > *272.*

1 ' (< *0.* **phase** line

For substances such as water, ***V2*** > ***V1,*** so

(b) The lowest temperature permitted for enjoyable skating is the temperature at which the pressure on the coexistence line is equal to the pressure exerted by the skater on ice. The triple point of water is at *To* = **273.16** K, ***po*** = 1 atm. For a skater of normal weight **p** *N*10 atm, ***so*** that

(P - Po)/(Trnin - ***TO)*** = ***-h/TminAv*** .

With *h* = 80 cal/g, AV = 0.091 cm3/g, we have

TO = (1 - 2.5 x 10-3)T0 = -0.06"C .

(P - PO) AV Tniin =

h

1131

The following data apply to the triple point of H20.

Temperature: 0.01"C; Pressure: 4.6 mmHg

Specific volume of solid: 1.12 cm3/g

Specific volume of liquid: 1.00 cm3/g

Heat of melting: 80 cal/g

Heat of vaporization: 600 cal/g.

(a) Sketch a **p** - T diagram for H20 which need not be to scale but which should be qualitatively correct. Label the various phases and critical points.

(b) The pressure inside a container enclosing H20 (which is maintained at T = -1.O"C) is slowly reduced from an initial value of lo5 mmHg. Describe what happens and calculate the pressure at which the phase changes occur. Assume the vapor phase behaves like an ideal gas.

(c) Calculate the change in specific latent heat with temperature *dL/dT* at a point **(p,** T) along a phase equilibrium line. Express your result in terms of *L* and the specific heat ***C,,*** coefficient of expansion **a,** and specific volume *V* of each phase at the original temperature T and pressure **p.**

(d) If the specific latent heat at 1 atm pressure on the vaporization curve is 540 cal/g, estimate the change in latent heat 10°C higher than the curve. Assume the vapor can be treated as an ideal gas with rotational degrees of freedom.

(MITI

Solution:

(a) The ***p*** - T diagram of H20 is shown in Fig. 1.35.

I mm
critical
ice point
vapor
T
27216
(K)

Fig. 1.35.

(b) The Clausius-Clapeyron equation gives

= **-2.4** cal/cm3 . - *L* K .

ice-water T(Vwater - Vice)

) (' > O **water-vapor**

When the pressure, which is slowly reduced, reaches the solid-liquid phase line, heat is released by the water while the pressure remains unchanged until all the water is changed into ice. Then at the vapor-solid line, the ice absorbs heat until it is completely changed into vapor. Afterwards the pressure begins to decrease while the vapor phase is maintained.

The pressure at which water is converted to ice is given by

T - To

.~ = **6.3** x 103cmHg

L

Pwater-ice = *PO* + **Vwater - h e TO**

where we have used the values **T = 272.15** K, **TO = 273.16** K and ***po*** = **4.6** mmHg. As **Vvapor = - > Kce,** we have

kT

Pm

-dP- -- *L* - *mLp*

dT TVvapor T2k .

The pressure at which ice is converted to vapor **is**

Pice-vapor *FJ* PO exP [*L-:* (- io- -k)] = **4.4** mmHg

where **rn** is the molecular **mass** of water.

(c) From *L* = *T(S1 - S2),* we have

As *dS1* = -**C***d***P***T* 1 - *alVldp,* where *a1* = - (S) **,** we have

T Vl

TJsing

L *dP* -

dT T(V1 - *V2)* '

_-

we obtain

dL L L

dT **Vl** - *v2*

- = *T* **1- (CPI** - *C,,)* - *(alvl* - *a2V2)-* **.**

(d) Let 1 and **2** stand for water and vapor respectively.

From *V2* >> *V1,* we know

where *012* = *1/T, so AL* = **(Cpl** - *C,,)AT.*

2

9

Letting *C,,* = *1* cal/g "C, C,, = -*R* cal/g.OC, *AT* = 10°C, we get

AL = ***6*** cal/g.

1132

(a) Derive an expression for the dependence of the equilibrium vapor pressure of a material on the toal pressure (i.e., how does the equilibrium partial pressure of a material depend on the addition of an overpressure of some inert gas?).

(b) Use this result to discuss qualitatively the difference between the triple point and the ice point of water.

(was ***co*** *nsin)*

Solution:

x << **1.** Thus the mole chemical potential of the solution is

(a) We assume the mole concentration of the solute in the solution is

1.11 ***(P, T)*** = ***1.1;*** ***(P,*** *T)* - *XRT* **,**

where *py(p,T)* is the mole chemical potential of the pure solvent. If the mole chemical potential of the vapor phase is *&(p,T),* the equilibrium vapor pressure of the solvent, ***P O*** **,** is determined by

1.1; *(Po, To)* = ***1.1;*** *(Po, To)* **.**

When the external pressure (the total pressure) is *p* , the condition of equilibrium of vapor and liquid is

Making use of Taylor's theorem, we have from the above two equations

Using the thermodynamic relation *dp* = -*SdT* + *Vdp,* we can write the above as

P - *Po* = *[(S2* - *S,)(T* - *To)* - *XRT]/(V2* - *Vl)* **,**

or

PO = *P* - **[L** ***(T***- *To)/T* - *zRT]/(V2*- *V I*)**,**

where *V* is the mole volume, *S* is the mole entropy, and ***L*** is the latent heat, *L* = *T(S2* - *S1).*

(b) The triple point of water is the temperature ***TO*** at which ice, water and vapor are in equilibrium. The ice point is the temperature T at which pure ice and air-saturated water are in equilibrium at **1** atm. Utilizing the result in (a) we have

$T - To = T(V2 - Vi)(p - po)/L + xRT2/L$,

where $V,$ and $V1$ are respectively the mole volumes of ice and water. From $V2 > Vl$ and $L < 0$, we know the ice point is lower than the triple point.

The first term of the above formula comes from the change of pressure, the second term appears because water is not pure. The quantitative result of the first term is -0.0075 K, of the second term is -0.0023 K.

1133

Some researchers at the Modford Institute of Taxidermy claim to have measured the following pressure-temperature phase diagram of a new substance, which they call "embalmium". Their results show that along the phase lines near the triple point

< (')sublimation < (-') fusion < (')vaporization

as indicated in the diagram. If these results are correct, "embdmiumn has one rather unusual property and one property which violates the laws of thermodynamics. What are the two properties?

(MIT)

P I

I - *T*

Fig. 1.36.

Solution:

The property (g) < 0 is unusual as only a few substances like

fu · n

water behaves in this way. yhe Clausius-Clapeyron equation gives

1(' -- (Sgas - Sliquid) vaporization Vgas

(') sublimation Vgas

- (Sgas - Ssolid) -

means Ssolid > S1iquid, i.e., the mole

entropy of the solid phase is greater than that of the liquid phase, which vi- (') vaporization > (') sublimiation

olates the second law of thermodynamics, since a substance absorbs heat to transform from solid to liquid and the process should be entropy increasing.

1134

The latent heat of vaporization of water is about **2 . 4 4 ~ 1 0**J/~k g and the vapor density is 0,598 kg/m3 at 100OC. Find the rate of change of the boiling temperature with altitude near sea level in "C per km. Assume the temperature of the air is 300 K.

(Density of air at $O°C$ and **1** atm is 1.29 kg/m3).

(wis ***co*** *nsin)*

Solution:

The Boltzmann distribution gives the pressure change with height:

where $p (0)$ is the pressure at sea level $z = 0$, m is the molecular weight of air, and $To = 300$ K is the temperature of the atmosphere. The Clausius-Clapeyron equation can be written as

dv *L L* (Y

with *p1* = 1000 kg/m3, *p2* = 0.598 kg/m3 and *L/M* = **2.44** x 106 J/kg, we have

(Y = ***Lp1p2*** = **1.40** x **lo6** J/m3 **.**
W P 1 - *P2)*
So the rate of change of the boiling point with height is
Using the equation of state for ideal gas *p* = ***pkTo/rn,*** we have near the sea level
where ***p*** = **1.29** kg/m3 is the density of air, g = 9.8 **m/s2** and *T(0)* = **100OC.**
d T
d z
Thus - = -0.87OC/km.

1135

A long vertical cylindrical column of a substance is at temperature *T* in a gravitational field ***g***. Below a certain point along the column the substance is found to be a solid; above that point it is a liquid. When the temperature is lowered by *AT,* the position of the solid-liquid interface is observed to move upwards a distance 1. Neglecting the thermal expansion of the solid, find an expression for the density *p1* of the liquid in terms of the density ***ps*** of the solid, the latent heat *L* of the solid-liquid phase transition, g and the absolute temperature *T* and *AT.*
Assume that *AT/T* << 1.

(Prince *ton)*

Soh t ion:

The Clausius-Clapeyron equation gives
do L L
In the problem, *dT* = *-AT, dp* = *-glp,.* Hence

1136

(a) Use simple thermodynamic considerations to obtain a relation between
--, the logarithmic rate of variation **of** melting point with change **of** pressure, the densities of the solid and liquid phases of the substance in question and the latent heat of melting. **(You** may find it convenient to relate the latent heat to the entropy change.)
(b) Use simple hydrostatic considerations to relate the pressure gradient within the earth to the earth's density and the acceleration of gravity. (Assume that the region in question is not at great depth below the surface.)
(c) Combine the foregoing to calculate the rate of variation of the melting point of silicate rock with increasing depth below the earth's surface
1 *dT,*
Tm dP

in a region where the average melting point of the rock is *1300°C.* Assume a density ratio
Pliquid/Psolid *e 0.9*
and a latent heat of melting of 100 cal/g. Give your answer in degrees C per kilometer.

(UC, **Berkeley)**

Soh tion:

(a) During the phase transtion, ***pr*** = ***pa,*** where *1* and 3 represent liquid phase and solid phase respectively. By thermodynamic relation

dp = *-SdT* **+** *VdP* **,**
we have *(S1 - S,)dT,* = (V, - *Va)dP, **so***

V, **- Va** V, - *V,* - - *1 dT,*
Tni dp Trn(Si - **Sa)** *L*

Substituting $V = l/p$ into the equation above, we get

dP

dz

(b) Denote the depth as **z,** we have - = pg.

(c) From the above results, we have

= 37 x "C/cm = **3.7"C/km .**

1137

The vapor pressure, in mm of Hg, **of** solid ammonia is given by the

The vapor pressure, in mm of Hg, **of** liquid ammonia **is** given by the

relation: lnp = $23.03 - 3754/T$ where T = absolute temperature.

relation: lnp = $19.49 - 3063/T$.

(a) What is the temperature **of** the triple point?

(b) Compute the latent heat of vaporization (boiling) at the triple point. Express your answer in cal/mole. (You may approximate the behavior of the vapor by treating it as an ideal gas, and may use the fact that the density of the vapor is negligibly small compared to that of the liquid.)

(c) The latent heat of sublimation at the triple point is ***7508*** cal/mole.

(UC, Berkeley)

What is the latent heat of melting at the triple point?

Solution:

$- 3754/T_0 = 19.49 - 3063/T_0$, which gives $T_0 = 195$ K.

(a) The temperature T of the triple point satisfies the equation ***23.03***

(b) From the relation between the vapor pressure and temperature of liquid ammonia

lnp = $C - 3063/T$,

we get $dp/dT = 3063p/T^2$.

The Clausius-Clapeyron equation $-dP$ = $-L$ then gives

dT TV

$L = 3063pV/T = 3063R = 2.54 \times 10^4$ J/mol

= ***6037*** cal/mol **.**

(c) Denote S_g, S_l and S_s as the entropy for vapor, liquid and solid at triple point. Then the latent heat of vaporization is $T_0(S_g - S_l)$, that of sublimation is $T_0(S_g - S_s)$, and that of melting is

$T(S_l - S_s) = T(S_g - S_s) - T(S_g - S_l)$

= ***7508 - 6037 = 1471*** cal/mol **.**

1158

The high temperature behavior of iron can be summarized as follows.

(a) Below 900°C and above ***1400OC*** a-iron is the stable phase.

(b) Between these temperatures T-iron is stable.

(c) The specific heat of each phase may be taken **as** constant: C_α = ***0.775 J/g*** . K; C_γ = 0.690 J/g . K.

What is the latent heat at each transition?

(UC, Berkeley)

Solution:

Referring to Fig. **1.37,** we regard the whole process as isobaric.

dS

Choose the entropy at T_1 as zero for the a-phase. Since $T- = C$,

dT

one has

S = C In T + const. : $S_\alpha = C_\alpha$ In , $S_\gamma = S_1 + C_\gamma$ In

The changes in chemical potential are

Since **Ap'** = **Ap,,** we have
= 1.60 x J/g.K
Therefore

= *(C, - C.,)T:!* In (g) *- SIT2*

= **23.7** J/g **.**
S I

Fig. **1.37.**

1139

Liquid helium-4 has a normal boiling point of **4.2** K. However, at a pressure of **1** mm of mercury, it boils at **1.2** K. Estimate the average latent heat of vaporization of helium in this temperature range.

*(UC, **Berkeley)***

Solution:

state for ideal gas
According to the Clausius-Clapeyron equation and the equation of
L
M- **,** *pVg=RT,*
L
dT T(Vg -Vl) TV,
_dP **--**
and assuming L to be constant, we get
L = R l n P*Po*/ (& - $) .
Therefore L = **93** J/mol.

1140

(a) The pressure-volume diagram shows two neighbouring isotherms in the region of a liquid-gas phase transition. By considering a Carnot cycle between temperatures *T* and *T* + *dT* in the region shown shaded in the diagram, derive the Clausius-Clapeyron equation relating vapor pressure and temperature, *dp/dT* = *L/ (TAV)* ,w here L **is** the latent heat of vaporization per mole and *AV* is the volume change between gas and liquid per mole.

(b) Liquid helium boils at temperature ***TO*** = **4.2** K when its vapor pressure is equal to *po* = **1** atm. We now pump on the vapor and reduce the pressure to a much smaller value *p.* Assuming that the latent heat L **is** approximately independent of temperature and that the helium vapor density is much smaller than that of the liquid, calculate the approximate temperature *T,,,* of the liquid in equilibrium with its vapor at pressure *p.* Express your answer in terms of L, *To, pol pm,* and any other required constants.

(CUSPEA)

Solution:

(a) From the *p* - *V* diagram, we can see that the work done by the working material on the outside world is *dW* = *dpAV* in this infinitesimal Carnot cyce. The heat absorbed in the process is Q = *L.* The formula for
dW dT
the efficiency of a Carnot engine gives **-** = *-L* ***T'***
Thus -*dP* = *-L dT TAV'*
(b) Since
Hence
Therefore

TO

L Prn

Tm = (1+- RTOlnP0)

I L

Fig. **1.38.** *V*

1141

When He3 melts the volume increases. The accompanying plot is a sketch of the He3 melting curve from 0.02 to 1.2 K. Make a sketch to show the change in entropy which accompanies melting in this temperature range.

(*wis* ***c o*** *nsin)*

Fig. 1.39.

Solution:

From the Clausius-Clapeyron equation, we have

d p AS and so *AS* = *AV-d P* . *dT - AV' dT*

When He3 melts, the volume increases, i.e., *AV* > 0.

When **0.02** K< *T* < **0.32** K, because - < *0,AS* < *0.*

When **0.32** K < ***T*** < **1.2** K, because - > *0,AS* > *0.*

When *T* = **0.32** K, *AS* = *0.* The results are shown in Fig. 1.39(b).

dP

dP

dT

dT

1142

The phase transition between the aromatic (a) and fragrant (f) phases of the liquid mythological-mercaptan is second order in the Ehrenfest scheme, that is, *AV* and *AS* are zero at all points along the transition line *p,-f(T).* Use the fact that *AV* = *V,(T,p)-Vf(T,p) = 0,* where *V,* and *Vf* are the molar volumes in phase a and phase **f** respectively, to derive the slope of the transition line, *dp,-t(T)/dT,* in terms of changes in the thermal expansion coefficient, ***a,*** and the isothermal compressibility, ***kT*** at the transition.

(MIT)

Solution:

Along the transition line, one has

Va(T1 P) = &(TIP)

Thus *dV,(T,p) = dVf(T,p).*

Since

we have

or

T

Fig. 1.40.

1143

State Curie's law for the magnetization of a paramagnetic gas. Why does the magnetization depend on temperature? What modification of the law **is** necessary as *T* -+ ***O?***

(wis **co *nsin)***

Solution:

Curie's law states that the magnetization of a paramagnetic substance in a magnetic field is inversely proportional to the absolute temperature: *M* = *CH/T,* where *C* is the Curie constant. As the temperature changes, so does the distribution of the directions of spins of the atoms and ions;

thus the magnetization is dependent on *T*.
At low temperatures the paramagnetic phase changes into the ferromagnetic phase. At this time, the external magnetic field B, produces a certain magnetization *M,* which in turn produces an exchange magnetic

field BE = ***XM*** (A is a constant). From *M* = x(Ba + BE) = x(Ba + *AM)*

and ***X*** = *C/T* (Curie's law), we have

M C x = -*B*=,- *T* - *Tc*

where *TC* = CX is the Curie temperature.

1144

A substance is found to have two phases, ***N*** and *S.* In the normal state, the ***N*** phase, the magnetization *M* is negligible. At a fixed temperature *T* < *T,,* as the external magnetic field *H* is lowered below the critical field

Hc(T) = *Ho* [1- (31 ,

the normal state undergoes **a** phase transition to a new state, the *S* phase. In the *S* state, it is found that *B* = 0 inside the material. The phase diagram is shown below.

(a) Show that the difference in Gibbs free energies (in cgs units) between the two phases at temperature *T* < *T,* **is** given by

1 *Gs(T,H)* - *GN(T,H)* = *K[H'* - *H:(T)]* **.**

(You may express your answer in another system of units. The Gibbs free energy in a magnetic field is given by *G* = ***U*** - *TS* - *HM.)*

(b) At *H* **I :** *Ho,* compute the latent heat of transition *L* from the ***N*** to the S phase. (Hint: one approach is to consider a "Clausius-Clapeyron" type of analysis.)

(c) At *H* = 0, compute the discontinuity in the specific heat as the material transforms from the ***N*** to the *S* phase.

(d) Is the phase transition first or second order at *H* = O?

(UC, **Berkeley)**

H

L

A/ **nhnca**

Ho h **G**

(***T*** :const < ***T,*** I

Fig. **1.41.** Fig. **1.42**

Solution:

(a) Differentiating the expression for Gibbs free energy, we find *.dG* = -*SdT* - *MdH,* where *B* = *H* + **47rM** in cgs units. Referring to Fig. **1.42,** we have

N phase: *M* = 0, *GN* = *Go(T),*

S phase: *B* = 0, *M* = *-H/4a.*

Integrating *dG* = *-MdH,* we obtain

Gs = *H2/87r* + const

Noting that *Gs* (H,, **7')** = *Go(T)* at the transition point, we have

1

871.

Gs = *Go(T)* **+** ***- (H 2*** *- H:)* **.**

It follows that

Gs - GN = **-1***(H* **2** *2 - H,)* **.** a71.

(b) Since S=- (g) *H* ,

we have

a2Hc

= **4a** [(***S)2*** + *H,* (aii)]

- *-H; -T* [3 **(f)2** - *11* -

2a *T, "*

When *H* = 0, *Cs - CN = H;/aT,*

(d) **At** *H = 0, L = 0, Cs* **-** *CN* **#** 0, therefore the phase transition is second order.

1145

The phase boundary between the superconducting and normal phases of **a** metal in the ***He*** - T plane *(He* = magnitude of applied external field) is given by Fig. *1.43.*

The relevant thermodynamic parameters are *T,p,* and *He.* Phase equilibrium requires the generalized Gibbs potential *G* (including magnetic paramters) to be equal on either side of the curve. Consider state ***A*** in the normal phase and ***A'*** in the superconducting phase; each lies on the phase boundary curve and has the same *T, p* and *He* but different entropies and magnetizations. Consider two other states *B* and *B'* arbitrarily close to ***A*** and ***A';*** as indicated by *PA = p g* .

(a) Use this information to derive a Clapeyron-Clausius relation (that is, a relation between the latent heat of transition and the slope *dHe/dT* of the curve). What is the latent heat at either end **of** the curve? (For a long rod-shaped superconducting sample with volume *V* oriented parallel to the field, the induced magnetic moment is given by ***Mfi*** = *-VHe/4r;* in the normal state, set *MH* = 0.)

(b) What is the difference in specific heats at constant field and pressure **(Cp , ~ ,**fo**)**r the two phases? What is the discontinuity in **C p , ~**a**c**t *H,=O,T=T,? AtT=O,H,=H,?*

(Prince *ton)*

Solution:

Fig. **1.43.**

(a) *dG* = ***-SdT*** **+** *Vdp - MHdH,.*

The condition of phase equilibrium is

Thus ***dG = dG'.***

With *dp* = 0, one obtains for the superconducting sample

where L = *T(S - S')* is the latent heat of phase transition. At the two ends of the curve: *He(T,)* = 0 at *T = T,* gives *L* = 0; *dHe/dT = 0* at *T* = 0 gives L = 0 also.

(b) From the above equation, we have

S' - S = -VH, . -dH,

41r *dT* ·

As *C = T(dS/dT)*

At *T = T,; He = 0,* we have

At *T* = 0, *He = H,,* we have

A C = -VHT, [F]d 2H, = o

47r *T = O*

1146

A simple theory of the thermodynamics of a ferromagnet uses the free energy F written **as** a function of the magnetization M in the following form: F = -HM + *FO* + *A(T - Tc)M2* + ***BM4,*** where *H* is the magnetic field, *Fo, A,* B are positive constants, *T* is the temperature and ***T,*** is the critical temperature.

(a) What condition on the free energy F determines the thermody-

(b) Determine the equilibrium value of M for *T* > *T,* and sketch a

(c) Comment on the physical significance of the temperature depennamically most probable value of the magnetization M in equilibrium?

graph of M versus *T* for small constant *H.*

dence of *M* as *T* gets close to *T,* for small *H* in case (b).

(*Wisconsin)*

Solution:

According to the problem *F* denotes the Gibbs function.

(a) *F* = minimum is the condition to determine the most probable value of *M* in equilibrium. Thus *M* is determined from *(~ F / ~ M) T=,* 0*H.*

(b) *(~ F / ~ M) T=, -HH* + *2A(T - Tc)M*+ *4BM3 = 0.* (*)

If *2A(T - T,)M* >> *4BM3,* that is, if T is far from *T,,* we have

H

2A(T - T,) ·

M =

This is the Curie-Weiss law. The change of *M* with *T* is shown in Fig. *1.44.*

(c) If *H = 0,* the equation (*) has solutions

M = 0 , M = i J A (T , - T) / 2 B .

For stability consider

(%) *= ZA(T - T,)* + *12BM2 . T,H*

When T > *T,,* the only real solution, *M* = 0, is stable;

'C

Fig. **1.44**

when ***T < T, ,*** the *M* = 0 solution is unstable, while the

when *T = T,,M = 0, T,* is the point of phase transition of the second order. (If ***T > T, ,*** the substance is paramagnetic; if *T* < *T,,* the substance is ferromagnetic.)

If *H* # 0, (*) requires *M* # 0. Then as long as ***M2*** > *A(Tc - T.)/6B,* the system is stable. When *T + TC,2A(T - T,)M* << *4BM2,* and (*) has the solution *M = (H/4B):.* Thus *T,* is the point of first-order phase transition.

M = i J A (T c - T)/ZB solution is stable;

1147

In the absence of external magnetic fields a certain substance is superconducting for temperatures *T* < *TO.* In the presence of a uniform field *B* and for *T* < *Td,* the system can exist in two thermodynamic phases: For *B* < *B,(T),* it is in the superconducting phase and in this phase the magnetization per unit volume is
(Superconducting phase) *M* = *-B/4s.*
For *B* > *B,(T),* the system is in the normal phase and here (Normal phase) *M* = 0.
The two phases can coexist in equilibrium along the curve *B* = *B,(T)* in the *B* - *T* plane.
Evidently there is a discontinuity in magnetization across the coexistence curve. There is also a discontinuity in entropy. Let *SN(T)* and *Ss(T)* be the entropies per unit volume respectively for the normal and superconducting phases along the coexistence curve. Given that *B,(T)* = *Bo* **1** - - **,** compute A S = *SN(T)- Ss (T)*a s a function of *T* and the other parameters.
(*CUSPEA)*

(*3*

Solution:

Comparing this magnetic system with a p-V system, we have *-B* -+ *P* and *M* -+ V. From the Clausius-Clapeyron equation of the ***p*** - V system,
dp AS
dT - AV '
-- -
we have for the magnetic system, on the line of two-phase coexistence,
-dB= - -AS
dT AM .
where A S = **SN** - ***Ss,*** A M = ***MN*** - ***Ms*** = *B/4s.*
Therefore
2s *T:*

5. NONEQUILIBRIUM THERMODYNAMICS (1148-1159)

1148

A tube of length *L* contains a solution with sugar concentration at time *t* = 0 given by
7rx 1 ***3TX*** **1**

n(z, *0)* = n o + n1 cos - + - cos - + - cos - *{ L 9 L 2 5 L*

Assume that n(x, *t)* obeys a one-dimensional diffusion equation with
(a) Write down the diffusion equation for n(z, *t).*
(b) Calculate ***n (x,*** *t)* for *t* > 0.
diffusion constant D.
(MITI

0 L

Fig. 1.45.

Solution:

(a) The diffusion equation is
and the condition **for** existence of solutions are
(b) Let *n(z, t)* = *X (z) T (t)* . We then have

X"(2) + ***XX(2)*** = 0 ,

T'(t) + *DXT(t)* = *0,* with X # 0 and *X'(0)* = ***X'(L)*** = *0* .

The conditions require X = *(ICT/L)****k****~ ,=* **1 , 2 , 3 , ...** The general solution is

The coefficients *ck* are obtained from the given concentration at *t* = 0, *n(z,* 0)

Hence

1149

(a) With neglect of viscosity and heat conductivity, small disturbances in a fluid propagate as undamped sound waves. Given the relation ***p*** = p(p,S), where p is pressure, ***p*** is the mass density, *S* is the entropy, derive an expression for the sound wave speed ***v.***

(b) **As** an example of such a fluid, consider a system of identical, noninteracting spin **1/2** particles of mass ***m*** at the absolute zero of temperature. The number density is *n.* Compute the sound speed *t~* in such a system.

(Princeton)

(a) The equations of continuity and momentum in a fluid are respec-

Solution:

tively

aP

- + V · ***(pv)*** = *0* , *at*

a -(pv) + (v . V)(pv) + VP = *0*

a t

For a fluid at rest, v = 0, ***p*** = *PO,* **p** = *PO,* Consider small disturbances,

the corresponding quantities are v = v',p = ***po*** + ***p', p*** = po + ***p'.*** We substitute them into the equations above, taking into consideration only first-order terms, and obtain

a *P'*

- + pov **.v'** = *0* **,** a t

av'

P o -a+t+ p '=o .

Hence

-*P p-'* - V2p' = v2 [**(2)** *PIJ* = ***(2)*** . V2P'

at2 *S*

Compare it with wave equation = **v2V2p',** we have **v2** = (EL

a2

at2

(Note: An assumption has been made here that the pressing of the fluid created by the disturbances is adiabatic for which *S* = const. Generally speaking, such approximation is reasonable as the heat conductivity is negligible.)

(b) At T = 0 K, for a system of spin 1/2 Fermioii gas we have

2 *NPo*

P = i v

1150

Gas, in equilibrium at pressure ***po*** and mass density *PO,* is confined to a cylinder of length *L* and cross sectional area ***A.*** The right hand end of the cylinder is closed and fixed. At the left hand end there is a frictionless and massless movable piston. In equilibrium the external force that must be exerted on the piston is of course *fo* = ***poA.*** However, suppose

a small additional force is supplied by an external agency: the harmonic force *f (t)* = fo cos(wt). This produces small motions of the piston and thus small amplitude disturbances in the gas. Let c be the speed of sound in the gas; neglect viscosity. Let *v (t)* be the velocity of the piston. Compute ***v (t) .***
(CUSPEA)

piston
/

. ,.* . . `.. x
-*L*Fig.
1.4F.

Solution:

whose origin is the equilibrium point (as shown in Fig. 1.46).
Consider the **gas** as **an** ideal fluid. We choose a coordinate system
Let the

velocity of the macroscope motion of the gas be ***u(x, t)*** and the pressure of the gas be ***p (x, t)***. Because the displacement of the piston is very small, we can solve ***u(z, t)*** and ***p (x, t)*** approximately in the region 0 5 x 5 L and consider ***u (0 , t) .*** The boundary conditions are *p (0 , t)* = ***f (t) / A*** and ***u(L, t)*** = 0 . **As** *f (t)* is a sinusoidal function of *t* and the frequency is w, the resulting ***u (z , t)*** and *p(z, t)* must be waves of frequency w and wave vector k = w/c. In fact, ***u(z, t)*** and *p(z, t)* both satisfy the wave equation with propagating velocity ***c.*** We can write

f (g) = Refoexp(iwt) ,

p = Re$(z) exp(iwt) ,

u = Reij(z) exp(iwt) .

Thus, to satisfy the boundary condition of ***p ,*** we have

$ (x) = -**fo** cos(kz) + Xsin(ks) , ***A***

where X is to be determined.
equation
On the other hand, the macroscope motion of fluid satisfies the Euler

au ap
Po- at = --ax

where ***po*** is the average density, ***u*** is the velocity and **p** is the pressure. Then

G(x) = -i(k-p osinkx+Xcoskz), where ***po*** = -f.o
WPO ***A***

Using the boundary condition ***u(L)*** = 0, we have

X = ***po*** tan(kL) .

Thus

ik % P O WL

c (x = 0) = -*PO* tan kL = -- tan - . WP3 c *PO* c

~ *(t=)* R e(6(0)eiwt)= - ("tan c
CPO

1151

Under normal conditions the temperature of the atmosphere decreases steadily with altitude to a height of about 12 km (tropopause), above which the temperature rises steadily (stratosphere) to about 50 km.

(a) What causes the temperature rise in the stratosphere?

(b) The warm stratosphere completely surrounds the earth, above the cooler tropopause, maintained as a permanent state. Explain.

(c) Sound waves emitted by a plane in the tropopause region will travel to great distances at these altitudes, with intensity decreasing, approximately, only as 1/R. Explain

(Columbia)

Solution:

(a) The concentration of ozone in the stratosphere formed by the action of the sun's ultraviolet radiation on the oxygen of the air increases with altitutde. The ozone absorbs the sun's ultraviolet radiation and raises the temperature of surrounding air.

(b) In the stratosphere, the ozone absorbs the ultraviolet radiation of the sun while the carbon dioxide COZ there radiates infrared radiation, resulting in an equilibrium of energy.

(c) Sound waves tend to deflect towards the region of lower velocity of propagation, i.e., of lower temperature. In the tropopause, temperature increases for both higher and lower altitudes. Hence the sound waves there are confined to the top layer of the troposphere, spreading only laterally in
1
fan-shape propagation so that the intensity decreases approximately as - R
1
instead of l.
R2

1152

Since variations of day and night in temperature are significantly damped at a depth of around 10 cm in granite, the thermal conductivity of granite is **5 x**

(Columbia)

lo-', lo2, lo5) cal/s.cm°C.

Solution:

Assume that the temperature at the depth of 10 cm below the surface of granite is constant at 2'0°C. When the temperature is the highest in a

day, the temperature of the ground surface is assumed to be TI *M* To+lO°C. The intensity of the solar radiation on the ground is

Q = 1400 W/m2 *M* **3.3** X calls. cm2 **.**

Q is completely absorbed by the earth within the first 10 cm below surface. Then from the Fourier law of heat conduction, we obtain an estimate of the thermal conductivity of granite:

Ax Ax
AT TI - To
K = *Q* . - = *Q* . -
= **3.3** x lop2 x (10/10) = **3.3** x cal/s . cm . **"C ,**

If we take into account reflection of the radiation from the earth's surface, the value of *K* will be smaller than the above estimate. Therefore we must choose the answer 5 x calls **.** cm **. "C.**

1153

The heat transferred to and from a vertical surface, such as a window pane, by convection in the surrounding air has been found to be equal to 0 . 4 1~0 -4(At)5/4 cal/sec.cm2, where At is the temperature difference between the surface and the air. If the air temperature is 25OC on the inside of a room and -15OC on the outside, what is the temperature of the inner surface of a window pane in the room? The window pane has a thickness of 2 mm and a thermal conductivity of **2 x** cal/sec. cm.OC. Heat transfer by radiation can be neglected.

(***Wisconsin)***

Solution:

inner and outer surfaces to be respectively t1OC and t2'C. Thus we have
We consider an area of 1 cm', and assume the temperatures of the

1

0.2

0.4 x 1 0 - ~ (+t ~ i q5l4= 2 x 1 0 -~x -(tl - ***t 2)***

= **0 . 4** x 10-4(25 - t1)5/4

The solution is tl = ***5OC.***

1154

The water at the surface of a lake and the air above it are in thermal equilibrium just above the freezing point. The air temperature suddenly drops by *AT* degrees. Find the thickness of the ice on the lake as a function of time in terms of the latent heat per unit volume *L/V* and the thermal conductivity **A** of the ice. Assume that *AT* is small enough that the specific heat of the ice may be neglected.

(MITI

Solution:

Consider an arbitrary area *AS* on the surface of water and let *h(t)* be the thickness of ice. The water of volume *ASdh* under the ice gives out heat *LASdhlV* to the air during time dt and changes into ice. So we have

L AT

ASdh V- = A-AhS dt

that is

Hence *h(t)* = **[** \$3 **1'2.**

1155

A sheet of ice 1 cm thick has frozen over a pond. The upper surface of the ice is at **-20°C.**

(a) At what rate is the thickness of the sheet of ice increasing?

(b) How long will it take for the sheet's thickness to double?

The thermal conductivity of ice *κ* is **5~**

heat of ice *L* is 80 cal/g. The mass density of water ***p*** is 1 g/cm3

cal/cm. sec.OC. The latent

*(SUNY, **BuflulIo)***

Solution:

(a) Let the rate at which the thickness of the sheet of ice increases be

vl a point on the surface of ice be the origin of z-axis, and the thickness of ice be ***z.***

The heat current density propagating through the ice sheet is *J* =

-κ ___ and the heat released by water per unit time per unit area

T - To

z

dz dz **dz**

dt dt dt

is *pL-.* Hence we obtain the equation ***pL-*** = *- j* , giving *q* = **-** =

***- j / p L* = n(T** *- **T o) / p L** z* **.**

(b) The above expression can be written as

dt = ***pL*** *zdz.*

n(T - To)

t = ***p L (~-i*** *z f) /2n(T- To)* **.**

If we take **z1** = 1 cm and *22* = **2** cm, then *At* = **1.2** x **lo3** *s* = *20* min.

1156

Consider a spherical black asteroid (made of rock) which has been ejected from the solar system, so that the radiation from the sun no longer

has a significant effect on the temperature of the asteroid. Radioactive elements produce heat uniformly inside the asteroid at a rate of ***q* = 3 x**
cal/g.sec. The density of the rock is ***p* = 3.5** g/cm3, and the thermal conductivity is *k* = **5** x The radius of the asteroid is
R = 100 km. Determine the central temperature ***T,*** and the surface temperature *T,,* of the asteroid assuming that a steady state has been achieved.

*(UC, **Berkeley)***

cal/deg.cmsec.

Solution:

The surface temperature satisfies

4rR3

4rR20T,4 = *Q* = **-3** ***P Q*** 1

80

T, = **(Z)'** = **22.5** K **.**

The equation of heat conduction inside the asteroid is

V .(-kVT) = ***Qp* .**

Using spherical coordinates, we have

and so

The central temperature is

T **--*9RP*** 2 + *T S* = *3 7 2 K .*

\- ***6k***

1157

Let *H* be the flow of heat per unit time per unit area normal to the isothermal surface through a point *P* of the body. Assunze the experimental fact

H=-kVT,

where *T* is the temperature and k is the coefficient of thermal conductivity. Finally the thermal energy absorbed per unit volume is given by *cpT,* where ***c*** is the specific heat and ***p*** is the density.

(a) Make an analogy between the thermal quantities **HI *k,*** T, ***c, p*** and

(b) Using the results of (a) find the heat conduction equation.

(c) **A** pipe of inner radius rl, outer radius r2 and constant thermal conductivity k is maintained at an inner temperature TI and outer temperature T2. For a length of pipe *L* find the rate the heat is lost and the temperature between rl and r2 (steady state).

the corresponding quantities **El J,** *V,* ***p*** of steady currents.

(SVNY, Bufiulo)

Solution:

(a) By comparison with Ohm's law **J** = **aE** = *-o* grad *V(V* is voltage) and conservation law of charge *dp/at* = *-V* . **J,** we obtain the analogy

cpT **u** ***p;H*** **J;** grad T grad *V ;* k tl ***u.***

(b) By the above analogy and charge conservation law, we have

cp- = -grad. *(-k* grad *T)*= kV2T **.** *aT*

at

Then the heat conduction equation is

aT k

_ _ _-V2T = *0* **.**

at pc

(c) When equilibrium is reached, ***aT/dt*** = 0; hence ***V2T*** = *0.*

The boundary conditions are *T(r1)* = TI and T(r2) = ***T2.***
Choosing the cylindrical coordinate system and solving the Laplace equation, we obtain the temperature between rl and *7-2:*

1 T(r) = -rl In -
r2
r
r2
TI In - - ***T2*** In -

we obtain the rate at which the heat is lost:
7-2
rl

q = 2wLH = 27rk(T1 - T2)L/ln - .

1158

A uniform non-metallic annular cylinder of inner radius **rl ,** outer radius r2, length *lo* is maintained with its inner surface at 100°C and its outer surface at 0°C.
(a) What is the temperature distribution inside?
(b) If it is then placed in a thermally insulated chamber of negligible heat capacity and allowed to come to temperature equilibrium, will its entropy increase , decrease or remain the same? Justify your answer.
(*Wisconsin)*

Fig. **1.47.**

Solution:

(a) Because the material is uniform, we can assume the heat conductivity is uniform too. According to the formulas dQ = -k(dT/dr)sdt and s = 27rlor, we have

dQ/dt = -27rlorkdT/dr .

Since dQ/dt is independent of r, we require dT/dr = A/r, where ***A*** is a constant. Then T(r) = Alnr + *B.*

F'rom the boundary conditions, we have
T2-T1,
In -r2 In *-r2*
rl rl
A=- - - - *B* = TI In r2 - T2 In r l 3
where TI = **373** K and T2 = **273** K, so that
1

T(r) = In rl - In r2 [(TI - T2) In r + T2 In rl - TI In r2]

(b) This is an irreversible adiabatic process, so that the entropy increase
s.

1159

When there is heat flow in a heat conducting material, there is an increase in entropy. Find the local rate of entropy generation per unit volume in a heat conductor of given heat conductivity and given temperature gradient.
(UC, Berkeley)

Solution:

then du = TdS. The heat conduction equation is
If we neglect volume expansion inside the heat conducting material,

duldt + V .q = 0 .

Hence

dS/dt = -V . q/T = -V . (q/T) + 9. V(l/T) , where q/T is the entropy flow, and 9. V (i) is the irreversible entropy increase due to the inhomogeneous temperature distribution. Thus, the local rate of entropy generation per unit volume is

According to **Fourier's heat conduction law, q =** *-kVT,* **the above gives**

2

S=k(y.)

PART I1
STATISTICAL PHYSICS

1. PROBABILITY AND STATISTICAL ENTROPY (2001-2013)

2001

A classical harmonic oscillator of mass m and spring constant ***k*** is known to have a total energy of *E,* but its starting time is completely unknown. Find the probability density function, ***p(x),*** where *p(z)ds* is the probability that the mass would be found in the interval *dx* at *x.*

(MITI

Solution:

From energy conservation, we have

where ***1*** is the oscillating amplitude. So the period is

Therefore we have

p(z)dz = - = -

2002

Suppose there are two kinds of E. coli (bacteria), "red" ones and "green" ones. Each reproduces faithfully (no sex) by splitting into half, red-+red+red or green+green+green, with a reproduction time of 1 hour. Other than the markers "red" and "green", there are no differences between them. A colony of 5,000 "red" and 5,000 "green" E. coli is allowed to eat and reproduce. In order to keep the colony size down, a predator is introduced which keeps the colony size at 10,000 by eating (at random) bacteria.

(a) After a very long time, what is the probability distribution of the number of red bacteria?

(b) About how long must one wait for this answer to be true?

(c) What would be the effect of a 1% preference of the predator for eating red bacteria on (a) and (b)?

(Princeton)

Solution:

(a) After a sufficiently long time, the bacteria will amount to a huge number *N* >> 10,000 without the existence of a predator. That the predator eats bacteria at random is mathematically equivalent to selecting *n* = 10,000 bacteria out of *N* bacteria as survivors. *N* ,> *n* means that in every selection the probabilities of surviving "red" and "green" E. coli are the same. There are ***2n*** ways of selection, and there are *Cg* ways to survive m "red" ones. Therefore the probability distribution of the number of "red" E. coli is

1 1 ***fl!***

-C” = - . , m=0,1, **...,** *n*
2n 2n m!(n - m)!

(b) We require ***N*** >> ***n.*** In practice it suffices to have *N/n* = **lo2.** As
N = ***2tn,t*** = 6 to 7 hours would be sufficient.
(c) If the probability of eating red bacteria is

eating green is (i ***-p)*** **,** the result in (a) becomes

C: (;+?I)” **(;-P)n-m**
--*n!* **n-m --**
m!(n - m)!
The result in (b) is unchanged.

200s

(a) What are the reduced density matrices in position and momentum
(b) Let us denote the reduced density matrix in momentum space by
spaces?
q5(pl, pz). Show that if q5 is diagonal, that is,
d4Pl)PZ) = f (P l) L m >

then the diagonal elements of the position density matrix are constant.
(SUNY, *Buflalo)*

Solution:

(a) The reduced density matrices are matrix expressions of density
operator *$(t)* in an orthogonal complete set of singlet states, where the
density operator *$(t)* is defined such that the expectation value of an arbitrary
operator 6 is (6) = tr[b$(t)]. We know that an orthogonal complete
set of singlet states in position space is {Ir)}, from which we can obtain
the reduced density matrix in position space (r’l;(t)lr). Similarly, the reduced
density matrix in momentum space is **(p’($(t)(p**w)h, ere **{(p))**i s an
orthogonal complete set of singlet states in momentum space.
P’ P
P
1
V
Then the diagonal elements (rI$(t)lr) = **--Cpf(p)** are obviously constant.

2004

(a) Consider a large number of ***N*** localized particles in an external
magnetic field **H.** Each particle has spin **1/2.** Find the number of states
accessible to the system as a function of *M,,* the z-component of the total
spin of the system. Determine the value of *M,* for which the number of
states is maximum.
(b) Define the absolute zero of the thermodynamic temperature. Explain
the meaning of negative absolute temperature, and give **a** concrete
example to show how the negative absolute temperature can be reached.
(SUNY, Buflalo)

Solution:

(a) The spin of a particle has two possible orientations **1/2** and **-1/2.**
Let the number of particles with spin **1/2** whose direction is along **H** be

NT and the number of particles with spin **-1/2** whose direction is opposite
to **H** be ***Ni;*** then the component of the total spin in the direction of **H** is
M, = ***-(NT*** - ***NL).*** By ***NT*** + ***Ni*** = ***N*** **,** we can obtain *Nt* = - + *M,* and
Ni = - - *M,*. The number of states of the system is
1 N

2 2
N
2
Using Stirling’s formula, one obtains
N!
Nt !***N L!*** In *Q* = In ___
BY *a* In Q
- = - I n N t + I n (N - N t) = O , *a* Nt
N
2
we get NT = **-,** i.e., *M,* = *0* when the number of states of the system is maximum.

(b) See Question 2009.

2005

There is an one-dimensional lattice with lattice constant ***a*** as shown in Fig. **2.1.** An atom transits from a site to a nearest-neighbor site every 7 seconds. The probabilities of transiting to the right and left are ***p*** and *q* = **1** - **p** respectively.

Fig. **2.1.**

(a) Calculate the average position Z of the atom at the time *t* = *NT,*

(b) Calculate the mean-square value (z - %)2 at the time *t.*

where ***N*** >> *1;*

(MITI

Solution:

the z-axis directing to the right. We have

(a) Choose the initial position of the atom as the origin z = 0, with

(2n - N)apnqN-n
N ***N !***
-
= 1 *n!(N* - n)!

= *2aPG*(*n ! (NN -! n) !p n q N P n) - N a*
n=O
a N
n=O a
a P

= *2ap-(p* + *q)N - Na* = *Na(p* - *q)* **.**

2006

(a) Give the definition of entropy in statistical physics.

(b) Give a general argument to explain why and under what circumstances the entropy of an isolated system ***A*** will remain constant, or increase. For convenience you may assume that ***A*** can be divided into subsystems *B* and *C* which are in weak contact with each other, but which themselves remain in internal thermodynamic equilibrium.

(UC, ***Berkeley)***

Solution:

(a) S = klnfl, where *Ic* is Boltzmann's constant and fl is the total number of microscopic states of the given macroscopic state.

(b) Assume that the temperatures of the two subsystems are *TB* and ***Tc*** respectively, and that *TB* 2 *Tc.* According to the definition of entropy, if there is a small energy exchange *A* > 0 between them (from *B* to C), then

When TB > *Tc,* there is no thermal equilibrium between the subsystems, and *AS* > 0;

When *To* = T,, i.e., the two subsystems are in equilibrium, AS = 0.

2007

Give Boltzmann's statistical definition of entropy and present its physical meaning briefly but clearly. **A** two-level system of ***N*** = *nl* +*n2* particles is distributed among two eigenstates 1 and **2** with eigenenergies *El* and *E2* respectively. The system is in contact with a heat reservoir at temperature *T.* If a single quantum emission into the reservoir occurs, population changes *n2* --+ *n2* - 1 and *n1* -+ *nl*+ 1 take place in the system. For *nl* >> 1 and *n2* >> 1, obtain the expression for the entropy change of

(a) the two level system, and of

(b) the reservoir, and finally

(c) from (a) and (b) derive the Boltzmann relation for the ratio *nl/nz.*

(UC, Berkeley)

Solution:

Physically entropy is a measurement of the disorder of **a** system.

S = k In R, where R is the number of microscopic states of the system.

(a) The entropy change of the two-level system is

N! N!

ASl = kln - lcln -

(n2 - l) ! (n l+ I)! *nl!n2!*

n2 n2

= kln kln -

nl + 1 *nl*

(b) The entropy change of the reservoir is

(c) From **AS,** + AS, = 0, we have

-***n2*** = exp (- ***E2*** k-T ***El***) .

nl

2008

Consider **a** system composed of **a** very large number ***N*** of distinguishable atoms, non-moving and mutually non-interacting, each of which has only two (non-degenerate) energy levels: 0,s > 0. Let ***E/N*** be the mean energy per atom in the limit ***N*** -+ 00.

(a) What is the maximum possible value of ***E/N*** if the system is not necessarily in thermodynamic equilibrium? What is the maximum attainable value of ***E/N*** if the system is in equilibrium (at positive temperature, of course)?

(b) For thermodynamic equilibrium, compute the entropy per atom,

(Prince ton)

SIN, as a function of ***E/N.***

Solution:

(a) If the system is not necesssarily in thermodynamic equilibrium, the maximum possible value of ***E/N*** is ***E;*** and if the system is in equilibrium (at positive temperature), the maximum possible value of ***E/N*** is *s/2* corresponding to T + *co.*

(b) When the mean energy per atom is ***E / N , E / s*** particles are on the level of energy *E* and the microscopic state number is

N! Q= (f) ! *(N -* :)! ·

So the entropy of the system is

N!

S = kln- (f) ! *(N -* f) ! ·

If *E/&* >> 1, ***N*** - *E/&* >> 1, we have

N

r 1

= k ICE\. -In-+ "E" (1-- *:E)* ln- *' E l '*

1-- ***EN***

2009

Consider a system of *N* non-interacting particles, each fixed **in** position and carrying a magnetic moment ***p,*** which is immersed in a magnetic field *H.* Each particle may then exist in one of the two energy states *E* = 0 or *E* = ***2pH.*** Treat the particles as distinguishable.

(a) The entropy, S, of the system can be written in the form S = klnR(E), where k is the Boltzmann constant and *E* is the total system energy. Explain the meaning of R(E).

(b) Write a formula for S(n), where n is the number of particles in the upper state. Crudely sketch *S(n).*

(c) Derive Stirling's approximation for large n:

Inn! = nlnn - n

by approximating In n! by an integral.

(d) Rewrite the result of (b) using the result of (c). Find the value of

(e) Treating *E* as continuous, show that this system can have negative

(f) Why is negative temperature possible here but not for a gas in a

(CUSPEA)

(a) R(E) is the number of all the possible microscopic states of the

n for which S(n) is maximum.

absolute temperature.

box?

Solution:

system when its energy is *E,* where

(b) **As** the particles are distinguishable,

N!

= n!(N - n)! ·

N!

n!(N - ***n) !***

Hence *S* = lcln

We note that S(n = 0) = S(n = N) = 0, and we expect *S,,,* to appear

= S(n) **.**

at n = N/2 (to be proved in (d) below). The graph of S(n) is shown in Fig. **2.2.**

n

(c) Inn! = *C* 1nm ***M*** lnzdz = n l n n - n + 1 ***M*** n l n n - n, (for

m= 1

large n).
S N n
(d) k m N l n - - n l n -
N - n N - n
dS
- = *0* gives
dn
n

1 - I n n - - + ln(N - n) = *0* -_N .
N - n N - n
Therefore, *S* = *S,,,,,* when n = N/2.
N/2 N
Fig. **2.2.**

1 1 *as* (e) As *E* = nc, *S* = *S,,,,,* when *E* = -NE. When *E* > -NE, - < *0*
2 2 *aE*
1 *dS*
T dE'

(see Fig. **2.2).** Because - = - we have ***T*** < 0 when *E* > N E / ~ .

(f) The reason is that here the energy level of a single particle has an upper limit. For a gas system, the energy level of a single particle does not have an upper limit, and the entropy is an increasing function of *E;* hence negative temperature cannot occur.

From the point of view of energy, we can say that a system with negative temperature is “hotter” than any system with a positive temperature.

2010

A solid contains ***N*** magnetic atoms having spin 1/2. At sufficiently high temperatures each spin is completely randomly oriented. At sufficiently low temperatures all the spins become oriented along the same direction (i.e., Ferromagnetic). Let us approximate the heat capacity as a function of temperature ***T*** by

C(T)= [c1 (%0- 1) i fTL/ 2< T < *TI*

| 0 otherwise ,

where ***TI*** is a constant. Find the maximum value c1 of the specific heat (use entropy considerations).

(UC, Berkeley)

Solution:

dS
dT
From C = T - , we have

S(o0)- S(0) = *l*- - dT = c l (1 - ln2) .

On the other hand, we have from the definition of entropy *S(0)* = 0, *S(o0)* = Nk In 2, hence

Nkln2
1 - I n 2
c1=-.

2011

The elasticity of a rubber band can be described in terms of a onedimensional model of polymer involving N molecules linked together endto-end. The angle between successive links is equally likely to be *0'* or 180'.

(a) Show that the number of arrangements that give an overall length of L = 2md is given by

2 ***N!***

g(N,m) = , where m is positive (; + (; - *m)!*

Indicate clearly the reasoning you used to get this result.

(b) For *m* << N, this expression becomes

g(N, m) ***w*** g(N, 0) exp(-2m2/N) **.**

Find the entropy of the system as a function of L for N >> 1, L < Nd.

(c) Find the force required to maintain the length L for L << Nd.

(d) Find the relationship between the force and the length, without using the condition in (c), i.e., for any possible value of L, but ***N*** >> 1.

(UC, **Berkeley)**

N **molecules**

[***N*** **= constant**)

d **= length of one link**

a

Fig. 2.3.

Solution:

angle then

N+ - N- = 2m,

Therefore ***N*** N

N + = - + m , ***N - = - - m .***

2

(a) Assume that there are N+ links of *0'* angle and ***N-*** links of 180'

N+ + N- = N .

This corresponds to ***N!/(N+!N-$*** arrangements. Note that for every arrangement if the angles are reversed, we still get the overall length of ***2md.*** Thus

2N!

g = (;+m)!(;-m)!

(b) When *m* << ***N, g(N,*** m) ***w*** g(N, 0) exp(-2m2/N), the entropy of the system becomes

kL2

S = klng(N,m) = kIng(N,O) - ***2 ~ d 2.***

(c) From the thermodynamic relations *dU* = TdS + fdL and *F* =

U - TS we obtain dF = -SdT + fdL. Therefore (g),= - (*g)T* = NkdL2 ,

kTL

Nd2+'

f=-

As f = 0 when *L* = 0,

f=- kT*L*

Nd2 ·

(d) Consider only one link. When an external force f is exerted, the probability that the angle is *0'* or 180' is proportional to *ea* or *ePa* respectively, where ***a*** = fd/lcT. The average length per link is therefore

The overall length of the polymer is then

L = Ni = Ndtanh(fd/kT) **.**

2012

Consider a one-dimensional chain consisting of ***n*** >> 1 segments as illustrated in the figure. Let the length of each segment be *a* when the long dimension of the segment is parallel to the chain and zero when the segment is vertical (i.e., long dimension normal to the chain direction). Each segment has just two states, a horizontal orientation and a vertical orientation, and each of these states is not degenerate. The distance between the chain ends is ***nx.***

(a) Find the entropy of the chain as a function of ***x.***

(b) Obtain a relation between the temperature T of the chain and the tension *F* which is necessary to maintain the distance ***nz,*** assuming the joints turn freely.

(c) Under which conditions does your answer lead to Hook's law?

(Princeton)

nx

Fig. 2.4.

Solution:

parallel to the chain; so the microscopic state number is

(a) When the length of the chain is ***nz,*** there are **rn** = ***nx/a*** segments

n!

m!(n - m)!

n=c" = ***in***

We have

S = k l n n

n!

= kln

(:n>! (n - En)! ·

(b) Under the action of stress ***F,*** the energy difference between the vertical and parallel states of **a** segment is ***Fa.*** The mean length of a segment is

aeFalkT

1 + ***eFa/kT***

I =

so that

(c) At high temperatures,

L = n x = n a (a + a g) ,

which is Hooke's Law.

201s

Consider an idealization of a crystal which has ***N*** lattice points and the same number of interstitial positions (places between the lattice points where atoms can reside). Let *E* be the energy necessary to remove an atom

from a lattice site to an interstitial position and let *n* be the number of atoms occupying interstitial sites in equilibrium.

(a) What is the internal energy of the system?

(b) What is the entropy *S?* Give an asymptotic formula valid when

(c) In equilibrium at temperature *T,* how many such defects are there

(Princeton)

n>> I?

in the solid, i.e., what is n? (Assume *n* >> 1.)

Solution:

(a) Let *Uo* be the internal energy when no atom occupies the interstitial sites. When n interstitial positions are occupied, the internal energy is then

U = U o + n E .

(b) There are *C,"* ways of selecting n atoms from ***N*** lattice sites, and *C,"* ways to place them to ***N*** interstitial sites; *so* the microscopic state number is n = ***(C z) 2 .***H ence

N!

n!(N - n)!

S = k l n n = 2kln

When n >> 1 and ***(N** - n)* >> 1, we have ln(n!) = nlnn - n, so that

S = ***2k[N*** In ***N*** - *n* In n - ***(N*** - n) In(N - n)] **.**

(c) With fixed temperature and volume, free energy is minimized at

From *F* = *Uo* + nE - *TS* and a F / a n = 0, we have

equilibrium.

N

,El 2 k T + 1 **.** n =

2. MAXWELL-BOLTZMANN STATISTICS (2014-2062)

2014

(a) Explain Boltzmann statistics, Fermi statistics and Bose statistics, especially about their differences. How are they related to the indistinguishability of identical particles?

(b) Give as physical a discussi6n as you can, on why the distinction between the above three types of statistics becomes unimportant in the limit of high temperature (how high is high?). Do not merely quote formulas.

(c) In what temperature range will quantum statistics have to be applied to a collection of neutrons spread out in a two-dimensional plane with

the number of neutrons per unit area being - 1012/cm2?

(SVNY, Buflafo)

Solution:

(a) *Boltzmann statistics.* For a localized system, the particles are distinguishable and the number of particles occupying a singlet quantum state is not limited. The average number of particles occupying energy level ***EL*** is

al = ***w1*** exp(-a - ***Pel)* ,**

where ***wl*** is the degeneracy of 2-th energy level.

Fermi statistics. For a system composed of fermions, the particles are indistinguishable and obey Pauli's exclusion principle. The average number of particles occupying energy level ***€1* is**

Wl

***a1* =**

ea+l)tl + 1 *

Bose statistics. For a system composed of bosons, the particles are indistinguishable and the number of particles occupying a singlet quantum state is not limited. The average number of particles occupying energy level *El* is

Wl a1* = *ea+B#r - 1 '

(b) We see from (a) that when ***ea*** >> 1, or exp(-a) << 1, three types of statistics vanishes.

, (n is the particle density), we see that

2rmkT

n2/3h2

the above condition is satisfied when ***T*** >> **-.** So the distinction among the three types of statistics becomes unimportant in the limit of high temperatures.

It can also be understood from a physical point of view. When ***ea*** >> 1, we have ***q / w I*** << 1, which shows that the average number of particles in

27rmk

any quantum state is much less than 1. The reason is that the number of microstates available to the particles is very large, much larger than the total particle number. Hence the probability for two particles to occupy the same quantum state is very small and Pauli's exclusion principle is satisfied naturally. As a result, the distinction between Fermi and Bose statistics vanishes.

(c) The necessity of using quantum statistics arises from the following two points. One is the indistinguishability of particles and Pauli's exclusion

principle, because of which *ePa* = n (-) is not very much smaller than 1 (degenerate). The other is the quantization of energy levels, i.e., *AEIkT,* where *AE* is the spacing between energy levels, is not very much smaller than 1 (discrete).

h2

2.rrmkT

For a two-dimensional neutron system,

h2 *- AE*

kT 2mkTLZ

--

Taking *L* **w** 1 cm, we have *T* rn K. *So* the energy levels are quasicontinuous at ordinary temperatures. Hence the necessity of using quantum statistics is essentially determined by the strong-degeneracy condition

e-a = ***n*** (-) ***h2*** 21 **.** *2~mkT*

Substituting the quantities into the above expression, we see that quantum statistics must be used when **Ts1Ov2** K.

2015

(a) State the basic differences in the fundamental assumptions under-

(b) Make a rough plot of the energy distribution function at two different temperatures for a system of free particles governed by MB statistics and one governed by FD statistics. Indicate which curve corresponds to the higher temperature.

(c) Explain briefly the discrepancy between experimental values of the specific heat of a metal and the prediction of MB statistics. How did FD statistics overcome the difficulty?

lying Maxwell-Boltzman (MB) and Fermi-Dirac (FD) statistics.

(wzs ***co*** nsin)

Solution:

tions:

distinguished from one another.

a quantum state.

st at ist ics.

(a) FD, as compared with MB, statistics has two additional assump-

1) The principle of indistinguishability: identical particles cannot be

2) Pauli's exclusion principle: Not more than one particle can occupy

In the limit of non-degeneracy, FD statistics gradually becomes MB

(b) ***P (E)*** gives the number of particles in unit interval of energy or at energy level ***E.*** Figure **2.5** gives rough plots of the energy distributions ((a) MB, (b) FD).

P (&) h - P (E) I ft&

,
72 T1
ı
E &F
(a) MB statistics (b) FD statistics
Fig. 2.5.

(c) According to MB statistics (or the principle of equipartition of energy), the contribution of an electron to the specific heat of a metal should be **1.5** K. This is not borne out by experiments, which shows that the contribution to specific heat of free electrons in metal can usually be neglected except for the case of very low temperatures. At low temperatures the contribution of electrons to the specific heat is proportional to the temperture 7′. FD statistics which incorporates Pauli's exclusion principle can explain this result.

2016

State which statistics (classical Maxwell-Boltzmann; Fermi-Dirac; or Bose-Einstein) would be appropriate in these problems and explain why (semi-quantit atively) :

(a) Density **of** He4 gas at room temperature and pressure.

(b) Density of electrons in copper at room temperature.

(c) Density of electrons and holes in semiconducting Ge at room tem-

(VC, **Berkeley)**

perature (Ge band-gap *w* **1** volt).

Solution:

(a) Classical Maxwell-Boltzmann statistics is appropriate because

h2 3/2

nX 3 *P x* **3** x l o r 6 << 1 . =-.(-----)

kT 21rmkT

(b) Fermi-Dirac statistics is appropriate because electrons are Fermions and the Fermi energy of the electron gas in copper is about 1 eV which is equivalent to a high temperature of **104K.** At room temperature (low temperature), the electron gas is highly degenerate.

(c) Classical Maxwell-Boltzmann statistics is appropriate because at room temperature the electrons and holes do not have sufficient average energy to jump over the 1 eV band-gap in appreciable numbers.

2017

Show that X = exp(p/kT) = *nVQ* for an ideal gas, valid where X << 1; here *p* is the chemical potential, *n* is the gas density and

VQ = (h'/21rmkT)~/~

is the quantum volume. Even if you cannot prove this, this result will be useful in other problems.

(UC, Berkeley)

Solution:

In the approximation X << 1, Fermi-Dirac and Bose-Einstein statistics both tend to Maxwell-Boltzmann statistics:

The density of states of an ideal gas (spin states excluded) is

2lr

h3

D(+ = - (2 m) 3 / 2 f i d e .

Therefore,

That is, X = *nVQ.*

2018

A long, thin (i.e., needle-shaped) dust grain floats in a box filled with gas at a constant temperature *T.* On average, is the angular momentum vector nearly parallel to or perpendicular to the long axis of the grain? Explain.

(MITI

Solution:

Let the long axis of the grain coincide with the z-axis. The shape of the grain indicates that the principal moments of inertia satisfy *I,* < I,, *I,*. When thermal equilibrium is reached, we have

-1I #; = **-1** I,w,2 = z1I ,w, 2 ₁**2 2**

1 /2 1 ***I2***

so that Iw,I = ($) Iw,I = (t) lwyl **.** Therefore

So the angular momentum vector is nearly perpendicular to the long axis of the grain.

2019

A cubically shaped vessel 20 cm on a side constains diatomic H2 gas at a temperature of 300 K. Each H2 molecule consists of two hydrogen atoms

with mass of 1 . 6 6~1 0 - '~**g** each, separated by - **lop8** cm. Assume that the gas behaves like an ideal gas. Ignore the vibrational degree of freedom.

(a) What is the average velocity of the molecules?

(b) What is the average velocity of rotation of the molecules around an axis which is the perpendicular bisector of the line joining the two atoms (consider each atom as a point mass)?

(c) Derive the values expected **for** the molar heat capacities C, and C, for such a gas.

(Columbia)

Solution:

have

(a) The number of the translational degrees of freedom is **3.** Thus we

so ***w*** *0* = ***w*** **2** x 103 m/s. *M*

(b) The number of the rotational degrees of freedom is **2.** Hence

1 *2*

-IG2 = *-kT* **,**

2 2

. 1 where *I* = *m* . *2* = **-mr2** is the moment of inertia of the molecules Ha, ***rn*** is the mass of the atom H and ***r*** is the distance between the two hydrogen atoms. Thus we get

(;I2 **2**

(c) The molar heat capacities are respectively

5

7

C **- - R** = **2 1** J / m o l . K ,

C - -*R* = **29** J/mol. K **.**

v - 2

p - 2

2020

The circuit shown is in thermal equilibrium with its surroundings at a temperature *T.* Find the classical expression for the root mean square current through the inductor.

(MIT)

Fig. **2.6.**

Solution:

Fluctuations in the motion of free electrons in the conductor give rise
to fluctuation currents. If the current passing through the inductor is *I (t) ,*

then the average energy of the inductor is **W** = ***- I 2 ,*** where i Z is the meansquare

current. According to the principle of equipartition of energy, we

L-

2

1

have **W** = - kT. Hence

2

2021

Energy probability.

Find and make careful sketch of the probability density, p(E), for the
energy E of a single atom in a classical non-interacting monatomic gas in
thermal equilibrium.

(MITI

Solution:

When the number of gas atoms is very large, we can represent the states
of the system by a continuous distribution. When the system reaches thermal
equilibrium, the probability of an atom having energy E is proportional
to exp(-E/kT), where E = p2/2m, ***p*** being the momentum of the atom.

So the probability of an atom lying between p and p + dp is

Aexp(-p2/2mkT)d3p **.**

From

A 1 exp(-p2/2rnkT)d3p = **1 ,**

A = (2 ~ m k T) - ~. f ~

we obtain

Therefore,

giving

2022

Suppose that the energy of a particle can be represented by the expression
E(z) = az2 where *z* is a coordinate or momentum and can take
on all values from *-oo* to *$oo.*

(a) Show that the average energy per particle for a system of such
particles subject to Boltzmann statistics will be ***E*** = *kT/2.*

(b) State the principle of equipartition of energy and discuss briefly its
relation to the above calculation.

Solution:

its distribution function is

(a) From Boltzmann statistics,

(wis ***co ns in)***

whether *z* is position or momentum,

So the average energy of a single particle is

-

E=

+m L

1

= *-kT.*

2

Inserting *E(z)* = *az2* in the above, we obtain

(b) Principle of equipartition of energy: For a classical system of particle in thermal equilibrium at temperature *T,* the average energy of each degree of freedom of a particle is equal to *-kT.* 1

2

There is only one degree of freedom in this problem, so the average

1

2

energy is *-kT.*

2023

A system of two energy levels *Eo* and *El* is populated by ***N*** particles at temperature *T.* The particles populate the energy levels according to the classical distribution law.

(a) Derive an expression for the average energy per particle.

(b) Compute the average energy per particle vs the temperature as

(c) Derive an expression for the specific heat of the system of ***N*** par-

(d) Compute the specific heat in the limits *T* + 0 and *T* -+ *oo.*

T + *0* and *T* + *oo.*

ticles.

(was ***co*** nsin)

Solution:

(a) The average energy of a particle is

Assuming *El* > *Eo* > *0* and letting *AE* = *El* - *Eo,* we have

EO + *El e-BAE*

1 + *e-BAE*

U=

(b) When *T* + *0,* i.e., *p* = *l / k T* -+ *oo,* one has

u M *(EO* + *Ele-OAE)(l* - ***e - o A E)*** = *Eo* + *AEe-BAE* ,

When *T* -+ *co ,* or *p* + 0, one has

P

4

1

u **CJ -2** *(Eo* + *El - PElAE)* + *El) - - (AE) 2* **.**

(c) The specific heat (per mole) is

When ***T*** -+ *oo,*

CM- *. R* ***(*** *%****)*** 2 **.**

4

2024

Consider a glass in which some fraction of its constituent atoms may occupy either of two slightly different positions giving rise to two energy levels **A;** > 0 and **-A,** for the ith atom.

(a) If each participating atom has the same levels **A** and **-A,** calculate the contribution of these atoms to the heat capacity. (Ignore the usual

Debye specific heat which will also be present in a real solid.)

(b) If the glass has a random composition of such atoms so that all values of **A,** are equally likely up to some limiting value **A0** > 0, find the behavior of the low temperature heat capacity, i.e., ***kT*** << **Ao.** (Definite integrals need not be evaluated provided they do not depend on any of the parameters.)

(Princeton)

Solution:

(a) The mean energy per atom is **Z** = **A** tanh (&). Its contribution to the specific heat is

1 *d?* 2

c, = - = *4k* (&) *dT* *(eA/kT* + *e - A / k T) 2*

Summing up the terms **for** all such atoms, we have

1 2

cv = *4Nk* (&) . *(eA/kT* + *e - A / k T) 2* '

(b) The contribution to the specific heat of the ith atom is

1 2

ci = *4k* *(2)* *(eA,/kT* + *e - A , / k T) 2* '

When ***kT*** << **A,,** we have

Summing up the terms for all such atoms, we have

where **p(A)** is the state density of distribution **of A;.**

2025

The three lowest energy levels of a certain molecule are *El* = 0, *Ez* = *E* , *E3* = 1 0 ~ .S how that at sufficiently low temperatures (how low?) only levels *El, E2* are populated. Find the average energy *E* of the molecule at temperature *T.* Find the contributions of these levels to the specific heat per mole, *C,,* and sketch *C,* as a function of *T.*

(*Wisconsin)*

Solution:

levels for low temperatures.

according to the Boltzmann statistics, we have

We need not consider energy levels higher than the three lowest energy

Assuming the system has *N* particles and

NI + *N2* + *N3* = *N* ,

hence

N

N3 = 1 + *eQcfkT* + *elOa/kT* '

When *N3* < **1,** there is no occupation at the energy level *E3.* That is, when *T* < *Tc,* only the *El* and *E2* levels are occupied, where ***T,*** satisfies

If *N* >> **1,** we have

lo€

klnN '

T, *w* -

The average energy of the molecule is

The molar specific heat is

where

For high temperatures, $kT >> \epsilon$,

= l/kT and N_A is Avogadro's number.

For low temperatures, $kT << \epsilon$,

The variation of C, with T is shown in Fig. 2.7

T

Fig. 2.7.

2026

Given a system of two distinct lattice sites, each occupied by an atom whose spin (3 = 1) is so oriented that its energy takes one of three values ϵ = 1,0, -1 with equal probability. The atoms do not interact with each other. Calculate the ensemble average values and ? for the energy U of the system, assumed to be that of the spins only.

(UC, Berkeley)

Solution:

For a single atom, we have

For the system, we have

Since = q' GI it follows

2027

Obtain the temperature of each system:

(a) 6.0 x atoms of helium gas occupy 2.0 litres at atmospheric pressure. What is the temperature of the gas?

(b) A system of particles occupying single-particle levels and obeying Maxwell-Boltzmann statistics is in thermal contact with a heat reservoir at temperature T. If the population distribution in the non-degenerate energy levels is as shown, what is the temperature of the system?

Energy (eV)	population
30.1 x lob3	3.1%
21.5 x	8.5%
1 2 . 9 ~	23%
4.3 x 10-3	63%

(c) In a cryogenic experiment, heat is supplied to a sample at the constant rate of 0.01 watts. The entropy of the sample increases with time as shown in the table. What is the temperature of the sample at t = 500 sec?

Time:	100	200	300	400	500	600	700	(sec)
Entropy:	2.30	2.65	2.85	3.00	3.11	3.20	3.28	(J/K)

(UC, **Berkeley)**

Solution:

(a) Using the equation of state for an ideal gas, we get

$T = pV/nk$ = 241 K .

(b) The population distribution is given by

Therefore

Using the given n1 and n_2, we get T as follows:

99.2; 99.5; 99.0; 99.5; 100.2; 98.8 K .

The mean value is T = 99.4 K.

(c) The rate of heat intake is q = - = T-, giving

dQ dS

d t d t

T =- 9

(%)

dS

dt

We estimate - by the middle differential at *t* = *500s,* and get

= 1.0 x 10-3J/sec.K

@ = (3.20 - 3.00)

dt 600 - **400**

Therefore *T* = 10K.

2028

Assume that the reaction H*p+e occurs in thermal equilibrium at *T* = 4000 K in a very low density gas (no degeneracy) of each species with overall charge neutrality.

(a) Write the chemical potential of each gas in terms of its number density [HI, **[p],** or [el. For simplicity you may ignore the spectrum of

excited bound states of H and consider only the ground state. Justify this assumption.

(b) Give the condition for thermal equilibrium and calculate the equilibrium value of [el as a function of [HI and T.

(c) Estimate the nucleon density for which the gas is half-ionized at T = 4000 K. (Note that this is an approximate picture of the universe at a redshift ***z*** = **lo3.)**

(UC, **Berkeley)**

Solution:

(a) From Boltemann statistics, we have for an ideal gas without spin

n = . (2 ~ m k T / h ~**.**) ~ / ~

Both the proton and electron have spin 1/2, therefore

[p] = 2 (2 ~ m , k T / h ~) ~ / ~ e ~ p / ~ ~

[el = 2 (2 ~ r n , k T / h ~) ~ / ~**.**e ~ ' . / ~ ~

For the hydrogen atom, p and e can form four spin configurations with ionization energy Ed. Hence

(HI = ***4 (2 r m ~ k T / h ~) ~ / ~ e x p (E***e***d***x/p***k***(p***T***H***)*** / kT) **.**

The chemical potentials ***p, ,*** ***p(le*** and ***p~*** are given by the above relations with the number densities.

(b) The equilibrium condition is ***p~*** = ***pe*** +**pp.** Note that as p 7 2 ~*M* mp and [el = [p] we have

[el = ***m.*** (2 ~ t n , k T / h ~ .) e~x/p~(- Ed/2kT) **.**

(c) **When** the gas is half-ionized, [el = [PI = [HI = **n.** Hence

n = (Z ~ r n , l c T / h ~). e~x/p~(-Ed/kT) = **3.3 x 1016 rn-' .**

2029

A piece of metal can be considered as a reservoir of electrons; the work function (energy to remove an electron from the metal) is **4** eV. Considering

only the 1s orbital (which can be occupied by zero, one, or two electrons) and knowing that the hydrogen atom has an ionization energy of 13.6 eV and an electron affinity of 0.6 eV, determine for atomic hydrogen in chemical equilibrium at ***T*** = 300 K in the vicinity of **a** metal the probabilities of finding H+ , Ho and H- **.** Give only one significant figure.

What value of the work function would give equal probabilities to Ho and H-?

(UC, ***Berkeley)***

Solution:

We have (see Fig. ***2 . 8)***

e + H + ~ H ,

e + H s H - .

Fermi sea

Fig. **2.8.**

The chemical potential of the electron gas is ***pe*** = -*W*. From classical statistics, we can easily obtain

where the factor **2** arises from the internal degrees of freedom of spin. For the hydrogen atom, electron and proton spins can have four possible spin states, hence

For H-, both electrons are in their ground state with total spin *0* (singlet), as the space wave function is symmetric when the particles are interexchanged. Therefore, the spin degrees of freedom of H- correspond only to the two spin states of the nucleon; hence

The conditions for chemical equilibrium are

so that

Thus, the relative probabilities of finding H+, Ho and H- are

If ***PH*** = ***PH-,*** o r [HO] = [H-I, we have

W = −***pe*** = ---***€a*** + ***kT*** In ***2 w 0.6*** eV .

2030

The potential energy V between the two atoms (m =~ ***1 .672x*** g) in a hydrogen molecule is given by the empirical expression

V = D{e-za(r--ro) - ***2 e - a (r - r ~)*** **1** .

where **r** is the distance between the atoms.

D = *7* x erg,

a = ***2 x*** 10' cm-'

ro = 8 x lo-' cm.

Estimate the temperatures at which rotation *(TR)*a nd vibration ***(Tv)*** be gin to contribute to the specific heat of hydrogen gas. Give the approximate values of *C,* and ***C,*** (the molar specific heats at constant volume and at constant pressure) for the following temperatures:

Neglect ionization and dissociation.

Solution:

librium distance. From

Ti = ***25*** K, *T2* = ***250*** K, ***T3*** = ***2500*** K, *T4* = 10000 K.

***(UC,* Berkeley)**

The average distance between the two atoms is approximately the equi-

(%) **r=d** = *0* ,

we obtain ***d*** = ro. The frequency of the radial vibration of the two atoms is *r*

where ***p*** = **m** ~ / i**2**s the reduced mass and

so

w = ***J?.***

The characteristic energy of the rotational level is then

= **7 5 K .** **A2 on** = ***kmH*** **ri**

The characteristic energy of vibration is ***kOv*** = ***Aw,*** then

Thus, rotation begins to contribute to the specific heat at *T* = **75** K, and vibration does so at T = **6250** K.

When ***TI*** = **25** K, only the translational motion contributes to C, then

3 5

C v = -2 *R* = **12.5** J/K, **2** *C,* = -*R* = **20.8** J/K

When ***Tz*** = **250** K, only translation and 'rotation contribute to C, then

5 7

2

Cv = *i R* == **20.8** J/K, *C,* = -*R* = **29.1** J/K **.**

When ***T3*** = **2500** K, the result is the same **as** for *T2* = **250** K.

When ***T4*** = 10000 K, vibration also contributes to C, then

C* - −7 *R* 9** = **29.1** J/K, ***C* - −*R = **37.4** J/K **.**

v - 2 p - 2

2051

Derive an expression for the vibrational specific heat of a diatomic gas as a function of temperature. (Let ***hwo/k*** = **0).** For full credit start with an expression for the vibrational partition function, evaluate it, and use the result to calculate Cvib.

Describe the high and low ***T*** limits of Cvib.

(*wi3* CO ***fMitL)***

Solution:

The vibrational energy levels of a diatomic gas are

E" = ***hwo(w* + 1/2)] u = 0,1,2,** ·. . **.**

The partition function is

where z = *Phwo.* The free energy of **1** mole of the gas is

and the internal energy is

The molar specific heat is

C = -dU= R **x 2e x** *x=−−h−w=o − 6' dT* **(e5 - 1)2** *' kT T '*

(a) In the limit of high temperatures, ***T*** >> **0,** or z << 1, we have

C,=R.

(b) In the limit of low temperatures, *T* << *6 ,* **or** *x* >> 1, we have

C, **w** *R(6/T)2***e xp(-B/T) .**

2032

A one-dimensional quantum harmonic oscillator (whose ground state energy is ***hw/2)*** is in thermal equilibrium with **a** heat bath at temperature T.

(a) What is the mean value of the oscillator's energy, *(E),* as a function

(b) What is the value of **AE,** the root-mean-square fluctuation in en-

(c) How do *(E)* and ***AE*** behave in the limits *kT* << hw and *kT* >> hw

of *T?*

ergy about *(E)?*

(MIT)

Solution:

The partition function is

(a) The mean energy is

(E)*= kT2-a* Inz = -*hw* coth (g)

aT **2**

(b) The root-mean-square fluctuation is

(c) When kT << *hw,*

When kT >> *hw,*

(E) → kT, AE → kT .

2033

Consider a system of ***No*** non-interacting quantum mechanical oscillators in equilibrium at temperature T. The energy levels of a single oscillator are

Em = (rn + 1/2)7/V with **rn** = 0, 1 , Z . . . etc.

(7 is a constant, the oscillators and volume *V* are one dimensional.)

(a) Find *U* and *C,* as functions of T.

(b) Sketch U(T) and C,(T).

(c) Determine the equation of state for the system.

(d) What is the fraction of particles in the m-th level?

(SUNY, Bufulo)

Solution:

(a) The partition function is

The internal energy is

a coth -7P *ap* 2v **2v**

U = ***-No*** - In ***z*** =

The specific heat at constant volume is

c, = (g) = ***Nok*** (2 -) a c s c h 2 *(L)*

v2V ***kT 2VkT***

(b) **As** shown in Fig. **2.9.**

Fig. **2.9.**

(c) The equation of state is

p = ***-NPo*** - ***-aav*** 1nz = ***-No'Y***c oth (&) , ***2v2***

where ***p*** is the pressure.

(d) The fraction of particles in the m-th level is

2034

The molecules of a certain gas consist of two different atoms, each with zero nuclear spin, bound together. Measurements of the specific heat of this material, over a wide range of temperatures, give the graph shown below.

(The values marked on the vertical scale correspond to the height of the curve in each of the 'plateau" regions.)

regions: above *T3;* between *T2* and *T3;* between *Ti* and *Tz;* below *Ti,*

(a) Account **for** each of the different results found in the temperature

(b) Given that the first excited state of the rotational spectrum of this molecule is at an energy *kTe* above the ground rotational state, and ***T,*** = 64 K, calculate from basic theory the rotational contribution to the specific heat capacity of this gas at *20K* at *100K,* at *300K.*

(UC, Berkeley)

Solution:

(a) When *T* > *T3,* the translational, rotational and vibrational motions are all excited, and C, = *7k/2.* When *T2* < *T* < *T3,* the vibrational motion is not excited and C, = *5k/2.* When *TI* < *T* < *T2,* only the translational motion contributes to the specific heat and C, = *3k/2.* When *T* < ***TI,*** a phase transition occurs, and the gas phase no longer exists.

(b) When *T* = **20** K, neglect the higher rotational energy levels and consider only the ground state and the 1st excited state. We have

When *T* = 100 K, consider the first two excited states and we have
When *T* = *300* K, all the rotational energy levels are to be considered and
C, = *1.0* **k**

2035

The quantum energy levels of a rigid rotator are

E? = **j(j + l)h2/8w2rna2 ,**

where **j** = **0 , 1 , 2 , . . .** The degeneracy of each level is *gj* = **2 j + 1.**

(a) Find the general expression for the partition function, and show that at high temperatures it can be approximated by an integral.

(b) Evaluate the high-temperature energy and heat capacity.

(c) **Find** the low-temperature approximations to ***z,*** *U* and ***C, .***

(S VNY, BufuIo)

Solution:

(a) The partition function is

00 03

j = O *j = O*

(b) At high temperatures **A,** E (h2/8n2rna2kT)1/2 < 1,

where

Hence

~j = (j + -3 **A,, A E=~** ~ j +-l ~j = **A, .**

(a,) = ***8w2ma2kT/h2*** **.**

The internal energy is

a ***U*** = kT2-lnz = kT *8T*

(c) For low temperatures, we need only take the first two terms of ***z,***

i.e., ***z*** = 1 + ***3e-'lT,*** where 6 = ***h2/4a2ma2k.***

so

2036

The quantum energy levels of a rigid rotator are

e j = j (j+ l)h2/8n2ma2,

where *j = 0,1,2,. . . ,* m and ***a*** are positive constants. The degeneracy of each level is ***gJ*** = ***2 j*** + 1.

(a) Find the general expression for the partition function ***zo.***

(b) Show that at high temperatures it can be approximated by an

(c) Evaluate the high-temperature energy ***U*** and heat capacity *C,,.*

(d) Also, find the low-temperature approximations to ***zo, U*** and *C,.*

integral.

(S ***UN Y, Bufulo)***

Solution:

(a) The partition function is

where,

h2

8a2ma2k ·

6 =

(b) At high temperatures ***BIT << 1*** and exp[-Oj(j + ***1)/T)*** changes slowly as *j* changes, so that we can think of (2 j + 1) exp[-Oj(j + 1)/T] as a continuous function of *j* . Let *x* = *j (j* + l), then *dx* = 2 j + 1, and we can write **zo** as an integral:

(c) At high temperatures, the internal energy is

a

aB

U = --lnzo = *IcT.*

The heat capacity is

C , = k .

(d) At low temperatures, we have *T* << 6, and exp[-6j(j + *1)/T]* is very small. We need only take the first two terms of *zo,* so

2037

The energy levels of a three-dimensional rigid rotor of moment of inertial *I* are given by

EJ,M = h2J(J + 1) / 2 I ,

where *J =* ***0 , 1 , 2 , . .*** . *; M* = - *J* , - *J* + ***1 , . . . ,*** J. Consider a system of ***N*** rotors:

(a) Using Boltzmann statistics, find an expression for the thermody-

(b) Under what conditions can the sum in part (a) be approximated

namical internal energy of the system.

by an integral? In this case calculate the specific heat *C,* of the system.

(*wis* **co** *nsin)*

Solution:

(a) The partition function of the system is

03

z = c (2 J + 1) exp[-h2J(J + 1)/2IkT] **.**

J=O

The internal energy is

d l n z

dT

U = NkT2-

(b) In the limit of high temperatures, kT >> h2/21, and the above sum can be replaced by an integral. Letting 3: = *J (J* + 1), we have

~ = ~ ~ e x h2p { - ~ **2** iI k T) d z = ~ ,

U = N k T .

Thus the molar specific heat is *C,* = NAk = *R.*

2038

Consider a heteronuclear diatomic molecule with moment of inertia *I.* In this problem, only the rotational motion of the molecule should be considered.

(a) Using classical statistical mechanics, calculate the specific heat **C (T)** of this system at temperature T.

(b) In quantum mechanics, this system has energy levels

h2 . .

E . *--3* (3 + 1) **,** j = 0,1,2, **. . . .**

- 21

Each j level is (2j + 1)-fold degenerate. Using quantum statistics, derive expressions for the partition function **z** and the average energy *(E)* of this

system, as a function of temperature. Do not attempt to evaluate these expressions.

(c) By simplifying your expressions in (b), derive an expression for the specific heat *C(T)* that is valid at very low temperatures. In what range of temperatures is your expression valid?
(d) By simplifying your answer to (b), derive a high temperature approximation to the specific heat *C(T).* What is the range of validity of your approximat ion?

(Prince *ton)*

Solution:

(a) For a classical rotator, one has

E = - **1** 1
21

***z* = / *e* - *pEd p a d p , dOd p* = *ꝑ8r21* ,**

a 1 *(E)* = --lnz = **- = *kT.***
ap @

Thus *C(T)* = ***k.***

(b) In quantum statistical mechanics,

@h **h2**

(c) In the limit of low temperatures, **- >> 1,** or -- **>> *kT,*** so only ***21 21***

the first two terms *j* = 0 and *j* = 1 are important. Thus

z = **1** + 3exp (− T) .

3h2 exp (-$)
(E) = **-** ·

I 1+3exp (− T) ·

Hence
2
= 3k
(&)2

[3 + exp (**&)I2**
h2
21

(d) In the limit of high temperatures, ***-ph2* << 1** or kT **>> -,** so the ***21*** sum can be replaced by an integral, that is,
21

z = /0,(2z + **1)** exp ***21***

(E) = - - l n z = k T . *a*
aB

Thus *C(T)* = k.

2039

At the temperature of liquid hydrogen, **20.4K,** one would expect molecular **HZ** to be mostly (nearly 100%) in a rotational state with zero angular momentum. In fact, if **H2** is cooled to this temperature, it is found that more than half is in a rotational state with angular momentum *h.* **A** catalyst must be used at **20.4K** to convert it to a state with zero rotational angular momentum. Explain these facts.

(Columbia)

Solution:

The hydrogen molecule is a system of fermions. According to Pauli's exclusion principle, its ground state electron wave function is symmetric. So if the total nuclear spin *1* is zero, the rotational quantum number of angular momentum must be even and the molecule is called parahydrogen. If the total nuclear quantum spin *I* is one, the rotational quantum number of angular momentum must be odd and it is called orthohydrogen. Since the spin *I* has the 21+ **1** orientation possibilities, the ratio of the number of orthohydrogen molecules to the number of parahydrogen molecules is **3:l** at sufficiently high temperatures. **As** it is difficult to change the total nuclear spin when hydrogen molecules come into collision with one another, the ortho- and parahydrogen behave like two independent components. In other words, the ratio of the number of orthohydrogen molecules to that of parahydrogen molecules is quite independent of temperature. So there are more orthohydrogen molecules than parahydrogen molecules even in the liquid state. **A** catalyst is needed to change this.

2040

A gas of molecular hydrogen H_2, is originally in equilibrium at a temperature of 1,000 K. It is cooled to 20K so quickly that the nuclear spin states of the molecules do not change, although the translational and rotational degrees of freedom do readjust through collisions. What is the approximate internal energy per molecule in terms of temperature units K?

Note that the rotational part of the energy for a diatomic molecule is

A1(1+ **1)** where *1* is the rotational quantum number and A **-** 90K for H_2.

Vibrational motion can be neglected.

(MITI

Solution:

Originally the temperature is high and the para- and orthohydrogen molecules are in equilibrium in a ratio of about **1:3.** When the system is quickly cooled, for a rather long period the nuclear spin states remain the same. The ratio of parahydrogen to orthohydrogen is still **1:3. Now** the para- and orthohydrogen are no longer in equilibrium but, through collisions, each component is in equilibrium by itself. At the low temperature

of 20 K, exp(-PA) **-** exp(-90/20) **<< 1,** ***so*** that each is in its ground state.

Thus $E_{r,p} = 0$, $E_{r,o} = A(1+1)1 = 2A = 180$ K, giving

From equipartition of energy, we have

$$\bar{E}_t = \frac{3}{2}kT = 30 \text{ K} .$$

The average energy of a molecule is

$$\bar{E} = \bar{E}_t + \bar{E}_r = 165 \text{ K} .$$

2041

The graph below shows the equilibrium ratio of the number of orthohydrogen molecules to the number of parahydrogen molecules, as a function of the absolute temperature. The spins of the protons are parallel in orthohydrogen and antiparallel in parahydrogen.

(a) Exhibit a theoretical expression for this ratio as a function of the temperature.

(b) Calculate the value of the ratio for 100 K, corresponding to the

The separation of the protons in the hydrogen

(UC, **Berkeley)**

point *F* on the graph.

molecule is **0.7415k**

Fig. **2.11.**

Solution:

(a) The moment of inertia of the hydrogen molecule is

and its rotational energy level is

with degeneracy **(21 + 1),1 = 0 , 1 , 2 , . . .** .For ortho-H, ***1*** **= 1 , 3 , 5 , . . .** ; for

para-H, **1 = 0 , 2 , 4 , 6 , ...** Thus in hydrogen molecules, the ratio of the number of ortho-H to that of para-H is

where the coefficient **3** results from spin degeneracy and

(b) When ***T*** **= 100** K, A = 0.88, since as ***1*** increases the terms in the summations decrease rapidly, we need consider only the first two terms.

Hence

s e - 2 ~+ ~ ~ - 1 2 ~

1 + 5e-GA

f *= 3* **= 1.52**

2042

In hydrogen gas at low temperatures, the molecules can exist in two states: proton spins parallel (orthohydrogen) or anti-parallel (parahydrogen). The transition betwen these two molecular forms is slow. Experiments performed over a time scale of less than a few hours can be considered as if we are dealing with two separate gases, in proportions given by their statistical distributions at the last temperature at which the gas **was** allowed to come to equilibrium.

(a) Knowing that the separation between protons in a hydrogen molecule is **7 . 4** l~o- ' cm, estimate the energy difference between the ground state and the first excited rotational state of parahydrogen. Use degrees Kelvin as your unit of energy. Call this energy *k60,* so that rrors in (a) do not propagate into the other parts of the question.

(b) Express the energy difference between the ground and first excited rotational states of orthohydrogen, ***kO1,*** in terms of ***k00.*** In an experiment to measure specific heats, the gas is allowed to come to equilibrium at elevated temperature, then cooled quickly to the temperature at which specific heat is measured. What will the constant-volume molar specific heat be at:

(c) temperatures well above **00** and **01**, but not high enough to excite

(d) temperatures much below **00** and **01** [include the leading temperature-dependent term]?

(e) T = ***60/2?***

vibrational levels?

(ZJC, **Berkeley)**

Solution:

The hydrogen nucleus is a fermion. The total wave function including the motion of the nucleus is antisymmetric. The symmetry of the total wave function can be determined from the rotational and spin wave functions.

For orthohydrogen, the spin wave function is symmetric when the nuclei are interchanged. Therefore, its rotational part is antisymmetric, i.e. *1* is odd. Similarly, for parahydrogen, *1* i.e. even. Then we have

, l = l , 3 , 5 ,...

, *1= **0 , 2 , 4 ,** ...*

1(1+ l)h2

l (1 + l)h2

21

21

orthohydrogen: ***El*** =

parahydrogen: ***El*** =

where ***I*** is the moment of inertia of the nucleus about the center of separa208

tion.

m

(a) ***I = ; d 2 ,***

;x *(2* + 1) ***h2*** *h2* - = *3-*

I I '

k6o =

2

6h

md2

then ***k6o*** = - - *7* . *3* x **J ,** *60* = ***530*** **K .**

As the hydrogen gas had reached thermal equilibrium at high temperature before the experiment, the ratio of the number of the para- to that of the orthohydrogen in the experiment is ***1:3,*** which is the ratio of the degrees of freedom **of** the spins.

(c) When *T* >> 60,01, the rotational energy levels are completely excited.

From equipartition of energy, ***E = nkT, or** C,* ***= nk,*** where ***n*** is the total number of the hydrogen molecules. (Note that here we only consider the specific heat associated with rotation.)

(d) When ***T*** << **00,01 ,** there are almost no hydrogen atoms in the highly excited states. Therefore, we consider only the 1st excited state for paraand orthohydrogen. Noting the degeneracy **of** the energy levels, we have

for orthohydrogen

Similarly we have for parahydrogen

2

Cip) ***x n p k .*** *5* ($) ***e-OoIT*** **.**

Note that

***3* 1**

no = zn, np = ***i n ,***

(e) When ***T*** = **00/2,** the partition functions for ortho- and parahydrogen are

where X = ***h2/4.1r2md2kT.*** It does not appear possible to solve these and calculate *C,* accurately, but we can estimate them using the approximate results of (d).

2043

Molecular hydrogen is usually found in two forms, orthohydrogen (“parallel” nuclear spins) and parahydrogen (“anti-parallel” nuclear spins).

(a) After coming to equilibrium at “high” temperatures, what fraction of H_2 gas is parahydrogen (assuming that each variety of hydrogen is mostly in its lowest energy state)?

(b) At low temperatures orthohydrogen converts mostly to parahydrogen. Explain why the energy released by each converting molecule is much

larger than the energy change due to the nuclear spin flip.
(was *co* ns in)

Solution:

(a) For the two kinds of diatomic molecules of identical nuclei, the vibrational motion and the degeneracy of the lowest state of electron are the same for both while their rotational motions are different. The identical nuclei being fermions, antisymmetric nuclear spin states are associated with rotational states of even quantum number 1, and symmetry nuclear spin states are associated with rotational states of odd quantum number ***1*** (the reverse of bosons). Thus

where s is the half-integer spin of a nucleon (for the hydrogen nucleus, s = **1/2), s (2 3 + l)** is the number of antisymmetric spin states and **(s + 1) (2 s + l)**

is the number of symmetric spin states.

where 6 = *h2/87r21k, I* being the rotational moment of inertia. For high temperatures, we have **Zpara** = **Zortilo,** and **npara/nH2 = 1/4.** According to the condition given in the problem (the temperature is not too high), only states ***1*** = 0 and ***1*** = 1 exist. The fraction of parahydrogen is then

(b) When ***T*** << *6,* orthohydrogen changes into parahydrogen. The energy corresponding to the change in nuclear spin direction is the coupling energy of the magnetic dipoles of the nuclei and the electrons ***AEsj*** *N* **lo8** Hz. Since the rotational states are related to the nuclear spin states, the rotational states change too, the corresponding energy change being

w **lol'** Hz ***h2* .**
8r21
AER= -

When orthohydrogen converts to parahydrogen, the total energy change is

AE = ***AER*** + ***A,, w AER.*** Thus the released energy is much greater than ***AEsJ.***

2044

A "14 nucleus has nuclear spin I = 1. Assume that the diatomic molecule **N2** can rotate but does not vibrate at ordinary temperatures and ignore electronic motion. Find the relative abundances of the ortho- and para-molecules in a sample of nitrogen gas. (Ortho = symmetric spin state; Para = antisymmetric spin state). What happens to the relative abundance `as` the temperature **is** lowered towards absolute zero? (Justify your answers!)

(SVNY, Bufialo)

Solution:

The wave function of N2 is symmetric **`as`** "14 is a boson. The spin wave functions of N2 consist of ***`six`*** symmetric and three antisymmetric functions. We know that the rotating wave function is symmetric when the spin wave function is symmetric, and the rotating wavefunction is antisymmetric when the spin wave function is antisymmetric. Hence, the partition function of ortho-N2 is

and *I* is the rotational moment of inertia of N2. Similarly, A2 where *B,* = -
2kT'

Zpara = 3(21+ **l)e-or'(i+l)/T .**
I **= 1,3,5.. . .**

As *B,/T* << 1 at ordinary temperatures, the sums can be replaced by integrals:
3T
e-erx/Tdx = -
20,

Therefore , the relative abundance is given by
At equilibrium, **portho = pparat**,h e above ratio is **2.**

B,/T ***B*** l,exp[-B,l(I + **1)/T] <<** 1. Hence
When the temperature is lowered towards the absolute zero, we have
The relative abundance is

Northo = (:) exp(2Br/T)
Npara

When *T* --+ 0, the relative abundance -+ *oo.* All the para-molecules become ortho-molecules.

2045

(a) Write down a simple expression for the internal part of the partition function for a single isolated hydrogen atom in very weak contact with a reservoir at temperature *T.* Does your expression diverge for T = 0, for T # O?
(b) Does all or part of this divergence arise from your choice of the zero of energy?
(c) Show explicitly any effects of this divergence on calculations of the
(d) Is the divergence affected if the single atom is assumed to be confined to a box of finite volume ***L3*** in order to do a quantum calculation of the full partition function? Explain your answer.
(UC, ***Berkeley)***
average thermal energy ***U.***
Solution:

degeneracy ***2n2,*** w here n = ***1,2,3,.. . .*** Therefore
(a) The internal energy levels of hydrogen are given by ***-Eo/n2*** with
oo

Z = *C* ***2n2*** exp
n= 1

When ***T*** = 0, the expression has no meaning; when T # 0, it diverges.
(b) The divergence has nothing to do with the choice of the zero of energy. If we had chosen
then
which would still diverge.

(c) When ***T*** # 0,

n= 1

That is to say, because of thermal excitation (no matter how low the temperature is, provided ***T*** # 0), the electrons cannot be bounded by the nuclei.
(d) The divergence has its origin in the large degeneracy of hydrogen's highly excited states. If we confine the hydrogen molecule in a box of volume ***L3,*** these highly excited states no longer exist and there will be no divergence.

2046

The average kinetic energy of the hydrogen atoms in a certain stellar
(a) What is the temperature of the atmosphere in Kelvins?
(b) What is the ratio of the number of atoms in the second excited
(c) Discuss qualitatively the number of ionized atoms. Is it likely to
atmosphere (assumed to be in thermal equilibrium) is 1.0 eV.
state (n = 3) to the number in the ground state?

be much greater than or much less than the number in n = 3? Why?

Solution:

(**wisco** *nsin)*

(a) The temperature of the stellar atmosphere is

T = -zE= 2 x 1.6 x 10-19 = 7.7 x lo3 K . 3k 3 x 1.38 x

(b) The energy levels for hydrogen atom are

En=(-.;;1.3-).6 e v .

Using the Boltzmann distribution, we get

Inserting ***El*** = **-13.6** eV, *E3* = **(-13.6/9)** eV, and ***kT*** = **(2/3)** eV into the above, we have *N3/N1 M* **1.33** x

(c) The number of ionized atoms is the difference between the total number of atoms and the total number of atoms in bound states, i.e., the number of atoms in the level n = *00.* Obviously, it is much smaller than the number in n = **3.** Thus **-*Nion*** = exp ($) *M* 0.1, i.e., ***Nion*** is about one-tenth of *N3.*

N3

2047

A monatomic gas consists of atoms with two internal energy levels: a ground state of degeneracy ***g1*** and a low-lying excited state of degeneracy ***92*** at an energy ***E*** above the ground state. Find the specific heat of this gas.

(CUSPEA)

Solution:

According to the Boltzmann distribution, the average energy of the atoms is

where *Eo* is the dissociation energy of the ground state (we choose the ground state as the zero point of energy). Thus

2048

Consider a system which has two orbital (single particle) states both of the same energy. When both orbitals are unoccupied, the energy of the system is zero; when one orbital or the other is occupied by one particle, the

energy is ***E.*** We suppose that the energy of the system is much higher, say infinitely high, when both orbitals are occupied. Show that the ensemble average number of particles in the level is

(UC, Berkeley)

The probability that a microscopic state is occupied is proportional to

Solution:

its Gibbs factor exp[(p - &) TI. We thus have

2049

(a) State the Maxwell-Boltzmann energy distribution law.

(b) Assume the earth's atmosphere is pure nitrogen in thermodynamic equilibrium at a temperature of 300 K. Calculate the height above sea-level **at** which the density of the atmosphere is one half its sea-level value.

Solution:

(a) The Maxwell-Boltzmann energy distribution law: For a system of gas in equilibrium, the number of particles whose coordinates are between r and r + dr and whose velocities are between v and v + dv is

Define

terms. Discuss briefly an application where the law fails.

(**wisco nsin)**

dN = *no (L3/2)* e-'l kTdvdr , ***27rkT***

where *no* denotes the number of particles in a unit volume for which the potential energy **cp** is zero, *E* = ~*k* + *E*~ is the total energy, dv = du,duydu,, dr = dxdydz.

It is valid for localized

systems, classical systems and non-degenerate quantum systems. It does not hold for degenerate non-localized quantum systems, e.g., a system of electrons of spin *1 / 2* at a low temperature and of high density.

The MB distribution is a very general law.

(b) We choose the z-axis perpendicular to the sea level and *z* = 0 at the sea level. According to the MB distribution law, the number of molecules

in volume element ***dxdydz*** at height *z* is ***dN' = noe-mg"/kTdzdydz.*** Then the number of molecules per unit volume at height *z* is

Thus

kT ***no*** RT ***no***

n *Pg.* **n**

z = -1n- = ---In-.

The molecular weight of the nitrogen gas is *1.1* = 28g/mol. With g = 9.8m/s2, R = 8.31J/K.mole, T = 300 K, we find *z* = 6297 m for ***no/n* = 2.**

That is, the density of the atmosphere at the height 6297m is one-half the sea level value.

2050

A circular cylinder of height L, cross-sectional area ***A,*** is filled with a gas of classical point particles whose mutual interactions can be ignored. The particles, all of mass **rn,** are acted on by gravity (let g denote the gravitational acceleration, assumed constant). The system is maintained in thermal equilibrium at temperature T. Let **c,** be the constant volume specific heat (per particle). Compute **c,** as a function of T, the other parameters given, and universal parameters. Also, note especially the result for the limiting cases, T -+ 0, T -+ *oo*.

(***C USPEA)***

Solution:

of the molecules is

Let *z* denote the height of a molecule of the gas. The average energy

e = 1.5 kT + mgZ **,**

where **Z** is the average height. According to the Boltzmann distribution, the probability density that the molecule is at height *z* is p(z) ***cx*** exp(-rngz/kT). Hence

and

5 mgL

e = -kT *- emgLlkT* - 1 ' 2

ae 5 k(rngL)2 emgLlkT

aT 2 (kT)2 (emgLlkT - 1)2

c" = - = - ***k*** -

5 Tk, for *T* + *O* ,

2k, for *T* + 03 .

-yL EII *----

Fig. 2.12

2051

Ideal monatomic gas is enclosed in cylinder of radius a and length *L*. The cylinder rotates with angular velocity *w* about its symmetry axis and the ideal gas is in equilibrium at temperature ***T*** in the coordinate system rotating with the cylinder. Assume that the gas atoms have mass rn, have no internal degrees of freedom, and obey classical statistics.

(a) What is the Hamiltonian in the rotating coordinates system?

(b) What is the partition function for the system?

(c) What is the average particle number density as a function of **r?**

(MIT)

Solution:

(a) The Hamiltonian for a single atom is

h ' = - +*PI*+*2* d - -mw1r *2 2* ,

2m 2

L

2 *0,* r I a , (z (< - ,

m, otherwise.

4 (W , Z) =

The Hamiltonian for the system is

(b) The partition function is

(c) The average particle number density is

AN/AV = *N* *1* **d3p'** exp[-P(pf2/2m **+ 4** - mw2r2/2)]/z

2052

Find the particle density as a function of radial position for **a** gas of *N* molecules, each of mass *M ,* contained in a centrifuge of radius *R* and length *L* rotating with angular velocity *w* about its axis. Neglect the effect of gravity and assume that the centrifuge has been rotating long enough for the gas particles to reach equilibrium.

(Chicago)

Fig. 2.13.

Solution:

r. But in the rotational system S‘, the energy of a particle is

In the rest system S, the energy *E* is independent of the radial distance

1 1

2 2

E(r) = - *I W* ~ = *-Mr2w2*

The effect of rotation is the same as that of an additional external field acting on the system of

1

2

U(r J)= - - ~ *r* ~ *w* ’.

Using the Boltzmann distribution we get the particle number density

n(r) = Aexp (−g) = Aexp (Mw2r 2 r)

where the normalization factor A can be determined by *Jn(rJ)dV* = ***N,***
Thus we have
Mw2r2
NMw2 (kT) *n (r) = 2.lrkTL*

2053

Suppose that a quantity of neutral hydrogen gas is heated to a temperature *T. T* is sufficiently high that the hydrogen is completely ionized, but low enough that *kT/m,c2* << 1 *(me* is the mass of the electron). In this gas, there will be a small density of positrons due to processes such as e-+ e- +-+ e-+e-+ e-+e+ or e-+ p +-+ e-+ p + e-+ e+ in which electron-positron pairs are created and destroyed.

For this problem, you need not understand these reactions in detail. Just assume that they are reactions that change the number of electrons and positrons, but in such a way that charge is always conserved.

Suppose that the number density of protons is 101'/cm3. Find the chemical potentials for the electrons and positrons. Find the temperature at which the positron density is l/cm3. Find the temperature at which it is 101°/cm3.

(Prince ***ton)***

Solution:

For kT/m,c2 << 1, nuclear reactions may be neglected. From charge conservation, we have **n- = np + n+**, where **n-, n+** are the number densities of electrons and positrons respectively. For a non-relativistic nondegenerate case, we have

n- = **2** (2 Tm***h2***,k T) **3/2** exp(p-;Tm'c2) **,**

where ***p-*** and ***p+*** are the chemical potentials of electrons and positrons respectively. From the chemical equilibrium condition, we obtain ***p-*** **=** ***-p+*** = ***p.*** Hence

n+/n- = exp(-2p/kT) **.**

For n+ = l/cm3, n- **fic** np = lo1' /cm3, we have exp(p/kT) = lo5 or p/kT ***M*** 11.5. Substituting these results into the expression of n-, we have

T ***M*** 1 . 2 ~ 1 K0 ,~ ***s op w*** 1.6XlO-'erg. For n = 101'/cm3, exp(p/kT) = ***a,*** ***p/kT*** NN 0.4. Substituting these results into the expression of n+, we get T ***w*** 1.5 x lo8 K, ***p M*** 8.4 x lo-' erg.

2054

Consider a rigid lattice of distinguishable spin 1/2 atoms in a magnetic field. The spins have two states, with energies *-poH* and *+poH* for spins up (1) and down (l),re spectively, relative to **H.** The system is at temperature T.

(a) Determine the canonical partition function ***z*** for this system.

(b) Determine the total magnetic moment ***M = po(N+ - N -)*** of the

(c) Determine the entropy **of** the system.

system.

(wis co *nsin)*

Solution:

(a) The partition function is

z = exp(x) + exp(-x) ,

where x = ***pgH/kT.***

(b) The total magnetic moment is

a

aH

M = ***po(N****+ -* ***N-)*** = NkT- Inz

= ***Npo*** tanh(x) .

(c) The entropy of the system is

S = Nk(ln ***z*** - *pa* In *./a/?)*

= Nk(ln **2** + In(cosh z)) - z tanh(z) .

2055

A paramagnetic system consists of ***N*** magnetic dipoles. Each dipole carries a magnetic moment ***p*** which can be treated classically. If the system at a finite temperature T is in a uniform magnetic field *H,* find

(a) the induced magnetization in the system, and

(b) the heat capacity at constant *H.*

(UC, Berkeley)

Solution:

(a) The mean magnetic moment for a dipole is

Jpcos6exp(xcos6)dfl S exp (x cos 6) *dn*

***p*.:S** cos 6 exp(z cos 6) sin 6d6 **S:** exp (z cos **0)** sin 6d6

(') =

--

= p c[o t h ~ I : - - ,

where x = pH/kT. Then the induced magnetization in the system is

(M) = N (p) = Np

a(u) - *-hT-* - Nk(1 - z2csch2z2) .

aT (b) c = - - dT

2056

Consider a gas of spin **1/2** atoms with density **n** atoms per unit volume. Each atom has intrinsic magnetic moment ***p*** and the interaction between atoms is negligible.

Assume that the system obeys classical statistics.

(a) What is the probability of finding an atom with ***p*** parallel to the applied magnetic field **H** at absolute temperature *T?* With ***p*** anti-parallel to **H?**

(b) Find the mean magnetization of the gas in both the high and low

(c) Determine the magnetic susceptibility *X* in terms of ***p*.**

temperature limits?

(SUNY, ***Bufulo)***

Solution:

(a) The interaction energy between an atom and the external magnetic field is ***E*** = ***-p.*** **H.** By classical Boltzmann distribution, the number of atoms per unit volume in the solid angle element dfl in the direction **(0, p),** is

gexp(-PE)dfl= gexp(pHcosO/kT)dfl **,**

where **0** is the angle between ***p*** and **H** and g is the normalization factor given by

i.e.,

2?rg **ln** e-@'sin *6dO* = n **,**

nCLH

P H

9 =

47rkT sinh **- *kT***

Hence the probability density for the magnetic moment of an atom to be parallel to **H** is

and that for the magnetic moment to be antiparallel to **H** is

(b) The average magnetization of the gas at temperature T is

At high temperatures, *-P H* << 1. Let *-PH* = *x,* and expand ***kT kT***

x x

s o x ***w*** *-**w**H.**2***

3kT

At low temperatures, *x* >> 1, then

1

coth ***x*** - - ***w*** 1

x

and *a* ***w*** **np.**

(c) The magnetic susceptibility of the system is

-

np2/3kT, at high temperature

at low temperature **.**

There is spontaneous magnetization in the limit of low temperatures.

2057

A material consists ***of n*** independent particles and is in a weak external magnetic field *H.* Each particle can have a magnetic moment ***rnp*** along the magnetic field, where **rn** = *J, J* - 1, . . . , *-J* + 1, *- J, J* being an integer, and ***p*** is a constant. The system is at temperature T.

(a) Find the partition function for this system.

(b) Calculate the average magnetization, *a,* of the material.

(c) For large values of T find an asymptotic expression for ***M.***

(MITI

Solution:

(a) The partition function is

J

= ***empHIkT*** = sinh

m=- ***J***

(b) The average magnetization is

-M = - (g) T = N k T (& l n i)

T

= *2* [(2J + **1)** coth (2.7 + 1)- - coth

2 [2kT 2kT

(c) When kT >> *p H*, using

c o t h x a*2*? (l + %) , for x < 1

we get

M **w** -1*N J (J* + 1)-**P 2** *H*

-

3 kT

2058

Two dipoles, with dipole moments MI and M2, are held apart at a separation *R,* only the orientations of the moments being free. They are in thermal equilibrium with the environment at temperature T. Compute the mean force **F** between the dipoles for the high temperature limit __ kT ***R3*** **1.** The system is to be treated classically.

Remark: The potential energy between two dipoles is:

MlM2 <<

(3(M1 .R)(M2 **.R)** - (MI .M2)R2)

4 = ***R5***

(Princeton)

Solution:

Taking the z-axis along the line connecting'M1 and M2, we hatre

4=- Ml ***M2*** [2 cos 81 cos **e2** - sin **81** sin 82 cos(pl - **p2)].**

R3

The classical partition function is

(2 cos 61 cos *82* - sin 81 sin *62* cos(pl - **p2))]***d n l d Q 2* **.**

As X = *pMlM2/R3* **<< 1,** expanding the integsand with respect to **A,** retaining only the first non-zero terms, and noting that the integral of a linear term of cos6 is zero, we have

1 **A2**

z = [1 + ~ (cos**2** O1 c os ***e2*** - sin 61 sin ***O2*** cos(pl - **p2))2**d nldn2

= 1 6 2 + **-**3**A**2**2**r 2 + **-**47P = **-4(a**327 + 8X *2*) **,** 9 9 9

1 *aZ* 16X .-*M iM 2* **u = =**

z a p 37+8X2 *R3*

2059

The molecule **of** a perfect gas consists of two atoms, of mass `rn,` rigidly separated by a distance *d.* The atoms of each molecule carry charges *q* and -*q* respectively, and the gas is placed in an electric field ***E.*** Find the mean polarization, and the specific heat per molecule, if quantum effects can be neglected.

State the condition for this last assumption to be true.

(UC, Berkeley)

Solution:

field is **0.** The energy of a dipole in the field is

Assume that the angle between a molecular dipole and the external

Then

The condition for classical approximation to be valid is that the quantizah' tion **of** the rotational energy can be neglected, that is, ***kT*** >> -

md2.

2060

The response of polar substances **(e.g.,** HC1, H20, etc) **to** applied electric fields can be described in terms **of** a classical model which attributes to each molecule a permanent electric dipole moment of magnitude **p.**

(a) Write down a general expression **for** the average macroscopic polarization *jj* (dipole moment per unit volume) **for** a dilute system of n molecules per unit volume at temperature T in a uniform electric field *E.*

(b) Calculate explicitly an approximate result for the average macroscopic polarization *jj* at high temperatures ***(KT > pE).***

(MITI

Solution:

(a) The energy of a dipole in electric field is

~ , = - p . E = - p E c o s B ,

The partition function is then

The polarization is

PE 1 1

(b) Under the condition -z = **-** << 1, coth *2* ***w*** --z **+ -,** and we have

kT 3 x

ji w np2E/3kT **.**

2061

The entropy of an ideal paramagnet in a magnetic field is given approximately

by *s=so-cu2,*

where *U* is the energy of the spin system and C is a constant with fixed mechanical parameters of the system.

(a) Using the fundamental definition of the temperature, determine

(b) Sketch a graph of *U* versus T for all values of T (-m < T < m).

(c) Briefly tell what physical sense you can make of the negative temthe energy *U* of the spin system as a function of T.

perature part of your result.

Solution:

(wis ***co*** *nsin)*

(a) From the definition of temperature,

1

we have *U* = --

2CT‘

(b) We assume *C* > 0. The change of *U* with T is shown in the Fig. **2.14.**

Fig. **2.14.**

(c) Under normal conditions, the number of particles in higher energy states is smaller than that in lower energy states. The physical significance of a negative temperature is that under such condition the number of particles in an excited state is greater than that in the ground state. That is, there are more particles with magnetic moments anti-parallel to the magnetic field than those with magnetic moments parallel to the magnetic field.

2062

Consider a system of ***N*** non-interacting particles ***(N*** >> 1) in which the energy of each particle can assume two and only two distinct values, 0 and *E (E* > 0). Denote by no and nl the occupation numbers of the energy levels 0 and *E,* respectively. The fixed total energy’ **of** the system is *U.*

(a) Find the entropy of the system.

(b) Find the temperature **as** a function **of *U*.** For what range of values

(c) In which direction does heat flow when a system of negative temperature is brought into thermal contact with a system of positive temperature? Why?

(Princeton)

Solution:

of *no* is ***T*** < O?

(a) The number of states is

N!

Hence S = k l n n = klnno!

nl!

(b) nl/no = exp(-E/kT), where we have assumed the energy levels to be nondegenerate. Thus

When no < N/2, we get T < 0.

(c) Heat will flow from a negative temperature system to a positive temperature system. This is because the negative temperature system has higher energy on account of population inversion, i.e., it has more particles in higher energy states than in lower energy states.

3. BOSE-EINSTEIN AND FERMI-DIRAC STATISTICS

(2063–2 115)

2063

A system of *N* identical spinless bosons of mass **rn** is in **a** box of volume *V* = ***L3*** at temperature T > 0.

(a) Write a general expression for the number of particles, n(E), having an energy between s and E + *ds* in terms of their mass, the energy, the temperature, the chemical potential, the volume, and any other relevant quantities.

(b) Show that in the limit that the average distance, *d,* between the particles is very large compared to their de Broglie wavelength (i.e., d >> **A)** the distribution becomes equal to that calculated using the classical (Boltzmann) distribution function.

(c) Calculate the 1st order difference in average energy between a system of N non-identical spinless particles and a system of *N* identical spinless bosons when d >> **A.** For both systems the cubical box has volume ***V*** = *L3* and the particles have mass ***rn.***

*(UC, **Berkeley)***

Solution:

(a) The number of particles is

(b) In the approximation of a dilute gas, we have exp(-p/kT) >> 1, and the Bose-Einstein distribution becomes the Boltzmann distribution. We will prove as follows that this limiting condition is just d >> A.

Since

we have

where X = *h / d m*is the de Broglie wavelength of the particle's thermal motion, and ***d*** = *m***.**

Thus the approximation exp(-p/kT) >> 1 is equivalent to ***d*** >> A.

(c) In the 1st order approximation

the average energy is

2064

Consider a quantum-mechanical gas of non-interacting spin *zero* bosons, each of mass ***m*** which are free to move within volume *V*.

(a) Find the energy and heat capacity in the very low temperature region. Discuss why it is appropriate at low temperatures to put the chemical potential equal to zero.

Prove that the energy is proportional to ***T4.***

Note: Put all integrals in dimensionless form, but do not evaluate.

Solution:

(b) Show how the calculation is modified for a photon (mass = 0) gas.

(UC, Berkeley)

(a) The Bose distribution

requires that ***p*** *5* 0. Generally

When T decreases, the chemical potential ***p*** increases until ***p*** = 0, for which Bose condensation occurs when the temperature continues to decrease with ***p*** = 0. Therefore, in the limit of very low temperatures, the Bose system can be regarded as having ***p*** = 0. The number of particles at the noncondensed state is not conserved. The energy density ***u*** and specific heat ***c*** are thus obtained as follows:

(b) For a photon gas, we have ***p*** = 0 at any temperature and ***E*** = ***hw.***

w2 dw

The density of states is - and the energy density is

lr2c3 '

u=-J* 1 *hw3 d W = L (T)) ' l ,* *o 3* *-x.3 d x

T2c3 ehw/kT - 1 ***A2C3 ex*** - 1

2065

A gas of ***N*** spinless Bose particles of mass m is enclosed in a volume *V* 'at a temperature *T*.

(a) Find an expression for the density of single-particle states ***D (&)*** as a function of the single-particle energy ***E.*** Sketch the result.

(b) Write down an expression for the mean occupation number of a single particle state, E ***,*** as a function of ***E,T,*** and the chemical potential *p (T)* . Draw this function on your sketch in part (a) for a moderately high temperature] that is, a temperature above the Bose-Einstein transition. Indicate the place on the &-axis where ***E*** = *1.1*.

(c) Write down an integral expression which implicitly determines *p (T)* . Referring to your sketch in (a), determine in which direction *p (T)* moves as *T* is lowered.

(d) Find an expression for the Bose-Einstein transition temperature, *T,,* below which one must have a macroscopic occupation of some singleparticle states. Leave your answer in terms of a dimensionless integral.

(e) What is *p (T)* for *T* < *T,?*

Describe E(E, ***7 ')*** for *T* < *Tc?*

(f) Find an exact expression for the total energy, U(TIV) of the gas for *T* < *Tc.* Leave your answer in terms of a dimensionless integral.

(MITI

Solution:

(a) From *e* = **p2/2rn** and

47rV

D(&)d&= -p*h23*d p

we find

27rv

h3 D (&) = **-(2rn)3/2E1/2 .**

The result is shown in Fig. *2.15*

(c) With *P2* E = - we have *N*= -

2m

or

dx

ex-%, - 1 '

2T

h3

N/V= - (2mkT)3/2

where *xcl.* = *p/kT 5* 0. **As** *N/V* remains unchanged when *T* decreases, *p (T)* increases and approaches zero.

(d) Let *n* be the number density and *T,* the critical temperature. Note that at temperature *T,* the chemical potential *p* is near to zero and the particle number of the ground state is still near to zero, so that we have

= -2(T2 mkT,)3/2

h3

where the integral

= *1 . 3 0 6 6 .*

Hence

T - -

(e) For bosons, *p* < 0. When *T 5 T,, p w* 0 and we have

n,>o = exp(iEji;) - 1 '

and

(f) When T < T,, we have

2aV *o3 x3f2dx*

e 2 - 1

U = F(2m)3/2(k~)5/2 1 -

312

= 0.770NkT **(6)** .

2066

(a) In quantum statistical mechanics, define the one-particle density

(b) For a system of *N* identical free bosons, let

matrix in the r-representation where r is the position of the particle.

where (Nk) is the thermal averaged number of particles in the momentum state **k .** Discuss the limiting behavior of **pl(r)** as **r** -+ *00,* when the temperature T passes from T > Tc to T < *T, ,* where T, is the Bose-Einstein condensation temperature. In the case lim *p1* **(r)** approaches zero, can you describe how it approaches zero **as** *r* becomes larger and larger?

Solution:

(a) The one-particle Hamiltonian is *H* = p2/2m, and the energy eigenstates are *IE).* The density matrix in the energy representation is then *p(E)* = exp(-E/koT), which can be transformed to the coordinate representation

(rlplr') = *C* *(rIE)(Ele-HIksTI~)(E'lr')*

r+m

(SVNY, Bufldo)

E,E'

= *C* (PE(r)e-E'kflT6EE!pfE, **(r)**
E,E'

= *C* p E **(r)e-ElkBTpfE(rP. ')**
E

where kg is Boltzmann's constant. The stationary one-particle wavefunction is

where E = A2k2/2m. Thus we obtain

,**a k. (r- r') -** hak'/8rr'mk~ T
k

p* = *0 when the temperature T passes from T > T, to T < T,, hence

When r -+ *oo,* we have approximately

mkgT, 1
27rA2 r

***w* _____-.**

2067

Consider a gas of non-interacting, non-relativistic, identical bosons. Explain whether and why the Bose-Einstein condensation effect that applies to a three-dimensional gas applies also to a two-dimensional gas and to a one-dimensional gas.

(Princeton)

Solution:

Briefly speaking, the Bose-Einstein condensation occurs when ***p*** = 0.

For a two-dimensional gas, we have

If ***p* = *0,*** the above expression diverges. Hence ***p* #** 0 and Bose-Einstein condensation does not occur.

For a one-dimensional gas, we have

If ***p*** = 0, the integral diverges. Again, Bose-Einstein condensation does not occur.

2068

Consider a photon gas enclosed in a volume *V* and in equilibrium at temperature T. The photon is a massless particle, so that ***E* = *pc.***

(a) What is the chemical potential of the gas? Explain.

(b) Determine how the number of photons in the volume depends upon the temperature.

(c) One may write the energy density in the form

Determine the form of *p(w),* the spectral density of the energy.

(d) What is the temperature dependence of the energy ***E?***

(UC, Berkeley)

Solution :

(a) The chemical potential of the photon gas is zero. Since the number of photons is not conserved at a given temperature and volume, the average photon number is determined by the expression (*$)T,v = 0,* then

(b) The density of states is *87rVp2dp/h3,* or *Vw2dw/7r2c3.* Then the number of photons is

Hence

and ***E*** *o:* ***T4***

2069

(a) Show that for a photon gas **p** = *U/3V.*

(b) Using thermodynamic arguments (First and Second Laws), and the above relationship between pressure and energy density, obtain the dependence of the energy density on the temperature in a photon gas.

(UC, Berkeley)

Solution:

(a) The density of states is

D(&)da = a!VE2ds **,**

where *a!* is a constant.

With

In E = - *1* *D (E)*ln (1- *e-BC)de* **,**

we have

U

3v

d E = - .

(b) For thermal radiation, we have

U(T,V) = u(T)V **.**

Using the following formula of thermodynamics

T du u

3dT **3**

we get *u* = -- - **-,** i.e. *u* = *7T4,* where *7* is a constant.

2070

Consider a cubical box of side *L* with no matter in its interior. The walls are fixed at absolute temperature *T ,* and they are in thermal equilibrium with the electromagnetic radiation field in the interior.

(a) Find the mean electromagnetic energy per unit volume in the frequency range from *w* to *w* + *dw* as a function of *w* and T. (If you wish to start with a known distribution function - e.g., Maxwell-Boltzmann, Planck, etc. - you need not derive that function.)

(b) Find the temperature dependence of the total electromagnetic energy per unit volume. (Hint: you do not have to actually carry out the integration of the result of part (a) to answer this question.)

(SVNY, Buflulo)

Solution:

p + *dp* is given by

(a) The mean electromagnetic energy in the momentum interval ***p*** -+

V 4 ~ p ' d p h w dE, = *2 . -, (2Th)3 e h w / 2 n k T* - 1 '

where the factor *2* corresponds to the two polarizations of electromagnetic waves and *V* = ***L3.***

Making use of *p* = *hw/c,* we obtain the mean electromagnetic energy

in the frequency interval *w -+ w* + *dw:*

Vh w3dw

dEw = ***z e h w / 2 n k T*** - 1 *

The corresponding energy density is

(b) The total electromagnetic energy per unit volume is

(kT)4 *oo oo z 3 d z* ***u*** = *l* *d u w = - /~ ' (h c) ~* - **e5. - 1**

Thus ***u*** *o(* **T4 .**

2071

A historic failure of classical physics is its description of the electromagnetic radiation from a black body. Consider a simple model for an ideal black body consisting of a cubic cavity of side L with a small hole in one side.

(a) Assuming the classical equipartition of energy, derive an expression for the average energy per unit volume and unit frequency range (Rayleigh-Jeans' Law). In what way does this result deviate from actual observation?

Fig. **2.16.**

(b) Repeat the calculation, now using quantum ideas, to obtain an expression that properly accounts for the observed spectral distribution (Planck's Law).

(c) Find the temperature dependence of the total power emitted from

(CUSPEA)

Solution:

(a) For a set of three positive integers *(nl,nz,ns),* the electromagnetic field at thermal equilibrium in the cavity has two modes of oscillation with the frequency *u(n1, n 2 , n 3)* = **- (n: + *nz* + ni)1/2.** Therefore, the number of modes within the frequency interval ***Au*** is

the hole.

C

2L

Equipartition of energy then gives an energy density

47r

1 dE **1 *8***

kT. -u'Au.

u, = -- -- - . ***Au L3*** *du* ***L3***

= ***87ru2kT/c3*** **.**

When ***u*** is very large, this expression does not agree with experimental observations since it implies **u,** *o< **u2.***

(b) For oscillations of freqeuncy ***u,*** the average energy is

Ln=

O

which is to replace the classical quantity ***kT*** to give

(c) The energy radiated from the hole per unit time is

00

ucc $\int$ *u,dvoc T 4 .*

2072

Electromagnetic radiation following the Planck distribution fills a cavity of volume *V* . Initially *w;* is the frequency of the maximum of the curve of *u;(w),* the energy density per unit angular frequency versus *w.* If the volume is expanded quasistatically to *2V,* what is the find peak frequency *wf* of the *uf (w)* distribution curve? The expansion is adiabatic.

(UC, **Berkeley)**

Solution:

As the Planck distribution is given by l/[exp(hw/kT) - 11 and the density of states of a photon gas is

D(w)dw = uw2dw (u = const) **,**

the angular frequency *w* which makes *U(W)* extremum is *w = 7T,* where **7** is a constant. On the other hand, from *dU = TdS - pdV* and ***U*** *= 3pV,* we obtain *V4p3* = const when *dS* = 0. Since *p o: T4,* we have

VT3 = const.,

2073

A He-Ne laser generates a quasi-monochromatic beam at *632863.* The beam has an output power of Imw
radians, and a spectral linewidth of 0.Ol.h. If a black body with an area of 1 cm2 were used to generate such **a** beam after proper filtering, what should its temperature **be** approximately?

(UC, **Berkeley)**

watts), a divergence angle of

Solution:

of photons in the interval *dadn:*
Considering black body radiation in a cavity we get the number density
The number of photons in the laser beam flowing through an area **A** per unit time is *dn' = cAdn,* and the output power is *W = Edn'.*
Introducing *E* = *hc/X* and *dn* = *n(dO)2* into the expression, we obtain
where
Therefore
2 *n A hc2 dX (do)*
A5

W, =

T = -hc- . **1**

Xk l n ($ + l)

Using the known quantities, we get

WO = 3.60 x lo-' W , *T = 6* x lo9 K .

2074

(a) Show that the number of photons in equilibrium at temperature *T* in **a** cavity of volume *V* is ***N*** = *V (k T / f t* ~tim*)* ~es a numerical constant.
(b) Use this result to obtain a qualitative expression for the heat ca-

(UC, Berkeley)

pacity of a photon gas at constant volume.

Solution:

(d) The density of states of the photon gas is given by

Thus
where
(b) The energy density is
therefore C, *rn T3.*

2075

As you know, the universe is pervaded by **3K** black body radiation. In a simple view, this radiation arose from the adiabatic expansion of a much hotter photon cloud which was produced during the big bang.
(a) Why is the recent expansion adiabatic rather than, for example,
(b) If in the next **lo1'** years the volume of the universe increases by a factor of two, what then will be the temperature of the black body radiation? (Show your work.)
(c) Write down an integral which determines how much energy per cubic meter is contained in this cloud of radiation. Estimate the result within an order of magnitude in joules per (meter)3.

(Chicago)

Soh t **ion** :

(a) The photon cloud is an isolated system, so its expansion is adiabatic.
is0 t hermal?
(b) Th energy density of black body radiation is ***u*** = *aT4, so* that the

total energy *E* ₒ₍ *VT4.* From t#he formula *TdS* = *dE* + *pdV,* we have

T (g) "₌(*d*E*E*) ~

o cVT3·

Hence *S* = *VT3.* const.

For a reversible adiabatic expansion, the entropy *S* remains unchanged. Thus when *V* doubles *T* will decrease by a factor ***(2)-'13.*** So after another **lo1'** years, the temperature of black body radiation will become

T = **3K/2'I3.**

(c) The black body radiation obeys the Bose-Einstein Statistics:

where the factor **2** is the number of polarizations per state. Hence

2076

Our universe is filled with black body radiation (photons) at a temperature *T* = **3** K. This is thought to be a relic, of early developments following the 'big bang".

(a) Express the photon number density n analytically in terms of *T* and universal constants. Your answer should explicitly show the dependence on *T* and on the universal constants. However, a certain numerical cofactor may be left in the form of a dimensionless integral which need not be evaluated at this stage.

(b) Now estimate the integral roughly, use your knowledge of the universal constants, and determine n roughly, to within about two orders of magnitude, for *T* = **3** K.

(C USPEA)

Solution:

(a) The Bose distribution is given by

n(k) = 1/bP(P&(k)) - 11

The total number of photons is then

where *E(k)* = *hkc* for photons and *p* = **&.** The factor **2** is due to the two directions of polarization. Thus

3

where

(b) When T = **3** K, n ***M*** 1000/cm3.

2077

We are surrounded by black body photon radiation at **3K.** Consider the question of whether a similar bath of thermal neutrinos might exist.

(a) What kinds of laboratory experiments put the best limits on how

(b) The photon gas makes up lowGof the energy density needed to close the universe. Assuming the universe is no more than just closed, what order of magnitude limit does this consideration place on the neutrino's temperature?

hot a neutrino gas might be? How good are these limits?

(c) **In a** standard big-bang picture, what do you expect the neutrino temperature to be (roughly)?

(Princeton)

Solution:

(a) These are experiments to study the neutral weak current reaction between neutrinos and electrons, ***vp*** + ***e-*** -+ ***vp*** + ***e -,*** using neutrinos created by accelerator at CERN. No such reactions were detected above the background and the confidence limit of measurements was

90%. This gives an upper limit to the weak interaction cross section of *o* < **2.6** *x 10-42E,* cm2/electron. With *E,* **-** *kT* we obtain *T* < *10'* K.

(b) The energy density of the neutrino gas is ***p, M*** *aT:,* and that of the photon gas is ***p.,*** = *aT4.* As ***p,*** *5 1O-'p,* we have *T, 5 T/101.5.* For *T N* 3 K, we get *T, 5 0.1* K.

(c) At the early age of the universe (when ***kTkrn,c2)*** neutrinos and other substances such as photons are in thermal equilibrium with *T,* = ***T7,p,,* xa *p.,*** and both have energy distributions similar to that of black body radiation. Afterwards, the neutrino gas expands freely with the universe and its energy density has functional dependence *p,(v/T),* where the frequency ***v*** a **-,** the temperature *T* a **-,** *R* being the "radius" of the universe. Hence the neutrino energies always follw the black body spectrum, just like the photons. However, because of the formation of photons by the annihilation of electron-position pairs, ***p.,*** > ***p,,*** and the temperature of the photon gas is slightly higher than that of the neutrino gas. As the photon temperature at present is 3 K, we expect ***T,*** < 3 K.

1 1

R R

2078

Imagine the universe to be a spherical cavity, with a radius of *lo2'* cm and impenetrable walls.

(a) If the temperature inside the cavity is 3K, estimate the total number of photons in the universe, and the energy content in these photons.

(b) If the temperature were 0 K, and the universe contained *10'* electrons in a Fermi distribution, calculate the Fermi momentum of the electrons.

(***Columbia)***

Solution:

(a) The number of photons in the angular frequency range from *w* to *w* + *dw* is

The total number of photons is

The total energy is

w 2.6 x ergs ,

(b) The Fermi momentum of the electrons is

2079

An n-dimensional universe.

In our three-dimensional universe, the following are well-known results from statistical mechanics and thermodynamics:

(a) The energy density of black body radiation depends on the temperature as ***TQ,*** where ***a*** = **4 .**

(b) In the Debye model **of** asolid, the specific heat at low temperatures

(c) The ratio of the specific heat at constant pressure to the specific

Derive the analogous results (i.e., what are *7,* ***a*** and /I) in the universe

depends on the temperature **as** ***Tfl,*** where /I = *3.*

heat at constant volume for a monatomic ideal gas is *7* = ***5 / 3 .***

with **n** dimensions.

P I T)

Solution:

(a) The energy of black body radiation is

E = 2 / / - dnpdnq AW

(2nh)n ***ehwl2nkT*** **- 1**

For **the radiation we have** ***p = A w / c ,*** so

where ***x*** = ***Aw/kT.*** **Hence** Q = n + 1.

(b) The Debye Model regards solid as an isotropic continuous medium with partition function

nN nN [i=i 1 *j = 1*

Z (T , V) = exp - A E w ; / 2 k T n[1- *e x p (- f ~ w i / k T)] - l*

The Holmholtz free energy is

nN h *nN*

F = - k T l n Z = - ~ *w ; + k T ~ l n [l - e x p (- h w ; / k T)] .*

i=l i=*1*

2

When N **is very large,**

nN

-+ $ ***lwD*** ***wn-'dw*** **,**

i=l

where *WD* is **the Debye frequency.** So **we have**

AWD + *(kT)n+i ___xn-'* ln[l- *e x p (- x)] d x* ,

*(f*ntw2*D*N*) n* ***n2N lXD***

2(n + **1)**

F = -

where *XD* = ***hwD/kT.*** **Hence**

c v = - T **a*(2*~F** ***) m T n ,***

i.e., ***B*** = n.

(c) The theorem of equipartition of energy gives the constant volume

1

specific heat of a molecule as c, = **−*k*** where 1 is the number of degrees **2**

of freedom of the molecule. For a monatomic molecule in a space of n

dimensions, 1 = ***n.*** With cp = c, + ***k,*** we get

2080

(a) Suppose one carries out a measurement of the specific heat at constant volume, C, for some solid **as** a function of temperature, **TI** and obtains the results:

T	C, (arbitrary units)
lOOOK	**20**
500 K	20
40 K	**8**
20 K	1

Is the solid a conductor or an insulator? Explain.

(b) If the displacement of an atom about its equilibrium position in a harmonic solid is denoted by *U ,* then the average displacement squared is given **by**

where *M* is the mass of the atom, *g (E)* is a suitably normalized density of energy states and **n(c)** is the Bose-Einstein occupation factor for phonons of energy *E*. Assuming a Debye model for the density of states:

g (E) = ~ E ~ / (A W ~) ~

g (E) = 0

for *E* < ~ W D,

for *E* > h w ,~

where *WD* is the Debye frequency, determine the temperature depeudence of ***(U2)*** for very high and very low temperatures. Do your results make sense?

(*Chica* g *0)*

Solution:

constant at high temperatures. So it is an insulator.

(a) For the solid we have *C,* ₒ₍ T3 at low temperatures and ***C,*** =

(b) The phonon is a boson. The Bose-Einstein occupation factor for

1

ea/kT - 1 ·

phonons of energy *E* is

n(E) =

SO

& -.-+-.- ***LhwD"**** er/kT - 1 ds . -- 9h2 1 9A2

4M AWD M

If the temperature is high, i.e., kT >> *E,*

If the temperature is low, i.e., kT << *E.*

These results show that the atoms are in motion at T = 0, and the higher the temperature the more intense is the motion.

2081

Graphite has a layered crystal structure in which the coupling between the carbon atoms in different layers is much weaker than that between the atoms in the same layer. Experimentally it is found that the specific heat is proportional to T at low temperatures. How can the Debye theory be adapted to provide an explanation?

(SUNY, Buflulo)

Solution:

Graphite is an insulator and its specific heat is contributed entirely by the crystal lattice. When the temperature *T* increases from zero, the vibrational modes corresponding to the motion between layers is first excited since the coupling between the carbon atoms in different layers is much weaker. By the Debye model, we have

w = c k .

The number of longitudinal waves in the interval *k* to *k+dk* is *(L / 2 ~) ~ 2 ~ k d k ,* where *L* is the length of the graphite crystal. From this, we obtain the number of the longitudinal waves in the interval *w* to *w* + *dw, L2wdw/2xci,* where *C I I* is the velocity of longitudinal waves. Similarly, the number of transversal waves in the interval *w* to *w* + *dw* is ----,

L2wdw

TC?

Therefore, the Debye frequency spectrum is given by

w < *WD* (Debye frequency) .

where

hW

z=- - *XD* = *twD_* , *kB* being Boltzmann's constant.

kBT' kB T

At low temperatures, ~ *W* >*D*> *k BT,* **i.e.,** *X D* >> 1, then,

oo ***x3ez***

dx

where

oo

((3) = C **n-3 *m*** 1.2 **.**

n= I

So that the specific heat is proportional to T2 at low temperatures, or more precisely,

C" = . ((3)T2 **.** ***3k38P(Ci2*** + **2 c p)**

7rh2

2082

One Dimensional Debye Solid.

Consider a one dimensional lattice of ***N*** identical point particles of mass **rn,** interacting via nearest-neighbor spring-like forces with spring constant **mu2.** Denote the lattice spacing by *a.* **As** is easily shown, the normal mode eigenfrequencies are given by

wk = w.\/2(1 - cos *ka)*

with *k* = ***Z?rn/aN,*** where the integer n ranges from ***-N/2*** to *+N/2 (N* >> 1). Derive an expression for the quantum mechanical specific heat of this system in the Debye approximation. In particular, evaluate the leading non-zero terms as functions of temperature T for the two limits T + *co,* T -+ *0.*

(Princeton)

Solution:

Please refer to Problem ***2083.***

2083

A one dimensional lattice consists of a linear array of ***N*** particles ***(N*** >> 1) interacting via spring-like nearest neighbor forces. The normal mode frequencies (radians/sec) are given by

w, = ***W J 2 (1*** *- cos(Znn/N))* **,**

where 6 is a constant and **n** an integer ranging from ***-N/2*** to ***+N/2.*** The system is in thermal equilibrium at temperature T. Let ***c,*** be the constant

uvolume" (length) specific heat.

(a) Compute ***c,*** for the regime ***T*** + *oo.*

(b) For ***T*** + ***0***

c, -+ ***Aw-"Tr*** **,**

where ***A*** is a constant that you need not compute. Compute the exponents (Y and **7.**

The problem is to be treated quantum mechanically.

(P r i n c e ton)

Solution:

T *1*

= 1 ***ehw,/kT*** - 1 ,

*n=- i Y*When

kT >> *hw,*

- ***NkT . U kT*** *c5* ***C h w n .*** - -

hwn

= *Nk.*

dU

Hence *c,* = **-** *dT*

(b) When *kT* << *hw,* we have

Y 1 *N/2*

c5 2 C *tiune-hWJkT* . = C *hwn* *ehw,/kT* - 1

n=-+ n=O

SO

Notice that as *N* >> 1 we have approximately

N/2 sin2 *G e - (h w / r r k T) s i n (n z / N) N*

cos *N*

N . *-d* (sin *y)* *T TX*

Because exp(-thw/rkT) decreases rapidly as t -+ 1, we have

where *A* = (16Nk2/h) t2exp(-[)dE.

Hence *a* = *7* = 1 .

2084

Given the energy spectrum

EP = *[(P c)* + ~ *mc, , 2* 4 1 112 + *p c* as *p* - + 00.

(a) Prove that an ultrarelativistic ideal fermion gas satisfies the equation of state *pV* = *E/3,* where *E* is the total energy.

(b) Prove that the entropy of an ideal quantum gas is given by

S= - k ~ [n ; l n (n ;) i (l f n ;) l n (l + n ,)]

a

where the upper (lower) signs refer to bosons (fermions).

(SUNY, *Buflulo)*

Solution:

(a) The number of states in the momentum interval *p* to *p* + *dp* is

87rV 1

F p 2 d p (taking S = -). From *E* = *cp,* we obtain the number of states in

2

the energy interval *E* to *E* + dE:

87rV

c3h3

N(e)de = -e2de .

So the total energy is

In terms of the thermodynamic potential In **Z,**

1

= - *E* .

3

Note that this equation also applies to an ultrarc.dtivistic boson gas.

(b) The average number of particles in the quantum state *i* is given by

n; = l/(exp(a + *PE,)* 11, from which we have

or

and

BY

we have

2085

Consider an ideal quantum gas of Fermi particles at a temperature *T.*

(a) Write the probability *p (n)* that there are *n* particles in a given

(b) Find the root-mean-square fluctuation ***((n- (n)) z)) ' /iz***n the occupation number of a single particle state as a function of the mean occupation number ***(n) .*** Sketch the result.

single particle state as a function of the mean occupation number, ***(n) .***

(MIT)

Solution:

potential. The partition function is

(a) Let *E* be the energy of a single particle state, ***p*** be the chemcial

z = exp[n(p- &) /kT]= 1 + exp[(p - ***&) / kT.]***

n

The mean occupation number is

The probability is

(b) ((n- **(n))2)=** kT-*a (n)* -- (n) (1 - *(n))*

aP

So we have *((n- **(n)) z)) ' /=z*** J(n)(l - ***(n))***

The result is shown in Fig. 2.17.

1

< (n - <n>,2>'

Fig. **2.17.**

2080

In a perfect gas of electrons, the mean number of particles occupying a single-particle quantum state of energy *E,* is:

1 ***N;*** =

.XP[(Ei - ***p)/kT]*** + 1 ·

(a) Obtain a formula which could be used to determine ***p*** in terms of

(b) Show that the expression above reduces to the Maxwell-Boltzmann distribution in the limit *nX3* << 1, where X is the thermal de Broglie wavelength

.

the particle density n and various constants.

(c) Sketch ***Ni*** versus *E;* for ***T*** = 0 K and for ***T = p/5*** K. Label

(UC, ***Berkeley)***

significant points along both axes.

Solution:

(a) The particle number density is

As

X

This formula can be used to determine **/l.**

(b) When nX3 << 1, we must have in the above integral

It follows that

i.e., it reduces to the Boltzmann distribution.

(c) The variation of ***Ni*** versus *Ei* is as shown in Fig. 2.18.

(a) *T* = *K* **(b)** *J* = *$* - *K*

Fig. **2.18.**

2087

Suppose that in some sample the density of states of the electrons *D(E)* is a constant ***Do*** for energy *E* > 0 ***(D (s)*** = 0 for *E* < 0) and that the total number of electrons is equal to ***N.***

(a) Calculate the Fermi potential ***po*** at 0 K.

(b) For non-zero temperatures, derive the condition that the system is

non-degenerate.
(c) Show that the electronic specific heat is proportional to the tem-
*(UC, **Berkeley)***
perature, *T,* when the system is highly degenerate.

Solution:

(a) When T = 0 K, all the low lying energy levels are occupied, while those levels whose energies *E* are greater than *PO* are all vacant. Taking the 1/2 spin of electrons into consideration, every state can accomodate two electrons, and hence 2DopoV = ***N*,** or
N
Po = -*2VD0* '
where *V* is the volume of the sample.

(b) The non-degeneracy condition requires that exp (fi)<< 1, then

In this approximation,

Tha t is, the non-degeneracy condition is ***kT*** >> (8) */2 Do* = PO.

(c) When ***T*** = *0* K, the electrons are in the ground state without excitation. When T # 0 K, but ***T*** << ***P o l k ,*** only those electrons near the Fermi surface are excited, ***N,H*** *M* ***kTDo,*** and the specific heat contributed by each electron is *Co* = **- *k* .** Therefore, when the system is highly degnerate, the specific heat C *o(* ***T*.**
3
2

2088

Consider a system of ***N*** "non-interacting" electrons/cm3, each of which can occupy either a bound state with energy *E* = *-Ed* or a free-particle continuum with *E* = **&.** (This could be **a** semiconductor like Si with ***N*** shallow donors/cm3.)
(a) Compute the density of states as **a** function of *E* in the continuum.
(b) Find an expression for the chemical potential in the low tempera-
(c) Compute the number of free electrons (i.e., electrons in the contin-
(UC, Berkeley)
Suppose that each bound state can at most contain a pair of electrons
N
with anti-parallel spins, and that the number of bound states is - That
2 '
is, when T = 0 K, all the bound states are filled up with no free electrons. When ***T*** is quite low, only a few electrons are in the free particle continuum so that we can use the approximation of weak-degeneracy.
ture limit.
uum) as a function of T in the low temperature limit.

Solution:

(a) The density of states in the continuum is
(b), (c) The number of electrons in the bound states are
N
Nb = *e - (E d + p) / k T* + 1

The number of electrons in the continuum (weak-degeneracy approximation) is
where
From (1) and **(2),** we get
Substitute **(3)** in **(2),** we get

Nf - kT *N Ed p* = kTln- - -1n - - - . *N, 2 N,* 2

2089

(a) For **a** system of electrons, assumed non-interacting, show that the probability of finding an electron in a state with energy **A** above the chemical potential ***p*** is the same as the probability of finding an electron absent from a state with energy **A** below ***p*** at any given temperature T.

(b) Suppose that the density of states ***D(E)***is given by

U (& - **"p**, *E > % ,*

O < E < E g ,

& < O ,

as shown in Fig. **2.19,**

Fig. 2.19

and that at T = 0 all states with *E* < 0 are occupied while the other states are empty. Now for T *3* 0, some states with *E* > 0 will be occupied while some states with ***c*** < 0 will be empty. **If** *a* = ***b,*** where is the position of ***p?*** For *a* # *b,* write down the mathematical equation for the determination of ***p*** and discuss qualitatively where ***p*** will be if a > *b? **a*** < *b?*

(c) If there is an excess of nd electrons per unit volume than can be accommodated by the states with *E* < 0, what is the equation for ***p*** for ***T*** = O? How will ***p*** shift as ***T*** increases?

(SUNY, Buflulo)

Solution:

pied is

(a) By the Fermi distribution, the probability for a level ***E*** to be occuso

the probability for finding an electron at ***E*** = ***p*** + **A** is

and the probability for not finding electrons at ***E*** = ***p*** - **A** is given by

1

1 - ***.F(p*** - **A)** = **- eBA+l** ·

The two probabilities have the same value as required.

(b) When T > 0 K, some electrons with *E* < 0 will be excited to states of ***E*** > *E* ~ T. h at is to say, vacancies are produced in the some states of *E* < 0

while some electrons occupy states of *E* > ***E*** ~ T. h e number of electrons with *E* > ***E***~ is given by

The number of vacancies for **e** < 0 is given by

By n, = np, we have ***p*** = **cg/2** when *a* = ***b.*** We also obtain the equation to determine ***p*** when ***a*** # ***b,***

For *a* > ***b,*** we have

so that ***B*** + eg **-** ***p*** > ***E*** + ***p,*** i.e., ***p*** < ~ ~ **1**H**2**en**.**ce ***p*** shifts to lower energies.

For *a* < *b,* ***p*** > E~ ***12, p*** shifts to higher energies.

(c) When ***T*** = 0, by

we obtain

p shifts to lower energies **as** T increases.

2090

(a) Calculate the magnitude of the Fermi wavevector for 4.2 x 1021

(b) Compute the Fermi energy (in eV) for this system.

(c) If the electrons are replaced by neutrons, compute the magnitude

*(UC, **Berkeley)***

electrons confined in a box of volume 1 cm3.

of the Fermi wavevector and the Fermi energy.

Solution:

(a) The total number of particles is

The Fermi wavelength is

= 1.25 x 10-gm = 12.5A ,

h 8rV **‘*I* *3***

X F = - = *(X)*

PF

(b) The Fermi energy is

(c) **If** the electrons are replaced by neutrons, we find that

= *XF* = 12.5A ,

m

m‘

and ***E&*** = ***-EF*** = **5.2** x 10-4eV.

2091

Calculate the average energy per particle, ***E,*** for a Fermi gas at T = 0,

*(UC, **Berkeley)***

given that ***EF*** is the Fermi energy.

Solution:

We consider two cases separately, non-relativistic and relativistic.

(a) For a non-relativistic particle, ***p*** << *mc* ***(p*** is the momentum and m is the rest mass), it follows that

P2 & = - .

2m

We have *D(E)* = fi. const.

Then

- *l e F & & d a* -

- *iEF* ⋆

& = *I* , ′′ *&de*

(b) For **p** >> *mc,* we have ***E*** = ***p c ,*** and *D(E)*= ***E'.*** const. Therefore,

2092

Derive the density of states *D(e)* as a function of energy ***E*** for a free electron gas in one-dimension. (Assume periodic boundary conditions or confine the linear chain to some length *L.)* Then calculate the Fermi energy ***EF*** at zero temperature for an ***N*** electron system.

(wis co *ns* ***in)***

Solution:

The energy of a particle is ***E*** = ***p2/2m.*** Thus,

Taking account of the two states of spin, we have

or

a(€=) ***L*** (F) ’’’ /. .

At temperature 0 K, the electrons will occupy all the states whose energy **is** from 0 to the Fermi energy ***EF.*** Hence

giving

2093

Consider a Fermi gas at low temperatures *kT* << ***p(O),*** where *p(0)* is the chemical potential at *T* = 0. Give qualitative arguments for the leading value of the exponent of the temperature-dependent term in each of the following quantities: (a) energy; (b) heat capacity; (c) entropy; (d) Helmholtz free energy; (e) chemical potential. The zero of the energy scale is at the lowest orbital.

(UC, Berkeley)

Solution:

At low temperatures, only those particles whose energies fall within a

thickness - *kT* near the Fermi surface are thermally excited. The energy of each such particle is of the order of magnitude *kT*.

E - E(0) a T2.

(a) *E* = *E(0) +akT.kT,* where Q! is a proportionality constant. Hence

GI

T (c) From *dS* = *-dT,* we have

T

S = i $ d T a T .

(d) From *F* = *E* - ***TS,*** we have *F - F(0) a T2.*

(e) From ***p*** = *(F* + *pV)/N* and **p** = *2E/3V,* where ***N*** is the total number of particles, we have ***p*** - ***p(0)*** *a T2.*

2094

Derive an expression for the chemical potential of a free electron gas with a density of ***N*** electrons per unit volume at zero temperature (T = 0 K). Find the chemical potential of the conduction electrons (which can be considered as free electrons) in a metal with ***N*** = **loz2** electrons/cm3 at T = O K .

(UC, Berkeley)

Solution:

From the density of states

D(c)de= *4 ~ (2 r n) ~ / ~ & d ,e / h ~*

we get

h2 3N 2f3

2m (G) Therefore, ***po*** = -

For *N* = loz2 electrons/cm3 = **lo2'** electrons/m3, it follows that

po = 2.7 x lo-" J = 1.7 eV .

2095

D(E) is the density of states in a metal, and *EF* is the Fermi energy. At the Fermi energy ***D(EF)#*** 0.

(a) Give an expression for the total number of electrons in the system at temperature *T* = *0* in terms of *EF* and ***D(EF) .***

(b) Give an expression of the total number of electrons in the system at *T* # 0 in terms of the chemical potential ***p*** and *D(E).*

(c) Calculate the temperature dependence of the chemical potential at low temperatures, i.e., ***p*** >> *kT.*

(Chicago)

Fig. **2.20.**

Solution:

The density of states is

47rV (2m)3/2

h3

D(E) =

(a) **If *T*** = 0, the total number of electrons is

2
3
EF

N = *l* *D(E)dE = -D(EF)EF* .

(c) At low temperatures *1.1* >> ***kT,***

= / , *'D(E)dE* + *7-r(2k T)'D'(p)* + *-7T* ***(4k T) 4D" ' (p)*** + . . . *6* 3 *60*

Fy ***87~V3h(32 rn)~p/3'/2*** [1+ f I " , ? (

where

2096

For Na metal there are approximately 2.6 x conduction electrons/ cm3, which behave approximately as a free electron gas. From these facts,
(a) give an approximate value (in eV) of the Fermi energy in Na,
(b) give an approximate value for the electronic specific heat of Na at
(UC, Berkeley)
room temperature.

Solution:

(a) The Fermi energy is
h2 312

EF **= -** ***(3r2*** F) 2m

N
V We substitute *h* = 6.58 x
1022/~mi3n to it and obtain ***EF*** ***w*** 3.2 eV.
eV.s, m = 0.511 MeV/c2 and - = **2.6** x
(b) The specific heat is
where **me = 9.11** x kg is the mass **of** the electron, ***k*** = 1.38 x
J/K is Boltemann's constant, and ***kT*** **w** - eV at room temperature.
We substitute *EF* and the other quantities in the above expression and obtain C **M** **11.8** J/K.g.
1
40

2097

The electrons in a metallic solid may be considered to be a threedimensional free electron gas. For this case:
(a) Obtain the allowed values of ***k,*** and sketch the appropriate Fermi sphere in k-space. (Use periodic boundary conditions with length *L).*
(b) Obtain the maximum value of k for a system of ***N*** electrons, and hence an expression for the Fermi energy at ***T*** = OK.
(c) Using a simple argument show that the contribution the electrons make to the specific heat is proportional to ***T.***

Solution:

(a) The periodic condition requires that the length of the container *L* is an integral multiple of the de Broglie wavelength for the possible states of motion of the particle, that is,
(Wisconsin)

L = In,lX , In,/ = O , l , 2 , ...

Utilizing the relation between the wavelength and the wave vector, ***k*** = 27r/X, and taking into account the two propagating directions for each dimension, we obtain the allowed values of ***k,***

2s

k, = -*Ln* , , *n,* = O , f 1 , * 2 , ...

Similarly we have

Thus the energies

p2 *h2k2* **c = - - - = -**

2m 2m

are discrete. The Fermi sphere shell is shown in Fig. 2.21.

L

2lr

(b) *dn,* = -*dk,* ,

r L *dn,* = -*dk,* ,

dn, = -*dk,* .

2T

L

2.n

Thus, in the volume *V* = L3, the number of quantum states of free

electrons in the region *k,* -+ ***k,*** + *dk,, k,* -+ *k,* + *dk,, k,* -t *k,* + *dk,* is (considering the two directions of spin)

V *dn* = *dn,dn,dn,* = **2** *dk,dk,dk* - -*dk,dk,dk,* .

r- *4n-3*

At *T* = 0 K, the electrons occupy the lowest states. According to the Pauli exclusion principle, there is at most one electron in a quantum state. Hence so that

113

k,,,, = (3 ~ ~ ;) .

The Fermi energy is

(c) At *T* = 0 K, the electrons occupy all the quantum states of energies from 0 to *EF*. When the temperature is increased, some of the electrons can be excited into states of higher energies that are not occupied, but they must absorb much energy to do so, so that the probability is very small. Thus the occupancy situation of most of the states do not change, except those with *kT* near the Fermi energy *EF.* Therefore, only the electrons in such states contribute to the specific heat. Let ***N,fi*** denote the number of such electrons, we have *N,R* = *kTN/EF.* Thus the molar specific heat contributed by the electrons is

2098

Sketch the specific heat curve at constant volume, *C,,* as a function of the absolute temperature, *T,* for a metallic solid. Give an argument showing why the contribution to *C,* from the free electrons is proportional to *T.*

(*wis* c *o ns* i *n)*

Solution:

As shown in Fig. 2.22, the specific heat of a metal is

C, = *rT* + ***AT3***

where the first term on the right hand side is the contribution of the free electrons and the second term is the contribution of lattice oscillation.

T2

Fig. **2.22.**

For a quantitative discussion of the contribution to *C,* of the free electrons see answer to Problem 2097(a).

2099

(a) Derive a formula for the maximum kinetic energy of an electron in a non-interacting Fermi gas consisting of *N* electrons in **a** volume V at zero absolute tempcrature.

(b) Calculate the energy gap between the ground state and first excited state for such a Fermi gas consisting of the valence electrons in **a** 100A cube of copper.

(c) Compare the energy gap with ***kT*** at 1 K.

The mass density and atomic weight of copper are **8.93** g/cm3 and 63.6 respectively.

(UC, ***Berkeley)***

Solution:

(a) When T = 0 K, the Fermi distribution is

The density of quantum states is

N **47r**

Therefore, -*V* = **sodF** **„(2m)3/2&de,** giving

h2 **213**

& F = - (2"m) ***87rV*** **,**

i.e.,

(b) **As** *nX/2 = a* and ***p*** = *h/X,* the quantum levels of the valence electrons in the cube of copper are given by

where ***n1, n2, n3*** = **0 , 1 , 2 , . . .** (not simultaneously 0). The 1st excited state of the Fermi gas is such that an electron is excited from the Fermi surface to the nearest higher energy state. That is

Hence

- 6.0 x J **.** ***h2***

8ma2

A&=--

A&

(c) -***Ic*** = **4.4** x **IO-'K 1K.**

2100

1

(a) For a degenerate, spin - non-interacting Fermi gas at zero tem-

2 '

perature, find an expression for the energy of a system of ***N*** such particles confined to a volume *V*. Assume the particles are non-relativistic.

(b) Given such an expression for the internal energy of a general system (not necessarily a free gas) at zero temperature, how does one determine the pressure?

(c) Hence calculate the pressure of this gas and show that it agrees with the result given by the kinetic theory.

(d) Cite, and explain briefly, two phenomena which are at least qualitatively explained by the Fermi gas model of metals, but are not in accord with classical statistical mechanics. Cite one phenomenon for which this simple model is inadequate for even a qualitative explanation.

(UC, **Berkeley)**

Solution:

(a) The density of states is given by

Hence

and

(b) From the thermodynamic relation

(g) = T (g)" - P 1

and T = 0 K, we have

p = - (g) T v2 = E .

(c) Assume that the velocity distribution is **D(v)dv,** then the number of the molecules which collide with a unit area of the walls of the container in a unit time, with velocities between **v** and **v** + **dv** is **nv,D(v)dv.** The force that the unit areas suffers due to the collisions is

dp = 2mv:nD(v)dv

Hence the pressure is

nD(v) .2mvgdv = nD(v) . rnvgdv

= I, , , 1 2E

= 2 / **nD(v) -mv2dv = -- .**

3 2 3v

For an electron gas

(d) The specific heat and the paramagnetic magnetization of metals

Superconductivity cannot be explained by the Fermi **gas** model.

can be qualitatively explained by the Fermi gas model.

2101

The free-electron model of the conduction electrons in metals seems naive but is often successful. Among other things, it gives a reasonably good account of the compressibility for certain metals. This prompts the following question. You are given the number density n and the Fermi energy e of a non-interacting Fermi gas at zero absolute temperature, T =0 K. Find the isothermal compressibility

where V is volume, **p** is pressure.

Hint: Recall that pV = - E, where E is the total energy.

2

3

(GUSPEA)

Solution:

p = - (g) , where F is the free energy, F = E - TS. When

T

T = 0 K, F = E, and p = - (g) T .

2

Using pV = -El we have

3

or

*p=-(g)T=-*a *[-.-(fpV)]T=-;[*, *V (g)T+* 5

1 ***av*** ***3***

Hence *K.* = -- **(-)** = - ***(T*** = *0* K).

ap ***T 5P***

At *T* = 0 K,

h2k2

d3k-

2E 2 V

3V 3V **(2 ~) ~ *I* , , , ,** ***2m***

p= - = - . *2* . -

we obtain

For an ideal gas, the energy of **a** particle is

h2 *k2*

2m

&(k) = - **.**

Thus

h2 *k;*

2m ***& F*** = - .

Therefore,

2

5 **p** = - ***n*** . ***& F*** , ***(T=*** *0* K) ,

and

3

K. = - **.** (T = O K)

2n&F

2102

Fermi gas. Consider an ideal Fermi gas whose atoms have mass ***m*** =

5 x grams, nuclear spin *I* = **i,** and nuclear magnetic moment ***p*** =

1 x erg/gauss. At *T* = 0 K, what is the largest density for which the gas can be completely polarized by an external magnetic field of **lo5** gauss? (Assume no electronic magnetic moment).

Solution:

(MZT)

After the gas is completely polarized by an external magnetic field, the Fermi energy is ***EF*** = -**A**(2 6 ~ ~ n) ~ w/ h~e,re n is the particle density.

2m

With ***EF*** *5* ***2pH,*** we have

1 ***4mpH*** ***3i2***

n.&F-) **.**

Hence, **nmax** = = *2* x 10"atoms/cm~ **.**

2103

State and give a brief justification for the leading exponent n in the temperature dependence of the following quantities in a highly degenerate three-dimensional electron gas:

(a) the specific heat at constant volume;

(b) the spin contribution to the magnetic moment *M* in a fixed magnetic

field *H.*
(MITI
Solution:
Let us first consider the integral *I:*

where *kTz* = ***-p*** + ***E.*** **As** *p/kT* >> 1, we can substitute *oo* for the upper limit of the second integral in above expression so that

(a) Let ***f (e)*** = ***c312,*** then the internal energy E ▬ I, *C,* = - ▬
TI i.e., *n* = 1. In fact, when T = 0 K, because the heat energy is so small, only those electrons which lie in the transition band of width about *kT* on the Fermi surface can be excited into energy levels of energies = *kT.* The part of the internal energy directly related to *T* is then

(:IV

-

NT ▬ *T2,* i.e., C, ▬ *T* **.**

(b) Let *f (~)* = **d12,** then *M* ▬ I, hence *M* = Mo(1 *-aT2) ,* i.e., **n** = 0.
When *T* = 0 K, the Fermi surface ***EF*** with spin direction parallel to **H** is
&Ft = ***p+pgH (pg*** is the Bohr magneton) while the Fermi surface ***EF*** with spin direction opposite to **H** is ***EFJ*** = ***p - p g H .*** Therefore, there exists **a** net spin magnetic moment parallel to **H.** Hence n = 0.

2104

electrons in a "box" of volume V =
1 cm3. The walls of the box are infinitely high potential barriers. Calculate the following within a factor of five and show the dependence on the relevant physical parameters:
Take a system of *N* = **2** x
(a) the specific heat, C,
(b) the magnetic susceptibility, *X* ***,***
(c) the pressure on the walls of the box, **p,**
(d) the average kinetic energy, *(Ek).*
(*Cham* ***g 0)***
Solution:
The density of states in **k** space is given by
4rk2
8 6 *d k '*
D(k)dk = ***ZV*** **. -**

ii2
2m
and the kinetic energy of an electron is ***E*** = ***-k2.*** Combining, we get
At ***T*** = 0 K, the *N* electrons fill up the energy levels from zero to *EF* =
h"
-k>, i.e.,
2m
E F **2**

N = D(&)d&=;D (EF)EF
Jo
2m
(a) The specific heat is
where *kB* is Boltzmann's constant.
(b) The magnetic susceptibility is
where ***pB*** is the Bohr magneton.
(c), (d) The average kinetic energy is

2 3 *ED(&)&= -D(EF)E; = -NEF* **,** *(Ek) =I'''* *5* ***5***

and the pressure on the walls of the box is
2105
fermions is confined to a volume *V.* Calculate
the zero temperature limit of (a) the chemical potential, (b) the average
An ideal gas of *N* spin

energy per particle, (c) the pressure, (d) the Pauli spin susceptibility. Show
that in Gaussian units the susceptibility can be written as ***3 p i* N/Zp(O)V,**
where *p(0)* is the chemical potential at zero temperature. Assume each
fermion has interaction with an external magnetic field of the form *2poHS,,*
where ***p~*** is the Bohr magneton and *S,* is the z-component of the spin.
(*was* **co** *flsifl)*
Solution:
As the spin of **a** fermion is $, its ***z*** component has two possible directions
with respect to the magnetic field: up (I) and down (I) **.** These
correspond to energies ***3 =p ~ H*r,e** spectively. Thus the energy of a particle
is

P2 & = - * ***pgH .***
2m
At T = 0 K, the particles considered occupy all the energy levels below
the Fermi energy *p(0).* Therefore, the kinetic energies of the particles of
negative spins distribute between 0 and *p(0) - ~ B H*th,os e of positive spins
distribute between 0 and ***p(0)*** **+** *~ B H*th,e ir numbers being
(a) The total number of particles is
With *H* = 0, we obtain the chemical potential
p(0) = tL" ***(3 2 ;) 2/3 .***
2m
1 1
2 2
(b) For particles with z-components of spin, - and **--,** the Fermi
momenta are respectively

The corresponding total energies are
Hence the average energy per particle is
E E++EN
- N
--
For *p(0) PBH,*
E 3
N

(c) The pressure is

2N 2

T ap(0) *av 5v*

(d) For *p(0)* > ~ *B H*th,e magnetization is given by

M *= p g (N- - N+) /V* = ***-3PiN H = x H .***

2P(O)V

3NPi

2P(O)V *

Hence *x* = -

2106

Consider a Fermi gas model of nuclei.

Except for the Pauli principle, the nucleons in a heavy nucleus are assumed to move independently in a sphere corresponding to the nuclear volume *V*. They are considered as a completely degenerate Fermi gas. Let A = N (the number of neutrons) +Z (the number of protons), assume *N* = 2, and compute the kinetic energy per nucleon, **Ekin/A,** with this model.

4s

3

The volume of the nucleus is given by V = ***-RiA, Ro*** *M* 1.4 x

Please give the result in MeV.

cm.

(Chicago)

Solution:

In the momentum space,

4v

h3 dn = -4n-p2dp,

where n is the number density of neutrons.

The total number of neutrons is

A = *1* dn = 16n-V **LPF** $dP

where PF is the Fermi momentum.

The total kinetic energy of the neutrons is

Hence **,**

The volume V can be expressed in two ways:

V 4n **3 (2 ~)**-3~ *h* = ***-R3A*** = - pF ***A,*** (putting *h z* - = 1)

3 O 16n **27r**

giving ***p~*** = *R,'* (2) *'I3,* and

2107

At low temperatures, a mixture of 3He and 4He atoms form a liquid which separates into two phases: a concentrated phase (nearly pure 3He), and a dilute phase (roughly 6.5% 3He for ***T*** *5* 0.1 K). The lighter 3He floats on top of the dilute phase, and 3He atoms can cross the phase boundary (see Fig. 2.23).

The superfluid He has negligible excitation, and the thermodynamics of the dilute phase can be represented as an ideal degenerate Fermi gas of particles with density ***nd*** and effective **mass** m* (m* is larger than *m3,* the mass of the bare 3He atom, due to the presence of the liquid 4He, actually ***m**** **= 2.4m3).** We can crudely represent the concentrated phase by an ideal

degenerate Fermi gas of density n, and particle mass 7733.
(a) Calculate the Fermi energies for the two fluids.
(b) Using simple physical arguments, make an estimate of the very
low temperature specific heat of the concentrated phase *c,(T, T F* ~w*)*hi ch
explicitly shows its functional dependence on T and ***TF,*** (where ***T F***i~s t he
Fermi temperature of the concentrated phase, and any constants independent
of T and *TF,* need not be determined). Compare the specific heats of
the dilute and concentrated phases.
(c) How much heat is required to warm each phase from ***T*** = *0* K to
T?

I--&-- **concentrated phase of 3He**

dilute phase of 3He
(in superfluid of &He)

Fig. 2.23.

(d) Suppose the container in the figure is now connected to external
plumbing **so** that 3He atoms can be transferred from the concentrated phase
to the dilute phase at a rate of ***N,*** atoms per second (as in a dilution
refrigerator). For fixed temperature T, how much power can this system
absorb?
(Princeton)

, we have ***EF,*** = -***h2 ($)'I3,*** and

Solution:

2m3

h2 *213*

E F . =2-m- - - (~) **.**

(b) For an ideal degenerate Fermi gas at low temperatures, only those
particles whose energies are within *(EF - kT)* and *(EF* + *kT* contribute to
the specific heat. The effective particle number is *n,ff* = *n-, so*

k *h*

EF

T T

c , c c n e f f ~ - = a -

EF *'TF'*

where ***a,*** is a constant.

(d) The entropy per particle at low temperature is

T

TF

= **A-** , where X is a constant.

The power absorbed is converted to latent heat, being

2108

A white-dwarf star is thought to constitute a degenerate electron gas
system at a uniform temperature much below the Fermi temperature. This
system is stable against gravitational collapse so long as the electrons are
non-relativistic.
(a) Calculate the electron density for which the Fermi momentum is
one-tenth of the electron rest mass *X C .*
(b) Calculate the pressure of the degenerate electron gas under these
(UC, Berkeley)
conditions.

Solution:

P<PP

. . giving n = - = -

With

meC

P F = **-10**

we have

8r **m,c** 3

n = 7 (X) = 5.8 x **lo3'** /m3 ,

(b) For a strong degenerate Fermi gas (under the approximation of zero valence), we get

- **3** *E* = ***-Npo*** , ***5***

and

p o **2 P;** = -n - = 9.5 x Nfm' **.** **p** = **-2-E** = -2n

3v 5 5 2m

2109

A white dwarf is **a** star supported by the pressure of degenerate electrons. **As a** simplified model for such an object, consider a sphere of an ideal gas consisting of electrons and completely ionized Si28, and of constant density throughout the star. (Note that the assumption of **a** constant density is inconsistent with hydrostatic equilibrium, since the pressure is then also constant. The assumption that the gas is ideal is also not really tenable. These shortcomings of the model are, however, not crucial for the issues which we wish to consider.) Let ***ni*** denote the density of the silicon ions, and let n, = **14n;** denote the electron density. (The atomic number of silicon is **14).**

(a) Find the relation between the mean kinetic energy ***E,*** of the electrons and the density n,, assuming that the densities are such that the electrons are "extremely relativistic," i.e., such that the rest energy is negligible compared with the total energy.

(b) Compute ***E,*** (in MeV) in the case that the (rest mass) density of the gas equals ***p*** = lo9 g/cm3. Also compute the mean kinetic energy **Ei** of the silicon ions in the central region of the dwarf, assuming that the

temperature is **lo8** K and assuming that the 'ion gas" can be regarded as a Maxwell-Boltzmann gas, and hence convince yourself that ***E,*** >> **Ei.**

(c) If *M* is the mass of the star, and if *R* is its radius, then the gravi*UC*

3GM2 = -

In the case in which the internal energy is dominated by extremely relativistic electrons (as in part **(t)** above), the virial theorem implies that the total internal energy is approximately equal to the gravitational potential energy. Assuming equality, and assuming that the electrons do not contribute significantly to the mass of the star, show that the stellar mass can be expressed in terms of fundamental physical constants alone. Evaluate your answer numerically and compare it with the mass of the sun, **2 x 1030** kg. (It can be shown that this is approximately the maximum possible mass of a white dwarf.)

(UC, **Berkeley)**

Solution:

(a) Use the approximation of strong degenerate electron gas and *E* = ***pc.***

From the quantum state density of electrons, it follows

tational potential energy is given by

5R '

2 *8T*

-dp = -E2ds* , *h3 h3c3
then

n, = /," ***%E2ds***

h3c3
Therefore
Psr
(b) When ***p* = 1o9** g/cm3,
n, = 14ni = 3 x 1032~m-3= **3** x
E, = 5 x
Ei = *-kT* = 2 x

rn-’ , **-**

J = **3** MeV **,**
3
2
-
J = **1 . 3 ~ 1 0 -**M**~** e V.

Obviously, **xi << *S*,.**

(c) F'rom the virial theorem, we have

***($R3 n e)** :hc* (2·) ***l* 2**= i3 *~GM 2* **.**

we obtain

M = -!!- . %/$ **= 8.5** x **lo3'** kg **= 4.1M, ,**
1 2 8 ~ Gm,
where Ma is the mass of the sun.

2110

(a) Given that the mass of the sun is **2** x g, estimate the number of electrons in the sun. Assume the sun is largely composed of atomic hydrogen.

(b) In **a** white dwarf star of one solar mass the atoms are all ionized and contained in **a** sphere of radius **2** x 109 cm. Find the Fermi energy of the electrons in eV.

(c) If the temperature of the white dwarf is lo' K, discuss whether the

(d) If the above number of electrons were contained in **a** pulsar of one solar mass and of radius 10 km, find the order of magnitude of their Fermi energy.

(Columbia)

electrons and/or nucleons in the star are degenerate.

Solution:

(a) The number of electrons is

1.2 x lo5' **. 2** x 1033
1.67 x 10-24
N =

(b) The Fermi energy of the electrons is

EJ* 4** x **lo4** eV **.** EF'=%h2***(GV3)***N* *2 J 3*** *xE(--)* **9 *N* 2/3**
2m, 32x2 *R3*

The Fermi energy of the nucleons is

E F , *~ m e* 1 **= *EFe-* = *-EFe* .** *m,* 1840

(c) ***EFc/k*** = **4** x lo8 K> lo7 K.

EF,/k << lo' K.

Therefore, in **a** white dwarf, the electrons are strongly degenerate while the nucleons are weakly degenerate.

(d) The Fermi energy of the electrons if contained in a pulsar is

2111

At what particle density does a gas of free electrons (considered at T = 0 K) have enough one-particle kinetic energy (Fermi energy) to permit the reaction

proton + electron + 0.8 MeV -+ neutron

to proceed from left to right? Using the result above estimate the minimum density of a neutron star.

*(UC, **Beskeley**)*

Solution:

electron gas are related as follows:

When T = 0 K, the Fermi energy and the number density of the

The condition for the reaction to proceed is ***EF*** *2* 0.8 MeV, then

nIlliIl= 3.24 x lo3' m-' **.**

Hence the minimum mass density of a neutron star is

plllilI = *m,rn,i,* = **5 . 4** x lo9 kg/m3 **.**

2112

Assume that a neutron star is a highly degenerate non-relativistic gas of neutrons in a spherically symmetric equilibrium configuration. It is held together by the gravitational pull of a heavy object with mass *M* and radius *ro* at the center of the star. Neglect all interactions among the neutrons. Calculate the neutron density as a function of the distance from the center, ***r,*** for *r* > *ro.*

(Chicago)

Solution:

For a non-relativistic degenerate gas, the density ***p*** *o(* ***p3I2,*** the pressure *p o:* ***p5I2,*** where ***p*** is the chemical potential. Therefore, ***p*** = ***ap5I3,*** where *a* is a constant. Applying it to the equation

-d p = MGd (i) ,

P

5

2

we find ***a*** *. -dp2I3 = MGd*

p(r) = [−*2 M5aG* **.** -***r***1 + const]312 **.**

As *r -+ co,p(r) --+ 0,* we find const. = 0. Finally, with ***r*** > *ro,* we have

2MG 1 **3'2**

P (d = [F ;]

2113

Consider a degenerate (i.e., T = 0 K) gas of ***N*** non-interacting electrons in a volume V.

(a) Find an equation relating pressure, energy and volume of this gas for the extreme relativistic case (ignore the electron mass).

(b) For a gas of real electrons (i.e., of mass m), find the condition on ***N*** and V for the result of part (a) t o be approximately valid.

(MITI

Solution:

The energy of a non-interacting degenerate electron gas is:

PP Ep2

E=8nVL ***z d p***

where ***E*** is the energy of a single electron, pp is the Fermi momentum,

p F = (3 N / 8 ~ V) ' / ~ h .

(a) For the extreme relativistic case, ***E*** = ***cp,*** so we have energy

E= -2 scv **4** ***h3*** **' F '**

which gives the equation of state

- _1-E and pressure ***p*** = -

T=O

1

3

pV= -*E*

(b) For a real electron,

where p is its momentum, giving

EM2 scV[p; + (m c p ~) ~]./ h ~

The condition **for** the result of part (a) to be approximately valid is **PF** >> mc. or

-*N*> +)a s mc 3 ***v 3***

Either ***N*** -+ *00* **or** V -+ 0 will satisfy this condition.

2114

Consider a box of volume V containing electron-positron pairs and photons in equilibrium at a temperature *T* = **l/kp.** Assume that the equilibrium is established by the reaction

7 + + e + + e - .

The reaction does not occur in free space, but one may think of it as catalyzed by the walls of the box. Ignoring the walls except insofar as they allow the reaction to occur, find

(a) The chemical potentials for the fermions.

(b) The average number of electron-positron pairs, in the two limits ***kT*** >> mec2 and ***kT*** << mec2. (You may leave your answers in terms of dimensionless definite integrals.)

(c) The neglect of the walls is not strictly permissible if they contain a matter-antimatter imbalance. Supposing that this imbalance creates a net chemical potential ***p # 0*** for the electrons, what is then the chemical potential of the positrons?

(d) Calculate the net charge of the system in the presence of this imbalance in the limit ***kT*** >> ***p*** >> m,c2. (Again, **your** answer may be left in terms of a dimensionless definite integral.)

(Chicago)

Solution:

(a) For a chemical reaction A +-+ B + C at equilibrium, ***p~*** = ***pg +pc.***

As the chemical potential of the photon gas ***p7*** = 0, we obtain

pe+ + *pe-* = 0 .

Considering the symmetry between particle and antiparticle, we have

Hence ***pe+*** = ***pe-*** = *0.*

(b) At the limit ***kT*** >> mec2, neglecting the electron mass and letting

E = cp, we obtain

V (kT)3 *oo* x2dx

7r2 *(h) 3* ***ez*** + 1 - - *Ne*+ **.**

At the limit ***kT*** << mec2, the "1" in denominator of the Fermi factor

1

[exP(PJ(cP)2 + (meC2)2) + 11

can be neglected and we also have

cp = *.\/(cp)2* + *(m,c2)2* ***M*** *m,c2* + *p 2 / 2 m* **.**

Thus

="(*2 ~m, k T* ***3 J 2*** **-m,ca** ***/kT h2*** **)**

(c) AS ***pe+*** + ***pe-*** = *0,* **pLe+**= ***-pe-*** = ***-p.***

(d) The net charge of the system is *q* = *(-e)(ne-* - ***n,+) ,*** where

87reV oo*x2ex*

`2115`

In the very early stages of the universe, it is usually a good approximation to neglect particle masses and chemical potential compared with

kT.

(a) Write down the average number and energy densities of a gas of non-interacting fermions in thermal equilibrium under these conditions. (You need not evaluate dimensionless integrals of order 1.)

(b) If the gas expands adiabatically while remaining in equilibrium, how do the average number and energy densities depend on the dimensions of the system?

when *T N* 10l1 K in parts (c) and (d) below.

Assume that the fermions are predominantly electrons and positrons

(c) Is the assumption made in (a) that the particles are non-interacting reasonable? Why? [Hint: What is the average coulomb interaction energy?

Positron charge = 1 . 6 ~ 1 0 - lc~ou lomb; Bolteniann's constant *k* = 1.38 x erg/K].

(d) If the interaction cross sections in the electron-positron gas are typically of order of magnitude of the Thompson cross section *UT* = 8mg/3 (classical electron radius ***70*** = 2.8 x cm), estimate the mean free time between collisions of the particles. If the expansion rate in part (b) ***M***

lo4 sec-', is the assumption that the gas remains in equilibrium reasonable? Why?

(SUIVY, Buffalo)

Solution:

(a) In the stated approximation, we have

P

kT

& = p c , ***- W O O .***

so

The average number density is

The average energy density is

(b) The quasi-static adiabatic expansion process satisfies the equation d(pV) = -pdV. Neglecting the particle mass, we have **p** = p/3 (analogous to a photon gas), then

-dp - 4 dV

P 3 v)

giving

from which we obtain *T CX* V-'l3.

n *cx* V-I.

p *cx* v-4/3 **,**

Hence the particle number density

(c) The average distance between particles ***r*** *cx* ***n-'/3.*** The ratio of the Coulomb interaction energy per particle to the particle kinetic energy is

e2/r e2n1I3 **e2** 1

-N- - - N -

kT kT hc - 137 '

This implies that the interaction energy is much less than the kinetic energy, which makes the approximation in (a) reasonable.

(d) The mean free time is *t* - ***l / n q v ,*** where the average speed

kT

Hence *t* - **(E)-3c7~1** (Z) - 10-z3 s.

The assumption that the gas remains in equilibrium is reasonable for the mean free time is much shorter than the expansion time which is of the order of **10-4s.**

4. ENSEMBLES (2116 - 2148)

2116

Heat Capacity.

The constant volume heat capacity of a system with average energy *(E)* is given by C,, =

Use the canonical ensemble' to prove that: C is related to the meansquare fluctuation in the energy as follows:

Solution:

The partition function **is**

Z = exp(-E,/kT) **.**

1

Therefore, *(E)*= -Z *C* ***E,e-EnIkT.*** Then

2117

(a) Give the thermodynamic definition of the Helmholtz free energy F, the classical statistical mechanical definition of the partition function Z, and the relationship between these quantities. Define all symbols.

(b) Using these expressions and thermodynamic arguments show that the heat capacity at consant volume ***c,*** is given by

(c) Consider a classical system that has two discrete total energy states

*(SUNY, **Buflalo)***

Eo and El. Find Z and ***c*****, .**

Solution:

(a) F = ***U*** **-** TS, Z = exp(-PE(p, *q))dw* **,** where ***U*** is the internal energy, T the absolute temperature, *S* the entropy, ***p*** = l/kT, E(p, *q)* the energy of the system and `dw` = ***dpdq*** an infinitesimal volume element in the phase space, p and *q* being the genera.lized momentum and coordinate respectively, and ***k*** Boltzmann’s constant.

The relation between F and Z is

I

$F = -kT\ln Z$.

(b) From dF = -SdT - *pdV,* we have

S=- (g) *v*

Hence

-- (El - EOl2

4kT2cosh2 (El2 -kT E o)

2118

Consider the energy and fluctuation in energy of an arbitrary system in contact with a heat reservoir at absolute temperature *T* = l/k,f?.

(a) Show that the average energy *3* of the system is

where ***z*** = C exp(-PE,) sums over all states of the system.

n

-

(b) Obtain an expression for E2 in terms of the derivatives of lnz.

(c) Calculate the dispersion of the energy, (AE)2 = ***E2*** - *E* **.**

(d) Show that the standard deviation

- - -2

= ((AE)2)1'2 can be expressed

in terms of the heat capacity of the system and the absolute temperature.

N_(e) Use this result to derive an expression for AE/E for an ideal

(UC, Berkeley)

monatomic gas.

(e) For an ideal monatomic gas,

- 3 3

E = *-NkT,*

2 2 c, = ***-Nk***

and thus

E

2119

A useful way to cool He3 is to apply pressure *P* at sufficiently low temperature T to a co-existing liquid-solid mixture. Describe qualitatively how this works on the basis of the following assumptions:

(a) The molar volume of the liquid VL is greater than that of the solid Vs at all temperatures.

(b) The molar liquid entropy is given by

SL = 7RT with 7 **- 4.6** K-' **.**

(c) The entropy of the solid *Ss* comes entirely from the disorder associated with the nuclear spins **(s** = 1/2).

Note: Include in your answer a semi-quantitative graph of the p-T diagram **of** He3 at low temperatures (derived using the above information).

(Chicago)

Solution:

The Clausius-Clapeyron equation is

dp **AS** SL - *Ss*

dT AV VL-VS ·

_ -- -- -

1 ı

ı z

Tmin *T*

Fig. **2.24.**

1 For particles of spin -, SS = kNA In 2. Thus

2

dp 7RT-kNAln2 - 7RT-Rln2 __ - -

dT - VL - VS VL - vs .

dP

dT According to the problem, *VL* - *Vs* > 0, thus when *T* -t 0, - < 0. Hence, when

Tnill In2 In2 - = - K

7 **4.6** '

the pressure reaches the minimum value. This means that at sufficiently low temperatures (*T* < T,,,i,,), applying compression can lead to a decrease in temperature of the solid-liquid mixture.

A semi-quantitative **p-** *T* diagram of He3 at low temperatures is shown in Fig. **2.24.**

2120

(a) Describe the third law of thermodynamics.

(b) Explain the physical meaning of negative absolute temperature. Does it violate the third law? Why?

(c) Suggest one example in which the negative temperature can actually be achieved.

(d) Discuss why the negative temperature does not make sense in classical thermodynamics.

(S ***VNY,*** *Buflulo)*

Solution:

can have its absolute temperature reduced to zero.

(a) The third law or the Nernst heat theorem signifies that no system

(b) According to the Gibbs distribution, at equilibrium the ratio of the particle number of energy level En to that of Em is Nn/Nm = exp[-(En - *E,)/kT].* Hence, the particle number in the higher energy level is smaller than that in the lower energy level for *T* > 0. If the reverse is the case, i.e., under population inversion, the equation requires *T* < 0 and the system is said to be at negative temperature. This does not violate the third law for **a** system at negative temperature is further away from absolute zero than a system at positive temperature, from the point of view of energy.

1

2

(c) One such example is a localized system of spin - particles. We can introduce a strong magnetic field to align all the spins in the same direction as, i.e., parallel to, the direction of the magnetic field. We then reverse the magnetic field quickly so that there is no time for most of the

spins to change direction. Thus negative temperature is achieved.

(d) In classical thermodynamics, a negative temperature system is mechanically unstable. We divide a substance at rest into several parts. Let the internal energy and entropy of part **z** be *U;* and *S;(V;)* respectively. We have

where *E;* is the total energy of the part, *M;* is its mass, and ***p;*** is its momentum with **xp,** = 0. Mechanical equilibrium requires all **p;** = *0*.

As we have for a negative temperature system *dS;(U;)/dU;* = 1/T < *0,*
S, will increase when *U,* decreases, i.e., ***p,*** increases. Thus the entropies
S;(U,) are maximum when the 1p;I's reach maximum. This contradicts the
mechanical equilibrium condition **p;** = 0.

a

2121

Consider a system of two atoms, each having ony **3** quantum states of energies 0, *E* and **2s.** The system is in contact with a heat reservoir at temperature T. Write down the partition function Z for the system if the particles obey

(a) Classical statistics and are distinguishable.
(b) Classical statistics and are indistinguishable.
(c) Fermi-Dirac statistics.
(d) Bose-Einstein statistics.

(SUNY, Buffalo)

Solution:

(a) Z1 = A2, where A = 1 + exp(-P&) + exp(-2P&).
(c) Z3 = Aexp(-pe).
(d) Z, = A (1 + exp(-ZP&)).

2122

(a) You are given a system of two identical particles which may occupy any of the three energy levels

E, = n ~ , n = O , l , 2, **.**

The lowest energy state, *EO* = 0, is doubly degenerate. The system is in thermal equilibrium at temperature *T.* For each of the following cases determine the partition function and the energy and carefully enumerate the configurations.

1) The particles obey Fermi statistics.
2) The particle obey Bose statistics.
3) The (now distinguishable) particles obey Boltzmann statistics.

(b) Discuss the conditions under which Fermions or Bosons may be treated as Boltzmann particles.

(SVNY, Buflalo)

Solution:

(a) Considering the systems as a canonical ensemble, the partition function is ***z*** = ~ w , e x p (- P E ,) , where w, is the degeneracy of energy level n.

n

1) The particles obey Fermi statistics. We have
The configurations are shown in Fig. 2.25(a)

a b

2- ▬ 1- -

n = o % *1*

E.0 2E 2E

2- -

I - -

a b

€= 0 0

Fig. **2.25.**

2) The particles obey Bose statistics. We have

The configurations are shown in Fig. 2.25(b).

3) The particles obey Boltzmann statistics. We have

The configurations are shown in Fig. 2.25(c).

(b) When the non-degeneracy condition is satisfied, i.e., when. ***e-a w***
<< 1, the indistinguishability of particles becomes unimport&
nt and Ferrnions and Bosons can be treated as Boltzmann particles.

2123

(a) Give a definition of the partition function ***z*** for a statistical system.

(b) Find a relation between the heat capacity of a system and -

a2 Inz

aa2 '

1

kT where ***P*** = -.

(c) For a system with one excited state at energy **A** above the ground state, find an expression for the heat capacity in terms of **A.** Sketch the dependence on temperature and discuss the limiting behavior for high and low temperatures.

(UC, ***Berkeley)***

Solution:

(a) The partition function is the sum of statistical probabilities.

For quantum statistics, ***z*** = x e x p (- P E ,) , summing over all the
8
quantum states.

For classical statistics, ***z*** = 1 e xp(-PE)dI'/h7, integrating over the phase-space where 7 is the number of degrees of freedom.

a *E* = -- In ***z*** ,

ap

-

1 *a* - ***1*** *a2*

d T kP2 *ap* ***kP2*** ***ap2*** *E* = - - - l n z , *aE*

cv = - =

(c) Assume the two states are non-degenerate, then

A

eA/kT + 1

-

- ***Ae-A/kT***

1 + ***e-AlkT***

E=

dz ***eA/kT***

(1 + ***eAlkT)2*** *

c, = - = ***k*** (&) dT

The variation of specific heat with temperature is shown in Fig. **2.26.**

f ***cv***

Fig. 2.26.

2124

Consider a collection of N two-level systems in thermal equilibrium at a temperature T. Each system has only two states: a ground state of energy 0 and an excited state of energy ε. Find each of the following quantities and make a sketch of the temperature dependence.

(a) The probability that a given system will be found in the excited state.

(b) The entropy of the entire collection.

(MIT)

Solution:

(a) The probability for a system to be in the excited state is P =
1

-e-'fkT, where ***z*** = 1 + ***e-'fkT,*** i.e.,
z

The relation between probability and temperature is shown in Fig. **2.27.**

Fig. **2.27**

(b) *ZN* = [1+ ***e-'fkTIN*** **,** *F* = -kTlnzrJ **,**

The relation between entropy and temperature is shown in Fig. **2.28.**

T

Fig. **2.28.**

2125

N weakly coupled particles obeying Maxwell-Boltzmann statistics may each exist in one oi the **3** non-degenerate energy levels of energies *-E,* 0, *+E.* The system is in contact with a thermal reservoir at temperature *T.*

(a) What is the entropy of the system at T = 0 K?

(b) What is the maximum possible entropy of the system?

(c) What is the minimum possible energy of the system?

(d) What is the partition function of the system?

(e) What is the most probable energy of the system?

(f) If *C(T)* is the heat capacity of the system, what is the value of lrn *C(T)dT?*

o T

(UC, **Berkeley)**

Solution:

(a) At *T* = 0 K, the entropy of the system is *S(0)* = 0.

(b) The maximum entropy of the system is

S,,,,, = klnn,,,,, = kln3N = Nkln3 **.**

(c) The minimum energy of the system is ***-NE.***

(d) The partition function of the system is

= (p / k T + 1 + ,-EIkT)N **.**

(e) When N >> 1, the most probable energy is the average energy

NE, ***M*** NE

2NEsinh -- - (s)

1 + **2** c o s ~ (g) ,

where a = exp(E/kT).

(f) J m m d T = l m d S = *S(o0)* - *S(0)* = Nkln3 **.**

o T

2126

Find the pressure, entropy, and specific heat at constant volume of an ideal Boltzmann gas of indistinguishable particles in the extreme relativistic limit, in which the energy of a particle is related to its momentum by *E* = **cp.** Express your answer as functions of the volume V, temperature T, and number of particle N.

(Princeton)

Solution:

Let *z* denote the partition function of a single particle, *Z* the total partition function, *p* the pressure, *S* the entropy, *U* the internal energy, and c the specific heat. We have

81rV

N

a

ap *u* = -- lnZ = *3NkT*

c = 3 N k .

2127

A vessel of volume *V* contains *N* molecules of an ideal gas held at temperature *T* and pressure *PI.* The energy of a molecule may be written in the form

where *&k* denotes the energy levels corresponding to the internal states of the molecules of the gas.

(a) Evaluate the free energy *F* = -kTlnZ, where Z is the partition function and k is Boltzmann's constant. Explicitly display the dependence on the volume *Vl.*

Now consider another vessel, also at temperature *T,* containing the same number of molecules of an identical gas held at pressure *PZ.*

(b) Give an expression for the total entropy of the two gases in terms of *Pi* , *P2,* T, ***N.***

(c) The vessels are then connected to permit the gases to mix without doing work. Evaluate explicitly the change in entropy of the system. Check whether your answer makes sense by considering the special case *Vl* = *V2 (z.e.,Pl* = **Pz) .**

(Princeton)

Solution:

(a) The partition function of a single particle is

where *zo* = xexp(-Cn/kT) refers to the internal energy levels. Taking account of the indistinguishability of the particles, the partition function of

n

the N particle system is

so

F = **-kTlnZ**

Thus

SI = **Nk** ($+ ;3I n (y+ :+) So) ,

where a

aP *So* = **lnzo** - ***P-*** **lnzo**

The total entropy is

S = s1 + *S,*

= 2Nk [ln-~ N+ ~ 2 l n (~) + ~ +. S o 1

(c) After mixing, the temperature of the ideal gas is the same as before, so that

S' = 2Nk [h + -3I n (2rmkT 7+ 5 +S) o] , 2N 2

When ***Vl*** = ***V2,*** AS = ***0*** as expected.

2128

(a) Calculate the partition function ***z*** of one spinless atom of mass *M* moving freely in a cube of volume ***V*** = ***L3.*** Express your result in terms of the quantum concentration

MkT 3/2

n,=(.> *

Explain the physical meaning of n,.

(b) An ideal gas of ***N*** spinless atoms occupies a volume V at temperature ***T.*** Each atom has only two energy levels separated by an energy A. Find the chemical potential, free energy, entropy, pressure and heat capacity at constant pressure.

Solution:

(SVNY, Buflulo)

(a) The energy eigenvalues are given by

h2

2mL2

2M

s = -(n2 + np + n;) ,

2 1 *2 2 - P* = - ***(P:*** + *Py* + ***P,)*** - ***2M*** 9

where **n,,ny,nl** = O , f l , ...

The energy levels can be thought of as quasi-continuous, so that the number of quantum states in the range ***p*** -+ ***p*** + ***dp*** is ***--p2dp,*** whence the number of states in the energy interval E + E + ***ds*** is ***- (2 M) 3 / 2 f i d e .***

Hence

4sv

h3

2sv

h3

is the average number of quantum states in unit

MkT 3/2 where n, = (7)

volume.

(b) The classical ideal gas satisfies the non-degeneracy condition. The partition function of a sub-system is ***z*** = exp(-PsI) + exp(-Ps2), ***e2*** =

~1 + A. Hence the partition function of the system is

The free energy is

F = -kTlnZ = -NkTln ***(e - p ' l + e--Bea)***

The chemical potential is

The pressure is

The entropy is

- k l n N ! = N k

N(&le-@'l + ~ 2 e - P ' ~)

+ *T (e - P c l* + **e-0'2)**

The heat capacity at constant pressure is

a

- N A 2 - N A 2

2kT2 (1 + cosh k)   4kT2 cash (&) .

2129

(a) Consider an ideal gas of N particles of mass **rn** confined to a volume *V* at a temperature T. Using the classical approximation for the partition function and assuming the particles are indistinguishable, calculate the chemical potential ***p*** of the gas.

(b) **A** gas of N particles, also of mass ***rn,*** is absorbed on a surface of area ***A,*** forming a two-dimensional ideal gas at temperature T on the

surface. The energy of an absorbed particle is ***E*** = lpI2/2m - ***EO,*** where **p = (pz,pv)**a nd ***€o*** is the surface binding energy per particle. Using the same approximations and assumptions as in part (a), calculate the chemical potential ***p*** of the absorbed gas.

(c) At temperature T, the particles on the surface and in the surrounding three-dimensional gas are in equilibrium. This implies a relationship between the respective chemical potentials. Use this condition to find the mean number n of molecules absorbed per unit area when the mean pressure of the surrounding three-dimensional gas is **p.** (The total number of particles in absorbed gas plus surrounding vapor is No) **.**

(Princeton)

Solution:

(a) The classical partition function is

N!

Thus

G = F + **pV** = ***-kT*** In ***z*** + NkT

= i V k T l n ~ - ~ l n (~ **,**)]

p = -kT [,nx + %In (y.)   ]

(b) The classical partition function for the two-dimensional ideal gas is

z* = -** ***AN (2T;kT) . ***eNco/kT*** **.**

N!

Thus

G = F + p A = - N k T [In-+ln ; (2T;kT) +%I ,

(c) The chemical potential of the three-dimensional gas is equal to that of the two-dimensional gas. Note that in the expression of the chemical

V kT

N v potential for the three-dimensional gas, - = **-**, and in that for the two-

A 1

N n

dimensional gas, - = -. Since the two chemical potentials have the same value, one obtains

2130

A simple harmonic one-dimensional oscillator has energy levels En = (n + *1/2)Aw,* where *w* is the characteristic oscillator (angular) frequency and n = 0 , 1 , 2 , **... .**

(a) Suppose the oscillator is in thermal contact with a heat reservoir at temperature *T,* with - << 1. Find the mean energy of the oscillator as a function of the temperature *T.*

kT

AW

(b) For a two-dimensional oscillator, n = n, + ny, where n, = **0 , 1 , 2 , . . .** and ny = *0 , 1 , 2 , . . . ,* what is the partition function for this case for any value of temperature? Reduce it to the degenerate case *w,* = **wy.**

(c) If a one-dimensional classical anharmonic oscillator has potential energy V(z) = ***cx2*** - gz3, where ***gx3*** << **cz2,** at equilibrium temperature *T,* carry out the calculations **as** far as you can and give expressions as functions of temperature for

1) the heat capacity per oscillator and

2) the mean value of the position z of the oscillator.

(UC, Berkeley)

tw

(a) Putting ***a*** = - = *Awp,* one has

kT

Solution:

(b) There is no difference between a two-dimensional oscillator and two independent one-dimensional oscillators, then the partition function is

eaz/2 eay/2 ***z=-.-***

eaz - **1**

When *w,* = ***wy, a,*** = ***ay*** = ***a,*** we have

eau - **1** ·

ea

2 =

(en - **1)2** ·

(c) 1) **We** calculate the partition function

z = / exp[-(cx2 - *gz3)/kT]dx* **.**

(Note that the kinetic energy term has not been included in the expression, this is done by adding - in the heat capacity later.) The non-harmonic term (exp(gs3/kT) - **11** is a small quantity in the region of motion. Using Taylor's expansion retaining only the lowest order terms, we get

k

2

The mean value of the potential energy is

The heat capacity per oscillator is

2) In the first-order approximation, the mean value of the position *x* of the oscillator is

2131

Consider a dilute diatomic gas whose molecules consist of non-identical pairs of atoms. The moment of inertia about an **axis** through the molecular center of mass perpendicular to the line connecting the two atoms is I. Calculate the rotational contributions to the specific heat and *to* the absolute entropy per mole at temperature T for the following limiting cases:

(a) *kT* >> h2/I,

(b) *kT* << h2/I.

Make your calculations sufficiently exact to obtain the lowest order

(CUSPEA)

non-zero contributions to the specific heat and entropy.

Solution:

The contribution of rotation to the partition function is

z$. = (zR)N 1

where N is the total number of the molecules in one mole of gas, and

The contribution to energy is

The contribution to specific heat is

The contribution to entropy is

(a) kT >> ***h 2/I*,** i.e., ph2/21 << 1. We have

ER = NkT ,

CR = Nk .

(b) *kT* << *h2/I.* We have

zR = 1 + *3e- a(h'/4 n a l)* + . ,. + *3 e - h 1 ~ 4 n 2 k ~ ~*

-"*e - h 2 1 4 n 2 1 k T*

I 3Nh2 e-h'14n21kT

En = ***3N*** 1+ *3 e - h a / 4 n 2 1 k T* -***I***

CR = ***-3N'4*** *e - h 2 / 4 n a I k T PkT2*

Nh2 *- h' / 4 n 2 IkT* S, = ***kN*** ln(1 + ***3e-ha/4n21kT***

h 2 / 4 n a I k T 3Nh2e ***- h 2 / 4 n 2 1 k T IT***

2132

1

2

An assembly of ***N*** fixed particles with spin - and magnetic moment

/.LO is in a static uniform applied magnetic field. The spins interact with the applied field but are otherwise essentially free.

(a) Express the energy of the system as a function of its total magnetic

(b) Find the total magnetic moment and the energy, assuming that

(c) Find the heat capacity and the entropy of the system under these

(UC, ***Berkeley)***

moment and the applied field.

the system is in thermal equilibrium at temperature *T.*

same conditions.

Solution:

(a) *E* = *-MH.*

(b) Assume that ***ii*** is the average magnetic moment per particle under the influence of the external field when equilibrium is reached, then *M* =

NjZ and

e ~ o H / k T- e - P oH/ k T

P = p o ***e ~ o H / k T+ e -@oH/ k T*** = /.Lo

Thus *E* = --*NpOH* tanli(poH/kT).

The partition function of the system is

z = *(a* + *l / a) N* with *a* = exp(poH/kT) .