A. M. D. G.

ST. JOSEPH'S COLLEGE
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NOTE BOOK

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Subject Zool

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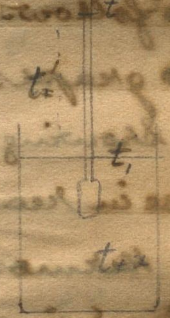
Notes on Heat

23-6-38 ## Thermometry.

cf (Page 1–10) B.A. Notes.

Correction for the exposed Column.



Let the reading of the thermometer be t, & the correction, t_1 the division at the level of the liquid, t' the average temp. of the exposed portion. If v_0 be the vol. at zero of each division, $v_0(1+gt'_*)$ is vol. in the exposed portion, $v_0(1+gt')(t-t_1)$ is total vol. of the exposed portion; if the mercury in it be raised from t'_* to $t+x$ its volume will be $v_0(1+gt')(t-t_1)\dfrac{1+m(t+x)}{1+gt'_*}$

This is the vol. of $(t+x-t_1)$ division at $(t+x)^\circ$ i.e. the above expn.

$$= v_0(t+x-t_1)(1+g\,\overline{t+x})$$

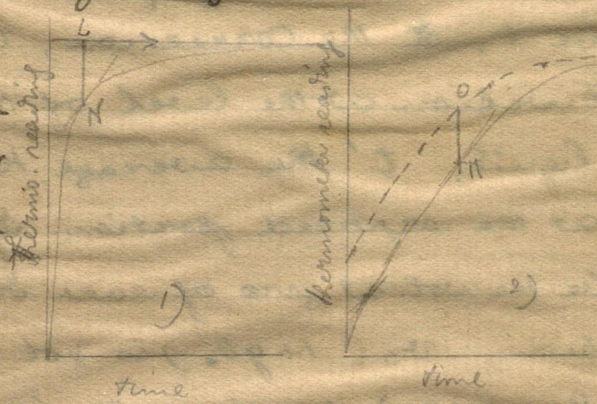
Putting $t-t_1=\theta$, $1+gt=G$, $1+gt'=G'$, $1+mt=M$, $1+mt'=M'$;

$$G'\theta(M+mx) = M'(G+gx)(\theta+x)$$

$$\text{ie } x\{G'\theta m - M'(g\theta+G)\} = M'G\theta - M\theta G'$$

$$= \theta(M'G - MG')$$

$$\therefore x = \theta\,\frac{M'G - MG'}{(G'm - M'g)\theta - M'G}$$



Lag A correction for lag can be made s follows. Let wo graphs be drawn) Showing the rate of ise in reading when e thermometer is laced in a ~~fixed~~ ath of steady temp.

& the 2) showing the rate when the thermo- meter is in the given bath whose temp. is ising. Take a pt R on (2) & find another on N ~~how~~ such that the slopes at R & N are equal. $\frac{d\theta}{dt}$ being equal the reading of the thermometer hould in both cases be equally below the mp. of the bath. Thus the pt O is plotted. n this way the temp. of the given bath corres ponding to any reading of the thermometer can be found.

Mathematically $\frac{d\theta}{dt} = k(\theta' - \theta)$

$$= -k(\theta - \theta')$$

$$\therefore \int \frac{d\theta}{\theta - \theta'} = -k \int dt$$

ie $\log(\theta - \theta') = -kt + \log A$.

When $t = 0$, let θ_0 be the reading of the thermometer.

$$\log(\theta_0 - \theta') = \log A$$

$\therefore A = \theta_0 - \theta'$

$$\therefore \frac{\theta - \theta'}{\theta_0 - \theta'} = e^{-kt}$$

ie $\theta' - \theta = (\theta' - \theta_0)e^{-kt}$.

The value of k can be found from graph ①.

27-6-38 Gas Thermometers. Assuming the gas to be perfect & the eqn $pv = RT$ to be true we can show that $\alpha_p = \alpha_v = \frac{1}{T_0}$, α_p & α_v being the coeffts of increase of press. & increase of vol.

$$\alpha_v = \frac{1}{v_0} \times \left(\frac{dv}{dT}\right)_p$$

Now $pv = RT$

$\therefore p\left(\frac{dv}{dT}\right)_p = R$. & $pv_0 = RT_0 \therefore \frac{1}{v_0}\left(\frac{dv}{dT}\right)_p = \frac{1}{T}$

ilarly $v\left(\frac{dp}{dT}\right)_v = R$ & $vp_0 = RT_0$

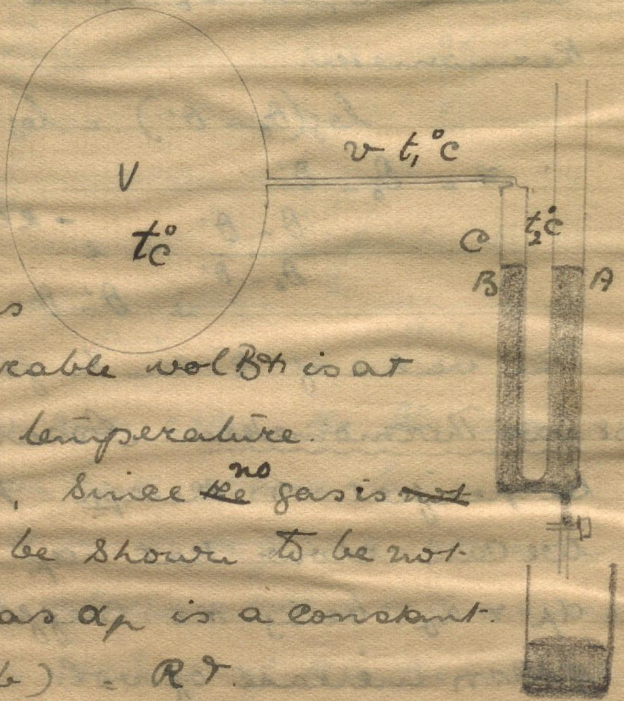
$$\therefore \frac{1}{p_0}\left(\frac{dp}{dT}\right)_v = \frac{1}{T_0}.$$

∴ The pressure coefft = vol. oefft & both are constants. Hence ither constant vol. or constant gas thermometers can be used for temp. measurements.

But constant ress. thermometers ave various isadvantages.

The expanding gas ccupies a considerable vol & is at n indeterminate temperature.

Apart from that, since ~~the~~ no gas is ~~not~~ erfect α_p can be shown to be not constant, whereas α_p is a constant.



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

$$\therefore p = \frac{RT}{v-b} - \frac{a}{v^2}.$$

$$\frac{dp}{d\tau} = \frac{R}{v-b}$$

$$\therefore \alpha = \frac{1}{p_0}\cdot\frac{dp}{d\tau} = \frac{\frac{R}{v-b}}{\frac{R\tau_0}{v-b} - \frac{a}{v^2}}$$

$$= \frac{Rv^2}{R\tau_0 v^2 - a(v-b)}$$

which is a constant independent of

$$\left(p + \frac{a}{v^2}\right)(v-b) = R\tau.$$

$$\therefore v - b = \frac{R\tau}{p + \frac{a}{v^2}} = \frac{R\tau}{p}\left(1 - \frac{a}{pv^2}\right)$$

$$= \frac{R\tau}{p}\left(1 - \frac{a}{p}\cdot\frac{p^2}{R^2\tau^2}\right)$$

$$= \frac{R\tau}{p} - \frac{a}{R\tau}$$

$$\therefore \left(\frac{dv}{d\tau}\right)_p = \frac{R}{p} + \frac{a}{R\tau^2} = \frac{R}{p}\left(1 + \frac{ap}{R^2\tau^2}\right)$$

$$(v_0 - b) = \frac{R\tau_0}{p}\left(1 - \frac{ap}{R^2\tau_0^2}\right)$$

$$\text{ie}\quad v_0 = \frac{R\tau_0}{p}\left(1 - \frac{ap}{R^2\tau_0^2}\right)\left(1 + \frac{b}{v_0}\right)$$

$$\therefore \alpha_v = \frac{1}{v_0}\cdot\left(\frac{dv}{dT}\right)_p = \frac{1}{T_0}\left\{1+\frac{ap}{R^2T^2}\right\}\left\{1+\frac{ap}{R^2T_0^2}\right\}\left\{1-\frac{b}{v_0}\right\}$$

In the above expression, $1+\frac{ap}{R^2T^2}$ is not a Constant, it depends on T $\therefore$ α_v decreases s temperature rises.

However, if T is very high, $\frac{ap}{R^2T^2}$ approxi-ates to zero & α_v is nearly Constant.

But it Can be shown that when the temperature is high the sensitivity dC/dt is Small (C being volume of gas in the Stem B & t temp. of the bulb.)

Let V, v, C be the volumes (at 0°C) of the bulb, leading tube & Stem B & let t, t_1, t_2 be the temperatures. t & C are variables.

When bulb is at zero, mass of gas

$$= \left\{V + \frac{v(1+gt_1)}{(1+\alpha t_1)}\right\}\frac{H}{760}\times\rho$$

where H is the atmosheric pressure & ρ density of the air t N.T.P.

Mass of gas when bulb is at t°C,

$$\left\{V\frac{1+gt}{1+\alpha t} + v\frac{1+gt_1}{1+\alpha t_1} + C\frac{1+gt_2}{1+\alpha t_2}\right\}\frac{H}{760}\times\rho.$$

The two expressions are equal

$$\therefore v = V\frac{1+gt}{1+\alpha t} + C\frac{1+gt_2}{1+\alpha t_2}.$$

Differentiating C w. r. to t,

$$0 = V\frac{(1+\alpha t)g-(1+gt)\alpha}{(1+\alpha t)^2} + \frac{dC}{dt}\cdot\frac{1+gt_2}{1+\alpha t_2}.$$

$$\text{ie } \frac{dC}{dt} = V\frac{\alpha-g}{(1+\alpha t)^2}\cdot\frac{\cancel{t}1+\alpha t_2}{1+gt_2}$$

$$= \left\{V(\alpha-g)\frac{1+\alpha t_2}{1+gt_2}\right\}\frac{T_0^{\,2}}{T^2}. = \frac{\text{Con}}{T^2}$$

where T is the absolute temperature. Hence the sensitivity reduces with increase of temperature.

Hence Constant vol. therm. only can be taken as the Standard & is what the Bureau international has taken.

<u>The gas Constant.</u>

In eqn $pv = RT$ & v is the vol. of 1 gm & R is different for different gases. But the gas Consta

hich is the same for all the gas is
iven by the eqn $pv_m = R_u T$
v_m being the vol. of one gram ~~atom~~ mole.
ule of the gas & = 22·4 litres at N.T.P.

∴ ~~$R_u =$~~ $\frac{v_m}{v} = M$ the molecular wt

∴ $R_u = M \times R$ or $R = R_u / M$.

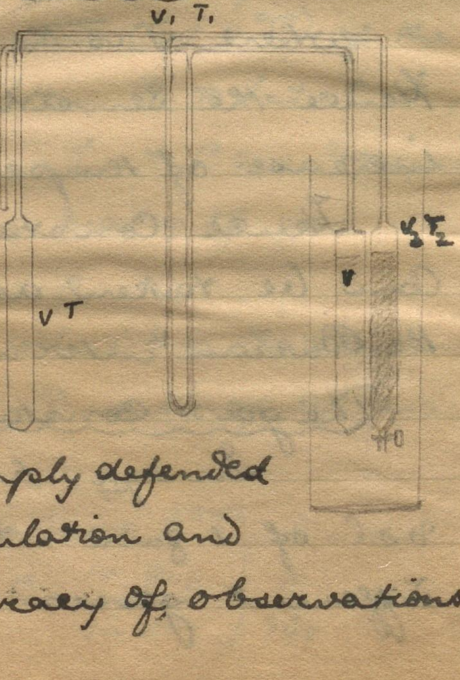
& $R_u = p v_m / T$

$= \frac{76 \times 13.6 \times 981 \times 22400}{273}$

$= 8.318 \times 10^7$ ~~de~~ ergs per degree.

$= 1.981$ calories per degree.

allendar's Compensated Const. Pres. thermometer 30-6-38



The compensation
orrects for the first
ource of error viz
he temp of the gas in
he leads & in the measuring
ulb. But the other two
ources are left uncorrected.
Yet the thermometer is amply defended
y its simplicity of manipulation and
alculation, by the accuracy of observations

(Since observations are made by weighing)

Since $PV = RT$, $P.\frac{V}{T} = R$ a constant

When V is the vol. of ~~unit~~ m gms ~~mass~~, R ~~or the~~ ha to be replaced by mR. Let the mass of gas in each part of the thermometer be m gms & the press. p

$$P\left(\frac{V}{T} + \frac{v_1}{T_1} + \frac{v_2}{T_2}\right) = mR = P\left(\frac{v_1}{T_1} + \frac{V}{T_2}\right)$$

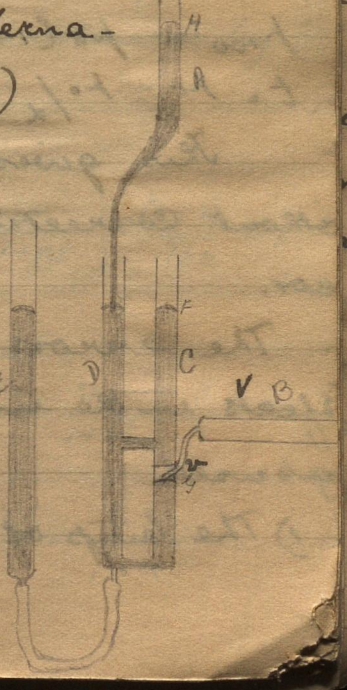
$$\text{ie} \quad \frac{V}{T} = \frac{V - v_2}{T_2} \quad \therefore \quad T = T_2 \Big/ \frac{V - v_2}{V}$$

T_2 is the temp of melting ice, V is a constan of the thermometer & v_2 is the only observation to be made.

Constant vol. Standard thermometer.

(adopted by the Bureau Internationale de poids et mesures,)

Consists essentially of a bulb B containing a certain fixed mass of gas, & the manometer arrangement ACDE. ~~Gas~~ C is partitioned into two, the lower level G of mercury serving to



eep the vol. of gas constant, & the upper level howing the pressure. In D is inserted a an barometer tube A bent as shown in the igure to facilitate cathetometer observations is the manometer which can be adjusted to e reqd ~~any~~ height till the level G touches a platinum eedle protruding from the ~~g~~ connecting tube f the gas bulb. Let the diff FH be H & FG be h. ressure of the gas is (H+h) The pressures re found at two known temperatures 0°C & 100°C at another ~~an~~ unknown temp t. Let the ressures be ~~p_1, p_2, p_3~~ p_0, p_{100} & p_t.

$$p_{100} = p_0(1+\alpha 100) \quad \text{ie} \quad \alpha = \frac{p_{100}-p_0}{100}$$

$$t = p_t - p_0/\alpha \quad \therefore \quad t = \frac{p_t - p_0}{p_{100}-p_0}\,100$$

This gives an approximate value of t ithout correcting for any of the sources of rror.

The errors are due to two sources efects in the instrument, 2) Defects in the as used

1) The temp of the leading tube & of the space

above gas is not the same of as of the bulb.

The vol. of the bulb increases with (1) temperature 2) with increase of internal pressure

Let V be the vol. of the bulb at 0°C & v that of the dead space at t° (the temp. of the dead space supposed to be constant). Let H & H+h be the pressures at ~~t°~~ zero & θ

At zero, $\left(V + \frac{v}{1+\alpha t}\right)\frac{H}{760}\rho$ is the mass of the gas

At θ the temp to which the bulb is raised its vol increases to $V(1+g\theta)$ g being coeff of exp. ~~due to~~ of the material of the bulb & an additional increase βh is caused by the increase of int. ~~press~~.

∴ Mass of the gas

$$\left\{\frac{V(1+g\theta)+\beta h}{1+\alpha\theta} + \frac{v}{1+\alpha t}\right\}\frac{H+h}{760}\times\rho.$$

The two masses being equal

$$\left(V+\frac{v}{1+\alpha t}\right)H = \left\{\frac{V(1+g\theta)+\beta h}{1+\alpha\theta} + \frac{v}{1+\alpha t}\right\}(H+h)$$

i.e. $$VH = \frac{V(1+g\theta)+\beta h}{1+\alpha\theta}(H+h) + \frac{hv}{1+\alpha t}$$

$$\theta = \frac{1}{\alpha}\left[\frac{\{V(1+g\theta)+\beta h\}(H+h)}{VH - \frac{hv}{1+\alpha t}} - 1\right]$$

In the term $g\theta$ which is small we can substitute an approximate value

$$\theta = \frac{p_\theta - p_0}{p_{100} - p_0} \times 100$$ & thus find

e correct value of θ.

Another source of error is that the gas

oes not obey Boyles law. ~~The~~ pv is not

a const RT, but some expression of

e form $A + Bp + Cp^2 + \ldots$ where $A, B, C \ldots$

e functions of temperature. The series is

rapidly converging one & ~~for~~ sufficient

ccuracy is obtained if we take $PV = A + BP$.

$$t = \frac{p_t - \cancel{p_{00}}}{p_{100} - p_0} 100$$

$$= \frac{p_t v_0 - p_0 v_0}{p_{100} v_0 - p_0 v_0} 100.$$

Now we have $p_0 v_0 = A_0 + B_0 p_0$

$$p_{100} v_{\cancel{00}} = A_{100} + B_{100} p_{100}$$

$$p_t v_0 = A_t + B_t p_t$$

We shall denote $A_{100} - A_0$ by δ, $A_t - A_{\cancel{00}}$

by ε, $\beta_{100}p_{100} - \beta_0 p_0$ by ζ, & $\beta_t p_t - \beta_0 p_0$ by η

$$\therefore\ t = \frac{\varepsilon + \eta}{\delta + \zeta}\,100$$

$$\equiv\ = \frac{\varepsilon}{\delta}\left\{\frac{1 + \frac{\eta}{\varepsilon}}{1 + \zeta/\delta}\right\} 100$$

$$= \frac{\varepsilon}{\delta}\left\{1 + \frac{\eta}{\varepsilon}\right\}\left\{1 - \frac{\zeta}{\delta}\right\} 100$$ if we neglect higher powers of $\beta_0 p_0/A_0$

$$= \varepsilon/\delta\left\{1 + \eta/\varepsilon - \zeta/\delta\right\}$$

Now in the limit $p \rightarrow 0$

$$p_0 v_0 = A_0, \quad p_{100} v_0 = A_{100}$$

$$\& \ p_t v_0 = A_t$$

$$\therefore\ \frac{\varepsilon}{\delta}100 = \frac{p_t - p_0}{p_{100} - p_0}100 = t_{lim}$$ t_{lim} being the temperature if the gas were perfect.

$$\therefore\ t = t_{lim}\left(1 + \eta/\varepsilon - \zeta/\delta\right)$$

$\therefore$ The correction necessary is $t_{lim} - t = t_{lim}\left\{\eta/\varepsilon - \zeta/\delta\right\}$

Now $\eta, \varepsilon, \zeta, \delta$ are known, & t al is known. The correction being a small quantity t can be substituted for t_{lim} on the right & $t_{lim} - t$ can be calculated

4 7-'88 Pyrometry. Gas thermometers cannot be used at temperatures above 500 °C

for though the gas itself may ~~exp~~ increase in bressure very regularly at these temperatures, he containers (which should be porcelain r platinum) become leaky, & the manoeters to be used at such temperatures are very unwieldy. ~~Hence~~ electrical resistance thermometers are used.

The platinum resistance thermometer

t first introduced by Sieman with a very omplicated formula was later made easy f manipulation by the simple Callendar and Griffith's bridge. For high ranges the inear formula $R_t = R_0(1+\alpha t)$ has tobe replaced by a hyperbolic one

$$R_t = R_0(1+\alpha t+\beta t^2)$$

nd a correction has therefore to be applied.

Let the ~~temp.~~ resistance be measured at 0, 100 & t°C. f the linear formula is supposed to olds good

$$R_{100} - R_0 = R_0 \alpha 100$$

$$R_t - R_0 = R_0 \alpha t_p$$

t_p being the temp as measured by the linear formula.

$$\therefore \cancel{R}\ t_p = \frac{R_t - R_0}{R_{100} - R_0} \times 100.$$

If t is the correct temperature of the bath

$$t_p - t = \frac{R_t - R_0}{R_{100} - R_0} \times 100 - t$$

$$= \frac{\alpha t + \beta t^2}{100\alpha - 100^2\beta} \times 100 - t$$

$$= \frac{\cancel{100}(\alpha t + \beta t^2) - t(\cancel{100}\alpha + 100\beta)}{\cancel{100}\ \alpha + 100\beta}$$

$$= \frac{-100\beta t + \beta t^2}{\alpha + 100\beta}$$

$$= \left(\frac{t^2}{100^2} \mp \frac{t}{100}\right) \frac{100^2\beta}{\alpha + 100\beta}$$

$$= \left\{\frac{t^2}{100^2} - \frac{t}{100}\right\} \delta$$

where $\delta = \frac{100^2\beta}{\alpha + 100}$

& is a constant factor in correction which can be calculated if α & β are known. α & β can be calculated if R_0 & the resistances at ~~both~~ & tw the known temperatures say the B. P of wa

& the melting point of Sulphur ~~& R_0~~ are known.

The advantages of the instrument are hat it is very handy, its Calculation is simple, it is free from all zero errors, ts degree of accuracy is very great, & $\frac{1}{100}$° up to 500°C & $\frac{1}{10}$° between 500 & 200°C. The one disadvantage is that e metal ~~to~~ should be ~~in~~ extremely un-lloyed, which is not an easy Condition. Slight mpurities affect the resistance to a large xtent especially at low temperatures.

Thermocouples have a range even bigger han the resistance thermometers. The Couple ements usually employed are platinum nd an alloy of platinum & Rhubidium. e formulae for the e.m.f. when one junc-ion is in melting ice & the other at t re for ranges

0 – 400°C $e = At - B(1 - e^{Ct})$

400 – 1200°C $e = -A' + B't + C't^2$

& 1200 – 1800°C $e = -A'' + B''t + C''t^2$.

For higher ranges radiation pyromete are employed which vide later.

Low temperature Thermometers

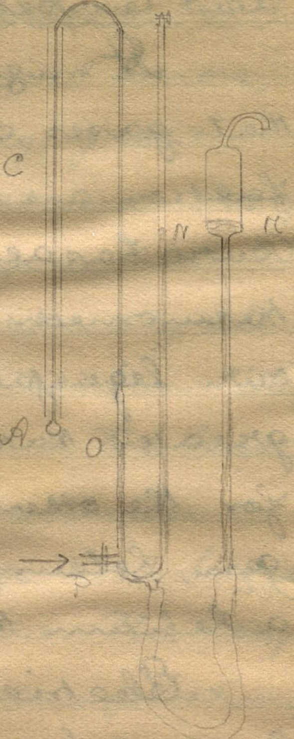
Saha 38

It might appear at first sight that gases as they approach their liquefaction are * unreliable for thermome But it has actually been found that an oxyge thermometer can be used to measure its own liquefaction point & the error is not greater than $\frac{1}{2}$ °C. The same is true for the other permanent gases like hydrogen, helium etc. Thus up to 5° Kelvin a helium thermometer is quite reliable.

Electrical resistance thermometers cannot be used at low temperature fo it is impossible to get a metal perfectly pure, & the slightest trace of impurity causes great discrepancy in behaviour.

Below 5°K (the liquefaction po of helium) gas thermometers canno

e used & they are supplanted by vapour
pressure thermometers They depend for
heir working on the exptly
bserved fact that the Satura-
ed vapour pressure of a
iquid has a Constant value
t each temperature. The
igure shows a model of the
hermometer used at Leyden.
A is a Small bulb ~~into~~
Contains The bulb & a
hich the liquid. ~~Can be~~ ~~A~~
apillary leading from it
Covered by a Copper tube C
o ensure uniform temper-
ture, Constitute the ~~ther~~-
other part which has to be ~~subj~~ placed
the bath whose temperature is required.
P is an inlet for the gas. By lowering
e manometer limb M mercury level can
e brought below & a certain amount
f gas (nitrogen or helium) Can be drawn



in. N is now raised & the pressure of the gas inside is increased thereby liquefying a part which goes to A. The saturated vapour pressure depresses the mercury level in O below that in N, & from a knowledge of the difference the temperature of the bath can be found.

Expansion The accuracy of determinations of the coefft of linear expansion is greatly affected by the actual expansi being very small. Hence the necessity of special arrangements to measure the expansion. One of the most accurate metho is that where interference fringes are made use of.

Pre 316 Fizeau's Interference method. This method is capable of very great accuracy and is especially suitable when small specime of the experimental substance are availab as in the case of crystals. The ~~flat~~ Crystal

Cut into a ~~parallel~~ plate P with parallel sides.
The plate is placed on a metal disc AB
hrough which project three levelling screws
These screws support a
lass plate CD whose
osition is adjusted
o that it lies very nearly
arallel to and at a short

istance from the upper surface of P. A beam
f monochromatic light falling normally on
D is partially reflected upwards ~~on~~ at the
ower surface of CD & partially reflected at
he upper ~~p~~ surface of ~~C~~ P. The crystal
hould be truly plane & polished. The two
eflected portions are in a position to interfere
nd the fringes are clear & formed at infinity
s ~~CD~~ the lower surface of CD is truly plane
s ∥ to P. They are ~~st~~ parallel st. lines ~~if~~ formed at the film
the plate is inclined. If the lower surface
f CD is convex, Newton's rings are seen
t the film. In Fizeau's expt the ~~sur~~ plate

was plane and inclined & 11 fringes were observed. The whole apparatus was subjected to a ~~diff~~ high temperature bath. The thickness of the film decrease due to the differential expansion of the crystal and the platino-iridium screw. When the diminution is $\frac{\lambda}{2}$ one fringe will pass across the reference line in the focal plane of the microscope. As the temperature rises, more & more fringes are displaced. If n be the total ~~num~~ number of displaced fringes (n being an integer + a fraction) $\frac{n\lambda}{2}$ is the expansi & ∴ ~~Δμ~~ Coefft of (apparent) linear expansion $= \frac{n\lambda}{2L} \times \frac{}{t_1}$ L being the total height of the crystal, t_1, t_2 the initial & final temperatures. The ~~real~~ Coefft of linear expansion is got by adding the Coefft of exp. of the levelling screws.

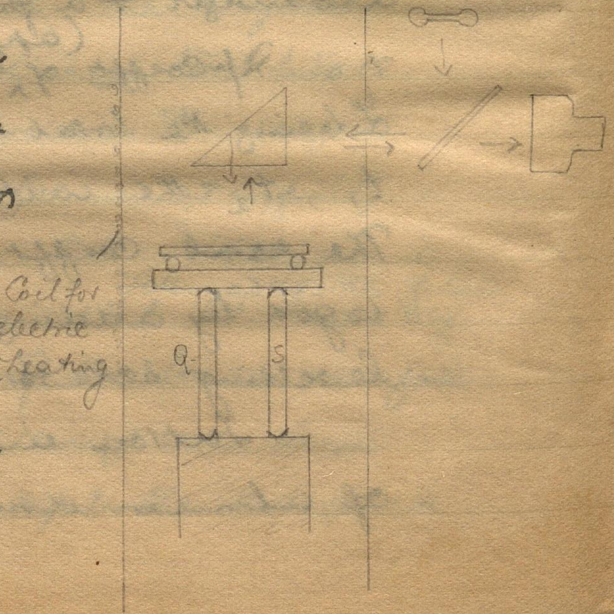
Sutton introduced a compensator of aluminium of sufficient thickness

Correct for the expansion of the screws.
ince μ for al. is nearly double that of iridio
latinum the thickness of al. was taken
alf the distance between AB & CD. The al.
late of which the upper surface is polished
s placed above the crystal. The Compensa-
ion is not accurate at all temperatures.

The chief defects of the instrument are
) a person has to be observing the fringes
he whole time taken by the crystal to
ome to a steady temperature 2) The method
is not absolute. Correction for the screws is
ecessary.

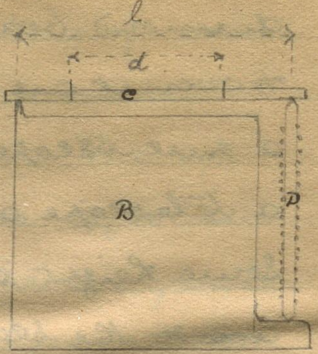
Robert's optic lever method

Accuracy by this expt is not
s great as in the former, &
urther it is not a standard
method. A Rods 6" long of
uartz & the given specimen
re placed side by side on
tainless steel, ~~over them~~

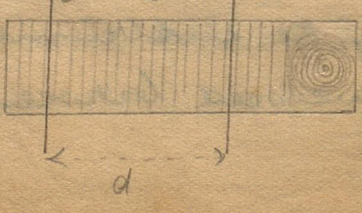


the ends of the rods being pointed & fitting into diamond bearings. The upper Cover plate is of glas & over it are three ~~bal~~ small balls supporti a microscope slide. A horizontal scale & a telescope are ~~fixed at~~ supported at some height above & the telescope views ~~an &~~ the scale as reflected from the upper surface. From the shift of the scale readi caused by differential expansion of the two rods & the consequent tilting of the microscope slide, the expansion of the specimen may be calculated.

A more perfect instrument designed in 1920 which corrects both Fizeau's ~~errors~~ defects is Priest's fringe width dilatometer. Here the specimen P is held between the cover-plate C & the base plate B as shown in the diagram. P can thus be heated by an electric coil without heating the rest of the instrument. The film of air enclosed between the cover plate & the ase plate Causes interference ~~of reflected~~



etween portions of the light eflected at the lower surface f C & the upper surface of . If the film is wedge shaped l lines are seen in the micro-cope. Two reference lines re drawn on the Cover plate & the no of ringes between them (an integer + a fraction) re Counted before & after ~~the expt~~ heating he rod. If n_1 & n_2 be the numbers, $\frac{(n_1 - n_2)\lambda}{2}$ s the increase or decrease in the difference f thicknesses of the film at the two reference lines. $\frac{(n_1 - n_2)\lambda}{2d} = \frac{e}{l}$ where e = expansion f the rod, l = distance between the rod & the ther end of the base plate, d = distance between he reference lines. ∴ $e = \frac{l(n_1 - n_2)\lambda}{2d}$ hence the Coefft of expansion Can be easily alculated. The shape of the fringes in hown in the diagram. e rings at one end are



Due to the curvature at the top of the specim
The temperature of the specimen is determined accurately by a thermocouple which has one of its junctions imbedded in the specimen.

<u>Grüneisen's law</u> Often it is ~~of~~ accurate to express expansion by the eqn $l_t = l_0(1+\mu t$
But a more exact definition of μ is $\mu = \frac{1}{l} \times \frac{dl}{dt}$. Expansion has been obser between different ranges of temperature & μ has been calculated at various temperatures. The results obtained led Grüneisen to state the empirical law μ / C_p is a constant. μ is the coefft of exp. at any temp. & C_p the sp. heat at constant press. at that temp. The value of the constant is different for different ~~a~~ substances. Expts have shown that the law is only approximately true at high temperatures.

Debyes T^3 law states C_v/T^3 is const.

Hence $\mu/\gamma 3$ is also a constant. ~~Hence~~ At temp. near ze absolute zero the coefft. f exp. must ∴ be very low.

Expansion of anisotropic materials.

ertain substances ~~which~~ like iceland par were observed to change in shape hen heated, thus a square face will ecome a parallelogram. The reason was asily seen to be ~~uneq~~ unequal coeffts f expansion along different directions. his class of substances ~~most~~ to which most rystals belong are called anisotropic or elotropic. Metals are also made up of ine grains of crystals but do not show nisotropic properties when taken in a lump ince the individual crystals are arranged n a haphazard manner.

In most crystals there are three mutually r directions such that if a ~~crystal be~~ cube e cut with its edges along these directions, s heated the ~~tempers~~ rt $\angle$s at the corners remain rt. ∠s though the cube may change into a rectangular parallelopiped. These three directions are called the principal axes of the crystal. The coeffts of linear expansi along these directions ~~is a~~ are constant & a called the principal coefficients of lin expansion. We shall denote them by λ_1, λ_2 In general λ_1, λ_2, λ_3 are all unequal. But in uniaxial crystals like quartz & Iceland spar, λ_1 along the optic axis is different from λ_2 & λ_3 which are equal. In crystals of the cubical system like ~~to~~ diamond, $\lambda_1 = \lambda_2 = \lambda_3$.

$$\text{Vol. Coefft} = \frac{V_t - V_0}{V_0 t}$$

$$= \frac{1}{V_0 t}\left\{V_0 (1+\lambda_1 t)(1+\lambda_2 t)(1+\lambda_3 t) - V_0\right\}$$

$$= \lambda_1 + \lambda_2 + \lambda_3.$$

The coeffts of lin. expn can be found by Fizeau's interference method or by Bragg's X-ray methods of space lattice. Fizeau found that for quartz $\lambda_1 = a + b(\theta -$
& $\lambda_2 = \lambda_3 = c + d(\theta - 40)$

where $a = -1{\cdot}06 \times 10^{-6}$, $b = 1{\cdot}14 \times 10^{-8}$

$C = 1{\cdot}37 \times 10^{-6}$ $\quad d = 1{\cdot}33 \times 10^{-8}$

The Coeff$\underline{t}$ of Cub. expansion

$$\alpha = a + 2C + (b + 2d)(\theta - 40)$$

$$= 1{\cdot}68 \times 10^{-6} + 3{\cdot}8 \times 10^{-8}(\theta - 40)$$

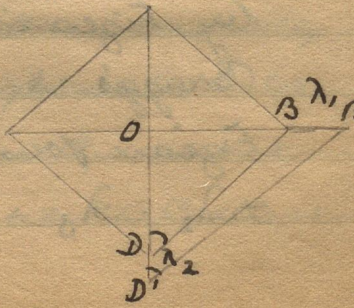
Thus when $\theta = \frac{-1{\cdot}68 \times 100}{3{\cdot}8} + 40 = -4{\cdot}2°C$

α becomes zero. Whether the body be heated
bove $-4{\cdot}2°C$, or cooled below $-4{\cdot}2°C$.
e body expands. Like water quartz has got
max. density at $-4{\cdot}2°C$.

In a similar manner expts showed
at emerald has got max. density at
$-40°C$ nearly.

Change in dihedral ∠s when the diagonals are
long the ~~optic~~ principal axes

Let a cube be cut having the diagonals
f its upper surface along two of the
rincipal axes of the crystal.
t l be the semidiagonal lengths
let λ_1, λ_2 be coeffs of expan-
ion along OB & OD. After



Heating let B expand to B' & D to D'.

The change in diahedral ($\angle OD'B' - \angle ODB$)

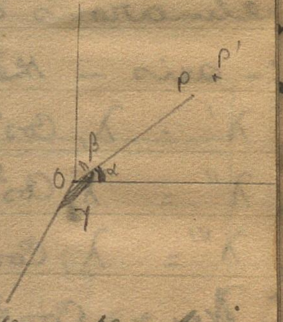
Now $\angle ODB = 45^\circ$. $\tan \angle OD'B' = \frac{OB'}{OD'}$

$$= \frac{l(1+\lambda_2 t)}{l(1+\lambda_1 t)} = (1+\lambda_2 t)(1-\lambda_1 t)$$
$$= (\lambda_2 - \lambda_1)t + 1$$

Thus change in dihedral ∠s can be express as a function of λ_1 & λ_2. The change can easily be measured by an optical metho say, by allowing a beam of light to be reflected from the face of the crystal.

To find coeff^t of linear expansion along any direction say OP

Let OX, OY, OZ be the principal axes through O. & let OP make ∠s α, β, γ with these directions. Due to a rise of temp t let P be displaced to P' O being fixed in space. Let OP $= r$, OP' $= r'$. ~~that~~ To a first approximation we shall suppose P' to be on OP produced so that the linea



Coeff^t $\lambda = \frac{r'-r}{rt}$.

Referring to the principal axes let P be

$x, y, z)$ & P' (x', y', z')

$r'^2 = (x'^2 + y'^2 + z'^2)$

$= x^2(1+\lambda_1 t)^2 + y^2(1+\lambda_2 t)^2 + z^2(1+\lambda_3 t)^2$

$= r^2 + 2t(x^2\lambda_1 + y^2\lambda_2 + z^2\lambda_3)$

neglecting higher powers of λ

$\therefore r'^2 - r^2 =$ ~~[illegible]~~ $(r'-r)\,2r$ nearly

s. $\therefore \lambda = \dfrac{r'-r}{rt} = \lambda_1 \dfrac{x^2}{r^2} + \lambda_2 \dfrac{y^2}{r^2} + \lambda_3 \dfrac{z^2}{r^2}$

$= \lambda_1 \cos^2\alpha + \lambda_2 \cos^2\beta + \lambda_3 \cos^2\gamma.$

Sum of linear Coeff^ts along any three utually ⊥r directions is a constant qual to the Cubical Coeff^t.

Let $\lambda', \lambda'', \lambda'''$ be linear Coeffts along the hree mutually ⊥r directions $\alpha_1, \alpha_2, \alpha_3$ the nclinations of these directions to the ~~x - axis~~

- axis — the 1st principal axis ...

$\lambda' = \lambda_1 \cos^2\alpha_1 + \lambda_2 \cos^2\beta_1 + \lambda_3 \cos^2\gamma_1$

$\lambda'' = \lambda_1 \cos^2\alpha_2 + \lambda_2 \cos^2\beta_2 + \lambda_3 \cos^2\gamma_2$

$\lambda''' = \lambda_1 \cos^2\alpha_3 + \lambda_2 \cos^2\beta_3 + \lambda_3 \cos^2\gamma_3$

. Now $\cos^2\alpha_1 + \cos^2\alpha_2 + \cos^2\alpha_3 = 1$ |||rly for

β & γ $\therefore \lambda' + \lambda'' + \lambda''' = \lambda_1 + \lambda_2 + \lambda_3 =$ Coeff^t of Cub. exp.

Linear coefft in a direction equally incline
to the three axes is $\frac{1}{3}$ Cub. Coefft.

$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$ & ∴ when inclinations are equal, $\alpha = \beta = \gamma$, $\cos^2\alpha = \frac{1}{3}$

$$\lambda = \lambda_1 \cos^2\alpha + \lambda_2 \cos^2\beta = \lambda_3 \cos^2\gamma$$
$$= (\lambda_1 + \lambda_2 + \lambda_3) \cos^2\alpha$$
$$= \frac{1}{3} \text{ Cub. exp. coefft}$$

~~Specific Heat~~ Expansion of liquids

~~Specific heat~~ Expansion by hydrostatic method:

Dulong's method was to balance two columns of the same liquid at two different temperatures

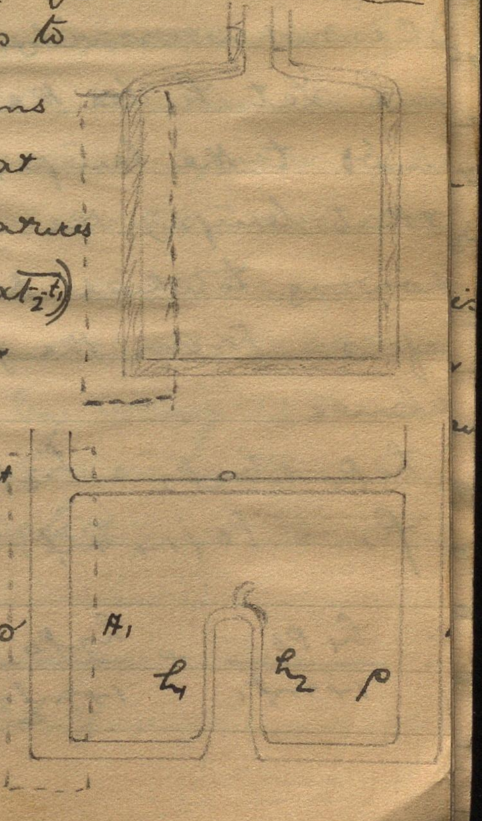
$h_1\rho_1 = h_2\rho_2$ & $\frac{\rho_1}{\rho_2} = (1 + \alpha\overline{t_2 - t_1})$

Regnault's method for abs. exp. of mercury was an improvement upon this method.

Here we have

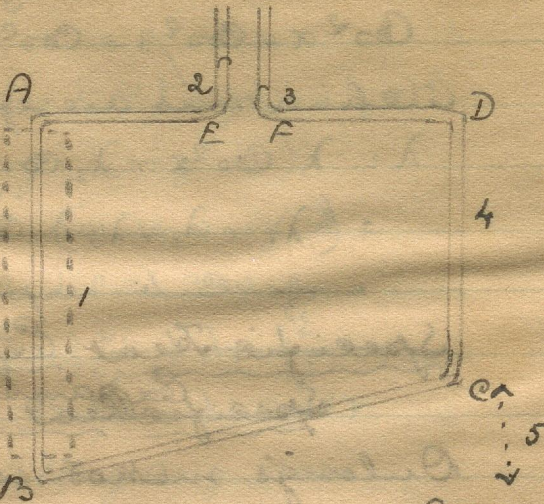
$$H_1\rho_1' - h_1\rho = H_2\rho - h_2\rho \quad \rho$$

$$\therefore 1 + \alpha t = \frac{\rho}{\rho_1} = \frac{H_1}{H_2 + h_1 - h_2}$$



$$\therefore\ a = \frac{1}{t}\,\frac{(H_1 - H_2) - (\cancel{th}h_1 - h_2)}{H_2 + h_1 - h_2}.$$

An improved method was later sed by Regnault



The tube used was of the shape hown in the diagram. Portions AE F D are on the same orizontal level; ~~B~~ but BC is not necessarily vel. Let h be the ~~vertical~~ height of ~~the~~ any limbs t the temp, ρ density m the coeff of exp. that temp, the subscripts 1, 2 etc howing to which portion each quantity refers. From the principle of hydrostatic alance

$$h_1\rho_1 + h_2\rho_2 = h_3\rho_3 + h_4\rho_4 + h_5\rho_5$$

$$\rho_1 = \rho_0 / 1 + m_1t_1 \quad \text{etc}$$

$$\therefore\ \frac{h_1\rho_0}{1+m_1t_1} + \frac{h_2\rho_0}{1+m_2t_2} = \frac{h_3\rho_0}{1+m_3t_3} + \frac{h_4\rho_0}{1+m_4t_4} + \frac{h_5\rho_5}{1+m_5t_5}.$$

ie $\frac{h_1}{1+m_1t_1} = h_4(1-m_4t_4)+h_5(1-m_5t_5)$

$+h_3(1-m_3t_3) - h_2(1-m_2t_2)$

$= h_4+h_5 - (h_4m_4t_4+h_5m_5t_5)$

$-(h_2-h_3)+h_2m_2t_2-h_3m_3t_3.$

$= h_1 - \Delta - (h_2-h_3)+\delta$

$\therefore m_1 = \left\{\frac{h_1}{h_1-\Delta-(h_2-h_3)+\delta}-1\right\}\frac{1}{t_1}$

$= \frac{(h_2-h_3)+\Delta-\delta}{h_1-\Delta-(h_2-h_3)+\delta}\times\frac{1}{t_1}$

m_2, m_3 etc being approximately known from other expts, m can be de by the method of successive approximati

Regnault's tube was on the whole 1·5 metre in length.

Callendar & Moss increased the accura in measuring (h_2-h_3) by using 12 turns each turn being 2 metres in length.

Coefft of exp. of a solid by wt. thermometer.

Two test tubes are supplied within one of hich the given solid is placed upon eads so as not to touch the sides of the ube. Both the tubes are drawn into wt. thermometers one for Coefft of exp. of mercury the other for Coefft of exp. of the solid terms of that of mercury. Let W_s be the wt of the solid, W_0 that of the mercury which fills the space in the wt thermo-eter left over by the solid. If ρ_s & ρ_0 be ensities of the solid & of mercury at zero apacity of the wt. thermometer at zero $\frac{W_s}{\rho_s} + \frac{W_0}{\rho_0}$. ~~After~~ ~~If~~ At t.°C capacity will be $\left(\frac{W_s}{\rho_0} + \frac{W_0}{\rho_0}\right)(1+gt)$. By raising e temp. let the ~~increase~~ amount of mercury owing out be w. The vol. of mercury $(W_0 - w)\frac{1+mt}{\rho_0}$ & the vol. of the solid $W_s \frac{1+\delta t}{\rho_s}$ m & δ being Coeffts of cub. exp. f ~~the~~ ~~solid~~ ~~& t~~ mercury & the solid.

$$\therefore \left(\frac{W_s}{\rho_s} + \frac{W_0}{\rho_0}\right)(1+gt) = W_s\frac{1+\delta t}{\rho_s} + \frac{W_0 - w}{\rho_0}(1+mt).$$

All the quantities being nown δ can be ~~at~~ found out.

Matheison's expt for temp of max. density

Water was taken in a glass bulb and heated to different temperatures, ~~The~~ the loss of wt being accurately determined at each stage. W_t W_t at temp. t was seen to be of the form $W_t = W_0\left(1+\alpha t+\beta t^2+\gamma t^3\right)$. Values of α, β, γ were ~~empirically~~ exptly determine

The volume of the bulb V_t was seen to be given by

$$V_t = V_0\left(1+at+bt^2\right)$$

$$\therefore \rho_t = \rho_0\left\{1+lt+mt^2+nt^3\right\}$$

$l, m,$ & n being ~~Con~~ functions of α, β, γ, a & b. ~~Matheison fo~~

ρ_t is a ~~minimum~~ maximum when $\frac{d\rho_t}{dt}$ is zer

ie $\rho_0\left(l+2mt+3nt^2\right)=0$

ie when $l+2mt+3nt^2=0$

i.e. when $t = \frac{-2m\pm\sqrt{4m^2-12ln}}{6n}$

Matheison calculated the values of

l, m & n & hence deduced t the temp. of maximum density.

His values were $l = 5{\cdot}2939 \times 10^{-5}$

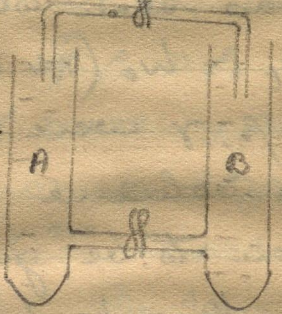
$m = -6{\cdot}5322 \times 10^{-6}$

$n = 1{\cdot}445 \times 10^{-8}$

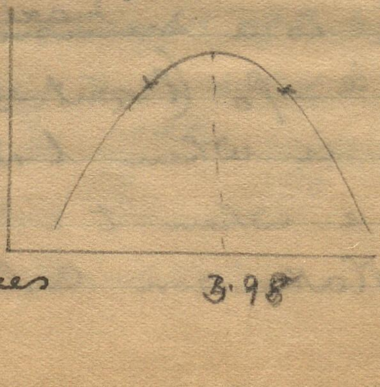
Hence t was calculated to be 3·98°C.

Joule and Playfair's expt for max. density

Two tubes A & B are ut in communication y a siphon arrangement. An airfilled glass bead of p. gr. one is placed in e horizontal siphon. ~~The~~ water is kept in both A & B, the temp of A being above 4°C & that of B being elow 4°C by an almost equal amount.



~~Then~~ If the densities f the two portions are nequal the bead noves from one side o the other. Temperatures



are adjusted by trial till the motion is least. The average of the temps &c at this stage gives the temp. of max. densit

The expt yielded the following results:-

Temp. of A °F	Temp of B °F	Velocity of the bea Divisions p
41·1	37·35	280
40·96	37·36	20
40·96	37·37	8
40·71	37·2	−40

The vel. is least when temps are 40·96 & 37·37. Their mean is 39·165°F = 3·98° C. Hence the temp. of max density is very nearly 3·98°C.

Specific Heats

If Q is the heat reqd to raise 1gm from 0°C to t°C, $\bar{s}$ the mean sp. heat of the interval, $Q = \bar{s}\,t$. If s is sp. heat at t°C, $dQ = s\,dt$

$$\therefore\ s = \frac{dQ}{dt} = \frac{d}{dt}(\bar{s}\,t)$$

$\bar{s}$ can be expressed in the form $a + bt + c$

$\overline{S} t = at + bt^2 + ct^3$

$\therefore s = \frac{d}{dt}(\overline{S} t) = a + 2bt + 3ct^2$.

Calorimetry.

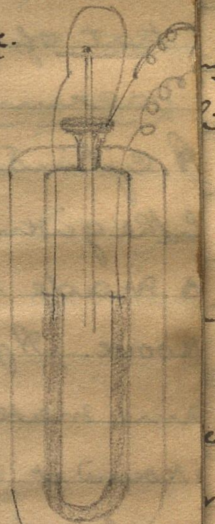
Berthelot's Calorimeter is ery convenient for latent eat. No steam condenses a during the transfer from oiler to condenser since the assage is through the oiling water. The wt of team condensed can be nown accurately since t remains in the condenser hich is of small wt. The ethod is applicable to liquids hich combine chemically.

Water as calorimetric Substance.

For accurate or universal use ater is inadequate as calorimetric ubstance. Its range is limited from ero to 100°C. At temperature above 60°C its use is attended with ~~several~~ much inaccuracy on account of the rapid vaporization and the consequent loss of heat. Lastly water has the largest thermal capacity and so when used in the method of mixtures the rise of temperature is very small.

Nernst's Copper block Calorimeter.

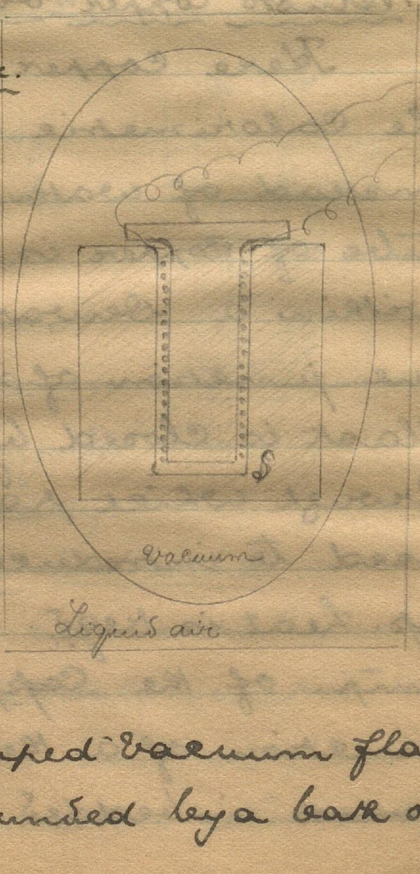
Saha 48



Here copper is used as the calorimetric substance instead of water. A thick tube of copper is enclosed within a Dewar flask. ~~and~~ ~~one junction of a ther~~ The flask is closed by a plug through which passes a tube used to introduce the substance whose sp. heat is reqd. For measuring the temp. of the copper calorimeter one junction of a thermocouple is ~~introduced~~ embedded in the ~~Cal~~ copper, the ther junction being on an outside block hich is at constant temperature. The iven substance is heated to a known mp. and then quickly introduced into the he copper vessel. Heat equilibrium is oon established & from the change in e.m.f. f the couple the sp. heat can be compared that of copper.

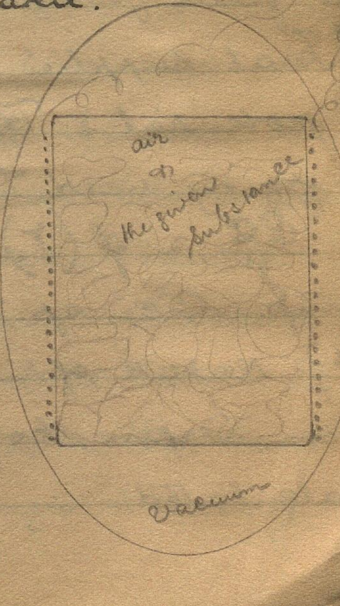
Vacuum Calorimeter.

A cylindrical block f the given material s made with a central roove. A plug of the ame material is taken round it is wound finely nsulated pure platinum ire. The plug when nserted just fits into e groove. The block



s kept in a pear shaped vacuum flask hich is further surrounded by a bath of liquid air or liquid hydrogen. Current is supplied through the coil thus heating it up. The ~~Cu~~ block & the plug also take up the temperature of the coil. By measu the current in the circuit & the p.d. betwe the ends of the coil ~~it to~~ the resistance of the coil is known & hence the temperature increase θ is calculated. If M be the mas S the sp. heat, k the water equiv. of the coil, $(MS + k)\theta$ is heat ~~supplied~~ taken i by the apparatus. Energy supplied = ECt jou $= \frac{ECt}{J}$ ~~ergs~~ cal E being e.m.f., C the mean current. Hence S is calculated.

If the given substance is a ~~non Co~~ poor conductor of heat the above arrangement is impracticable. A thin silver vessel was used round which the heating coil was wound. The given substance is



ken in as loose fragments as possible &

ut into the vessel with much air space

etween so that there may be sufficient Conduction

nd Convection of heat.

Simons used an arrangement by

hich radiation was Completely avoided

y Surrounding the Calorimeter with a

ath whose temp. varied ~~as~~ exactly as

at of the Calorimeter itself.

Corbino studied the sp. heat of tungsten

t 2000°C & above from the rate of rise

f temp when a ~~given~~ known Current

t fixed potential was sent into the wire.

Heat supplied p.s. $= \frac{EC}{J}$ E being Current

potential. This heat is partly radiated

partly used to raise the temperature.

$$\frac{EC}{J} = f(T) + Cm\frac{dT}{dt}$$ T being the

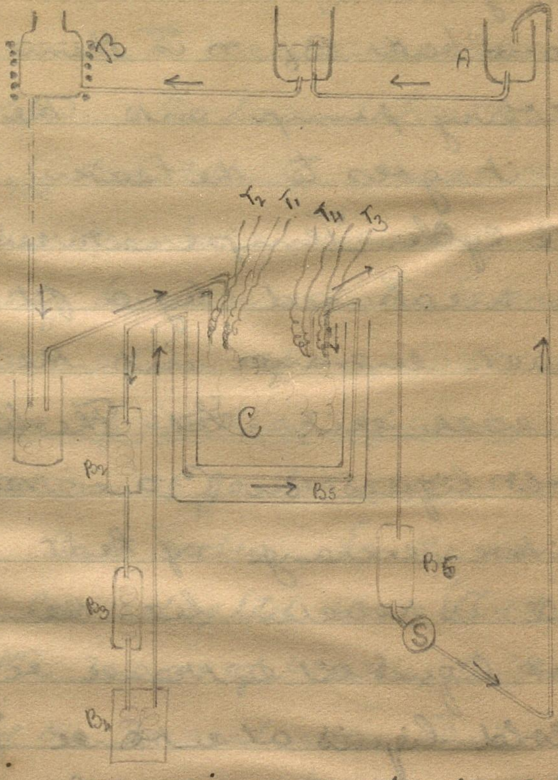
mp. C the sp. heat, m the mass of the wire,

$\frac{dT}{dt}$ the rate of rise of temp. If f (T) be assumed

om Stefan Boltzman law C Can be

alculated.

Callendar's Continuous flow method.



The expt is intended~~a~~ to Compare the Sp. heats of a given liquid at two differen temperature ranges. Heated liquid is supplied ~~fr~~ at a Constant hydrostatic pressure of 15 feet from the heater B to the Calorimeter C through a hot bath B_1: From C it passes through 3 cooling

aths B_2 B_3 B_4, then through a bath B_5 surround-
g C & lastly into C From C it again
asses into a bath B_6 & is then pumped
p by a rotary pump into the reservoir
) whence it goes to the heater & thus
epeats the cycle. Temperatures of the
iquid are measured by a pt. resistance
lug at each entrance into the Calorimeter
nd at the each exit. ~~Let~~ The tubes of
ot and cold liquid in C are so intertwined
s to facilitate exchange of heat. When
teady state is reached let the temperatures
~~g~~ ~~T~~ of hot liquid at entrance ie T_1, at exit
& of Cold liquid at entrance T_3, at exit
4. If S_{12} & S_{34} are sp. heats at the
wo ranges

$$(T_1 - T_2) S_{12} = (T_4 - T_3) S_{34}.$$

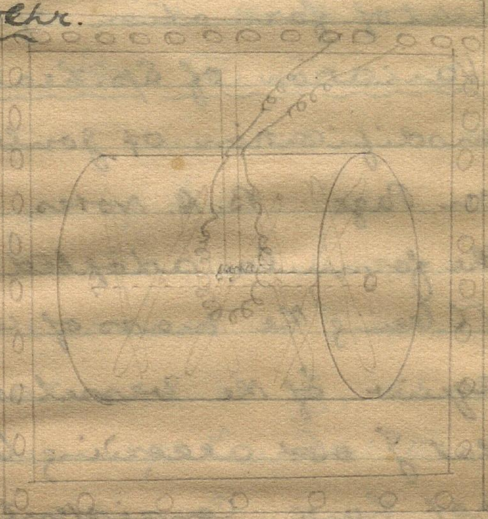
Liquid air & liquid hydrogen Cal. ~~At~~
The method of mixtures is utilized here.
he latent heat of liquids of permanent
ases. can be found by these. ~~The latent heat~~

The method employed is to drop a heate substance ~~into~~ at zero °C into the liquid and to measure the amount of gas evolved. The latent heat of liquid hydrogen is $\frac{1}{100}$ cal. nearly. Since such small quantities can be measured, the apparatus has largely been used to determine the heat of formation of radioactive substan

Variation of Sp. heat of water. Rowland's modification of Joule's expt described on Page B. A. Notes. In the earlier expts the formula adopted was $(M+k)\,\theta = Wg\,\frac{[illegible]}{J}$ M being the mass of water, k the water equiv. of the vessel etc. But it was seen that J ~~obt~~ according to this formula did not have consistent values. ~~But~~ By the law J. should have only value whatever be the temp. of the water. Hence it was concluded that the sp. heat of water is different at different temps. Expts showed that sp. heat was a min. at 30 °C nearly.

Griffith's Expt. is a modifications of oule's expt. Water is heated by a coil of nown resistance & the e.m.f. between the nds of the coil is measured by a potentio- ter calibrated by a Clarke cell. A separ- te expt. was conducted to find the vari- tion of resistance with temperature. —

Jaegar and Steinwehr.



age 63 Saha) This xpt aimed at a ery great degree of ccuracy, the probable error being only 1 %. A large mass f water is taken in cylindrical calo- imeter. A set of paddles are kept otating in it in order to keep the temp- rature ~~cons~~ uniform within the calori- eter. Heat is supplied to the water by n insulated coil within the calorimeter

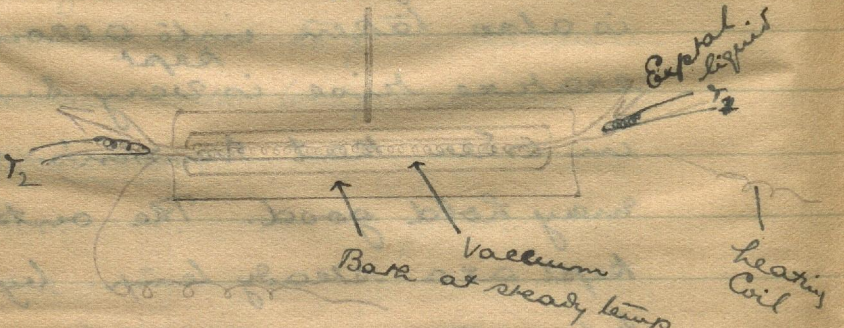
the ends of which are ~~adjusted~~ subjected to a known potential difference. ~~Electrical energy~~ Res tance of the Coil being known the no. of watts spent can be calculated. The energy spent in turning the paddl is also taken into account. The temperature rise is kept very small (1·4 °C) in order that Newton's law of radiat may hold good. The outside bath is kept at a steady temp. by a system of tubes through which water is passing. The temp. is* measured by a carefully calibrated resistance thermom The time is automatically recorded on a chronograph. The heat lost or gained through radiation is estimate both at the beginning & at the end of the expt. The value of sp. heat at diff. te is calculated from the formula

$$\frac{E^2 t \cancel{J}}{RJ} = (Ms + k)\,\theta$$

k being water equiv. of the Cal. Stirrer ndividual expts showed variations of nly 100ths of a per cent, which is attri-utable to the pt. thermometer being not ensitive enough.

Callendar and Barnes Steady flow method.

An equally high degree of accuracy was achieved y Callendar nd Barnes.



e exptal liquid passed at a steady rate rough a tube & was heated by a spiral ithin the tube. Pt. resistance thermo-eters measured the temps T_1 & T_2 on entrance & xit. The tube was enclosed in a Dewar lask which was further covered by a ath of constant temp. so as to keep the adiation perfectly steady. When T_1 & T_2 re quite steady, the eqn for loss & gain heat is $\frac{ECt}{J} = Ms(T_2 - T_1) + h$ --- (1)

where s is the sp. heat over the range T_1, T_2, M mass of water that has pass through, h is the heat lost through radiation

The advantages of the instrument are

1) the water equiv. of cal. has not be taken into account; the temp. is steady & so it does not gain or lose heat.

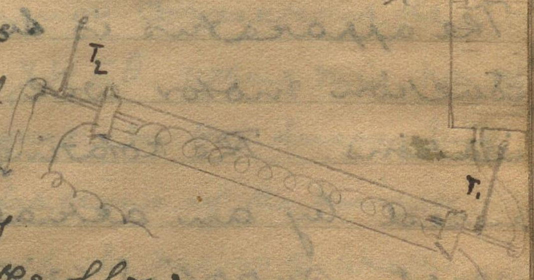
2) Since T_1 & T_2 are quite steady, there is no thermometer lag, & personal eqn also is eliminated.

3) h can be easily eliminated, for by causing a higher rate of flow & a larger current, T_1, T_2 & t being the same as before

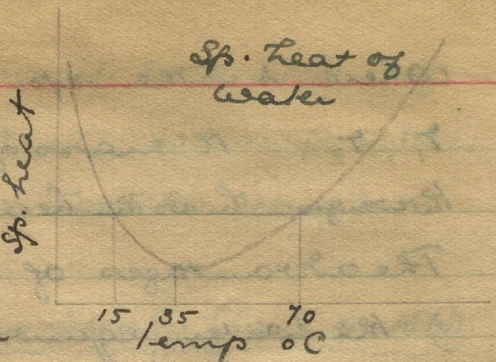
$$\frac{EC't}{J} = M's(T_2 - T_1) + h \qquad (2)$$

Subtracting (1) from (2) h is eliminated.

The figure shows a laboratory model of the same apparatus, with an easy device to regulate the flow.

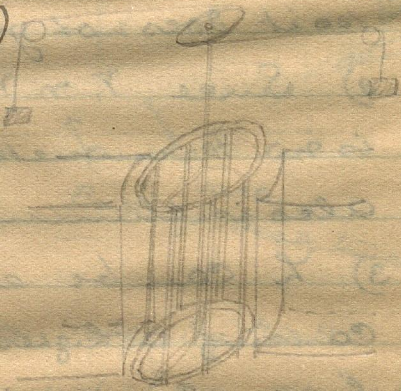


he variation of sp.
eat of water is shown
y this graph. The
in. is at 35 °C; &
p. heat at 15 °C is taken
be unity.



Laby and Hercus. (Saha 109)

The previous expts
quate calories to elec-
rical units & the value
f J. ∴ depends on the
ccuracy of the electric
units. This expt equates
alories to mechanical units.
he accuracy aimed at was of the order of
·01 %.



The apparatus is similar to a polyphase
nduction motor with the following modi-
ications. The rotating magnetic field is
aused by an actually rotating electro-
agnet supplied with suitable slip rings

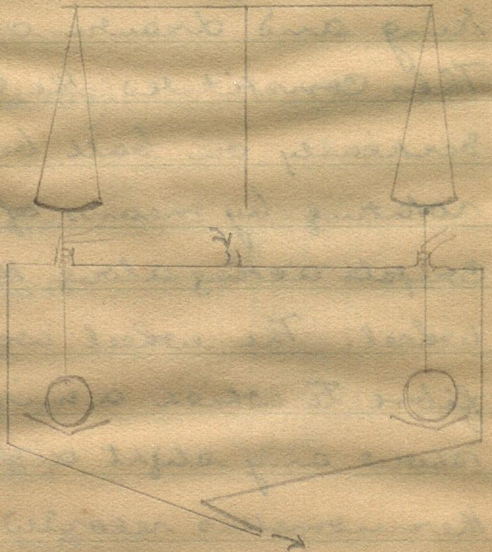
and brushes. In place of the squirrel Cage rotor we have an upper ~~ring~~ holl ring, & ~~anothe~~ a Similar lower hollow ring Connected together by 14 ~~hollow~~ vertical Copper tubes. Water is let into the lower ring and drawn out from the upper ring This Constitutes the Calorimeter. It is mou vertically on ball bearing & prevented fro rotating by means of a ~~disc~~ Constant Couple acting along the rim of a torsion wheel. The wheel was suspended by a torsi fibre to which a mirror was attached to show any slight displacement. Platinum thermometers recorded the temp. of water on entry & exit. ~~The approximat~~ The Calorimeter was ~~suspended by~~ surrounded by a Dew flask. Neglecting minor Corrections the eqn is $n \pi m g d = J W \delta \theta$ where n is no. of revol. p.s. of the magnet, m the Suspending wts Corrected for deflections of the mirror, d Diameter of the Wheel, W mass of water nning out p.s. $d\theta$ the rise of temp. The value

as got J at 15°C = 4.1860 Joules per Cal.

Sp. heat of gases

Joly's differential Calorimeter for C_v. (Saha 59)

Two similar hollow



pheres are suspended
rom the pans of a pre-
ision balance (i.e
ne which ~~deals with~~ can weigh
ange of masses & yet
ives great accuracy)
ne of the spheres is
filled with the gas &
e other is vacuum.
team is ~~Ca~~ let in & the extra steam condensed
n the gas sphere found out. The approximate
eqn ~~was~~ is $M C_v (\theta_{st} - \theta) = wL$
w being mass of steam condensed. Correction
ad to be applied for the following

1) Expansion of the sphere at θ_{st} & consequent
ork done ~~in~~ by the expanding gas.

2) Expansion of the sphere due to increase pressure

3) Thermal effects due to stretching of the material of the sphere

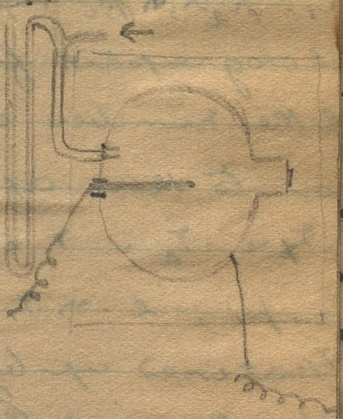
4) Increased buoyancy due to increased volume

5) Wt of the water condensed in an atmosphere of steam reduced to its wt in vacuo.

The expt is suited only for low rang of temperature.

Saha 86

Pier's Bomb Calorimeter.



The bomb is a strong metallic shell ~~one~~ with an orifice closed by a membrane. To the membrane is fixed a ~~st~~strip of mirror which reflects a spot of light on to a photographic film wound on a revolving drum. Variations of pressure within the bomb are thus recorded n the film. The bomb is filled with say n gms of the exptal gas & m grams of some ombustible gas say a mixture of oxygen & ydrogen. An electrode is fused into the bomb, the walls of the bomb act as the other lectrode. When sparks are produced the eat of combustion raises up the temperature f the ~~g~~ bomb. ~~The~~ Let the temperature ise from T_1 to T_2 & the pressure from p_i p_2. On cooling again let the pressure be p_1. p_2, & p_i ~~& T~~, can be known from the hotographic film. $\frac{p_1}{p_i}$ is the ratio e f the number of molecules before combustion to those after combustion

~~T_x~~ $= T_2 = T_1 \times \frac{p_2}{p_1} = T_1 \times \frac{p_2}{e\, p_i}$ Thus knowing p_2, p_i, e & T_1, T_2 can be calculated.

Heat used up by the gas in the bomb $= (T_2 - T_1) \times (m\, C_{vx} \times n\, C_v)$ C_{vx} being sp. heat at const. ol. of the exploding gas. Heat generated $m\, Q_2$ Q_2 being heat of explosion per gm.

. C_v can be calculated if C_{vx} is known.

C_v ~~is the sp. h~~ is observed ~~from~~ by comparison with the standard gas argon which has C_v constant at all temp.

The instrument can be used for very high ranges — as far as 3000°C. But the disadvantage is that only the mean ~~temp~~ C_v over a very wide range can be known from the instrument.

Eucken's Expt for C_v at very low temperatures. The expts were conducted with Nernst's vacuum calorimeter the calorimeter being placed in a bath of liquid hydrogen. The expt owes its imporatance to the fact that by this means he demonstrated the existence of two kinds of hydrogen.

Expts for C_p.

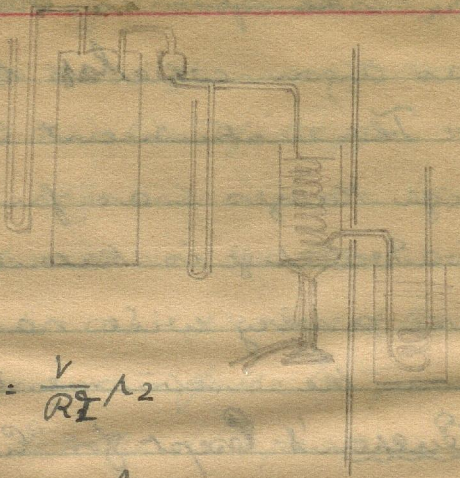
Regnault's expt for C_p at ordinary temps. Gas from a reservoir was passed at constant pressure through a heater & then into a calorimeter. The eqn ~~of~~ for C_p is

$lc_p\left(\theta_1 - \frac{\theta_2+\theta_3}{2}\right)$

$= (m + k)(\theta_3 - \theta_2)$

simple method for

is as follows.



$\frac{V}{m_1} = R\tau$

$p_2 \frac{V}{m_2} = R\tau$

ie $m_1 = \frac{V}{R\tau} p_1$; $m_2 = \frac{V}{R\tau} p_2$

$\therefore M = (p_1 - p_2)\frac{V}{R\tau}$.

Regnault saw from Amagat's curves that ~~as law~~ Boyle's law was not exactly observed & hence proceeded as follows:-

For any pressure p the mass m contained in the reservoir at temp θ is given by

$m(1+\alpha\theta) = Ap + Bp^2 + Cp^3$ A, B, C being constants determinable from Amagat's curves

$\therefore m_1(1+\alpha\theta) = Ap_1 + Bp_1^2 + Cp_1^3$

$m_2(1+\alpha\theta) = Ap_2 + Bp_2^2 + Cp_2^3$

$\therefore M = \frac{1}{1+\alpha\theta} A(p_1 - p_2) + B(p_1^2 - p_2^2) + C(p_1^3 - p_2^3)$.

Corrections were applied chiefly for the following:-

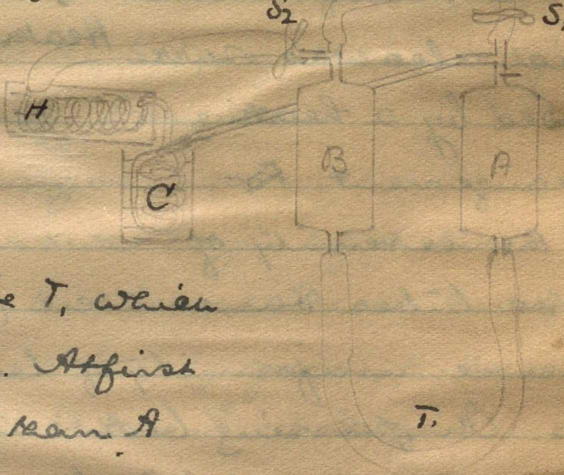
1) Radiation loss from the cal:

2) Conduction gain through the gas tubes

3) Radiation gain from the heater.

Lussana's Expt for C_p at high ~~temp~~ pres

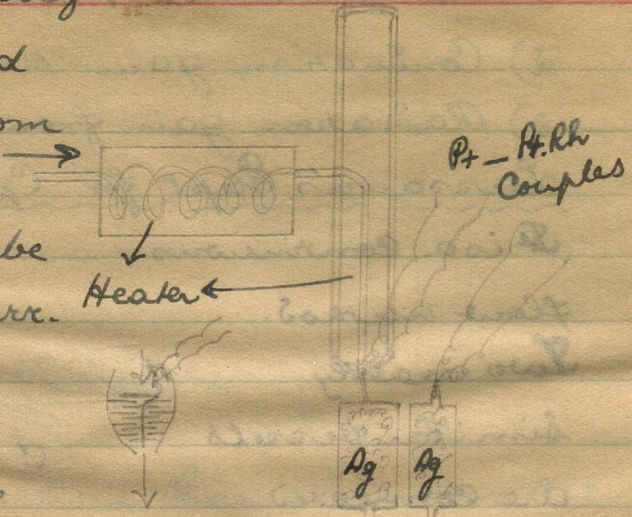
It is a continuous flow method. Two exactly similar vessels are connected through a tube ~~be~~ T_1 which contains mercury. At first B is ~~very~~ higher than A & contains the experimental



gas. T_1 & A are filled with mercury. The S is closed. As B is lowered the gas passes through the heater H into the calorimeter & then into A. Mercury passes from A to B. Then S_2 is closed, S_1 opened & B raised up to let the gas repass into B. The calculation is similar to Regna

Holborn and Henning C_p at high temper

tures: The method of ixtures was used ere also. Gas from n electric heater assed through a tube hich also was surr-unded by a heating rrangement. ~~Fr~~ At the extremity of e ~~se~~ tubes vanes were provided to nsure uniformity of temp. for the whole as. On passing between the vanes the emp. was recorded by a thermocouple. he Calorimeter consisted of two silver essels protected from radiation, ~~Covered~~ ith filled with loose silver filings to elp rapid transfer of heat.



ontinuous Electrical method for Cp i.e. the sage of a heater coil to heat the gas was irst devised by Swan in 1910 and later erfected in 1919 by Scheele and Heuse. The

latter apparatus is shown in the figure. The exptal gas enters at J, passes through the bent tube into the spiral. An~~tes~~ Pt electrical resistance thermometer reads the temp of the gas at this stage. From the spiral ~~&~~ ~~the~~ gas goes up through the outermost layer of a three walled cylinder, then comes down through the 2nd ~~central~~ layer & lastly goes up through the ~~central of the~~ c tube. Here the gas is heated by a coil, its temp. is made uniform by a system of wire gauzes & then the temp. T_2 is recorded by a platinum coil. The special feature is that ~~as~~ most of the heat radiated by the heated gas is received by the outer layers of gas ~~s~~ which are on the way to get heated.

The eqn is $J m C_p d\theta = C^2 R t - h$ where $d\theta = T_2 - T_1$; m is the mass of gas passing

rough the apparatus p.s. & h a small
orrection for radiation.

Ratio of Specific heats.

Eq^n for the adiabatic state & ~~the~~
~~ala~~ may be obtained analytically as follows:-

Let a quantity of heat dQ be supplied
1 gm of a gas at constant pressure. Its
emp. rises by dT

$\therefore dQ = C_p dT.$

Now the rise in temp. is accompanied by
n increase dv in vol. & $\therefore$ work done
gainst pressure is $p\,dv$ while internal
ork done to increase K.E. of molecules
s $C_v dT$ $\therefore dQ = C_p dT = C_v dT + p\,dv$
dv being expressed in thermal units.

$\therefore C_p - C_v = p\frac{dv}{dT}.$

But $pv = RT$ & since the pressure is
onstant $p\frac{dv}{dT} = R$ $\therefore C_p - C_v = R$ --(1).

Now suppose the change in the state of
e gas is adiabatic.

~~C_p~~ $dQ = 0$ ie $C_v dT + p\,dv = 0.$ ---(2)

Here both pressure & volume are variabl

$p\,dv + v\,dp = R\,dT$

$\therefore \quad C_v\,dT + p\,dv = C_v \cdot \dfrac{p\,dv + v\,dp}{C_p - C_v} + p\,dv$

$= C_v(p\,dv + v\,dp) + (C_p - C_v)\,p\,dv$

$= C_v\,\cancel{p}\,dp + C_p\,p\,dv$

Which by eqn 2 is zero

$\therefore \quad v\,dp + \dfrac{C_p}{C_v}\,p\,dv = 0$ & denoting $\dfrac{C_p}{C_v}$ by γ

$v\,dp + \gamma\,p\,dv = 0$

ie $\dfrac{dp}{p} + \gamma\dfrac{dv}{v} = 0$ Integrating

$\log p + \gamma \log v = \log k$

ie $p v^\gamma = k.$ (A)

Which is the eqn for the adiabatic Sta

The relation bet. pres. & ~~vo~~ temp.

is given by $p.\left(\dfrac{RT}{p}\right)^\gamma = \text{Constant}$

ie $T^\gamma / p^{\gamma-1} = \text{Constant.}$ (B)

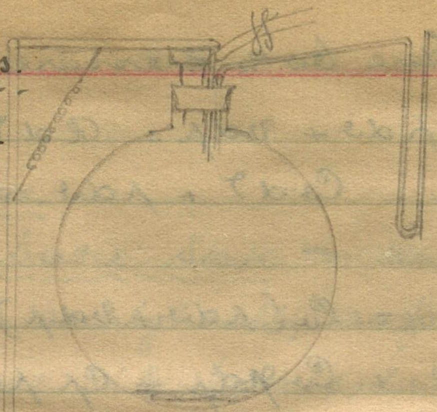
& relation between temp. & vol. is

given by $\dfrac{RT}{v}\,v^\gamma = \text{Constant.}$

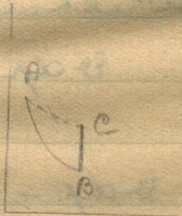
ie $T v^{\gamma-1}$ is Constant (C)

The above eqns can be used to determine γ

Clement and Desormes.

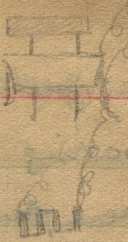


Gas at high pressure
is introduced into the
arboy & the orifice
uddenly opened and
en closed.
The changes are repre-
ented on the indicator
iagram by the adiabatic AB &
e constant volume rise in pressure
BC. γ can hence be easily calculated.



Lummer and Pringsheim sought to remedy
he chief source of error in the above expt.
iz. When the orifice is being closed we
re not sure that the manometer levels
e equal. The oscillations set up in the
anometer makes it highly improbable that
he levels are equal.

The experimenters introduced a
olometer into the carboy & noted the
all in temperature due to a sudden decrease

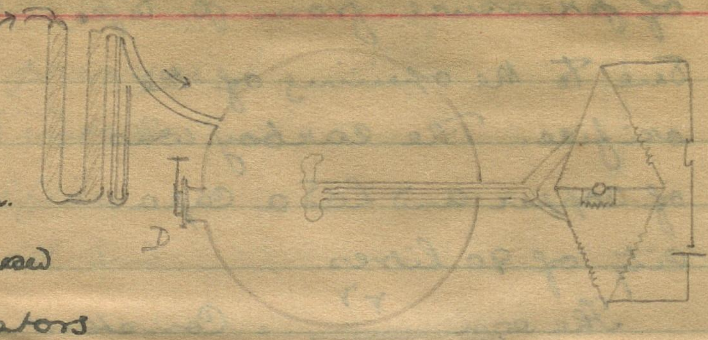


of pressure from p, to p.
due to the opening of the orifice. The carboy was of copper and had a capacity of 90 litres.

The eqn $\frac{T^{\gamma}}{p^{\gamma-1}}$ = Constant was used & γ Calculated.

Partington introduced a further improved form. To ~~avoid~~ lessen Conduction & Convection of heat from the walls of the vessel he increased the capacity of the vessel. For the bolometer thin wires were used instead of metal strip so that there is no temperature lag. The galvanometer used could record changes in resistance within ·01 of a secon
The leads of the bolometer were of very thin wires in order to minimize ~~Cond~~ heat Conduction through the leads. Further he used a null method. ~~S~~ ~~[illegible]~~ that is, the initial ~~pressure~~ deflection of the galvanometer was so adjusted that when the carboy was opened the deflec

ecame zero.



mpensating
leads were put
r the bolometer.
e gas was passed
rough dessicators
its ~~bump no~~ pressure noted by a sulphuric
cid manometer. The orifice was closed
y a diaphragm of adjustable aperture.
f the aperture is too large oscillations are
et up in the manometer & the bolometer
eading is not steady. If too small the
diabatic conditions are not satisfied so
~~mea~~ & the aperture was gradually made
maller till the oscillations just disappeared.

γ from ~~ratio of Specific heats~~ velocity of Sound

The usual eqn for velocity of sound
$v = \sqrt{\frac{\gamma p}{\rho}}$ is deduced on the assumption
hat the gas laws are obeyed & ∴ the iso-
thermal elasticity $\left(\frac{dp}{dv}\right)_T \times v$ is equal to p.
But the gas laws are not actually obeyed.

We shall put $pv = RT + Bp$ where B is a constant

$$\therefore\ p\,dv + v\,dp = B\,dp$$

$$\therefore\ dp/dv = \frac{p}{v-B}.$$

$$\therefore\ V^2 = \frac{\gamma\left(\frac{dp}{dv}\right)_T \times v}{\rho} = \frac{\gamma\,pv}{\rho(v-B)}$$

$$= \frac{\gamma\,p^2v^2}{\rho pv(v-B)} = \frac{\gamma(RT+Bp)^2}{RT\times M}$$

where $M = \rho v =$ gm molecular wt

$$= \frac{\gamma RT}{M}\left(1+\frac{Bp}{RT}\right)^2.$$

We shall substitute for B from Bertholet's eqn $pv = RT\left\{1+\frac{9}{128}\frac{T_c}{P_c}\cdot\frac{p}{T}\left(1-\frac{6T_c}{T^2}\right.\right.$

$$\therefore\ V = \sqrt{\frac{\gamma RT}{M}}\left\{1+\frac{9}{128}\frac{T_c}{P_c}\cdot\frac{p}{T}\left(1-\frac{6T_c^2}{T^2}\right)\right\}$$

Experimenters have used the above formula to calculate γ knowi the velocity of sound at any temp.

ressure. The velocity given by the ormula is that in free air & so if the xpt is by a tube method, say, Regnault's xpts in pipes, or & Kundt's tube method en the ~~val~~ value has to corrected for that free air by the following eqn

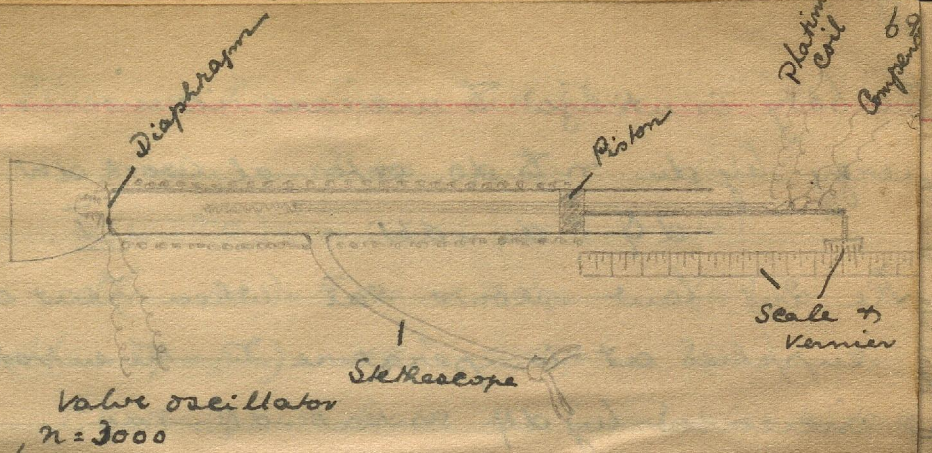
$$V' = V(1 - kc)$$

Where V' is vel. in tube, V in free air, & ~~R~~ k are constants given by

$$k = \frac{1}{2r\sqrt{\pi n}} \quad \& \quad c = \sqrt{\frac{\eta}{\rho}}\left\{1 + \frac{\varepsilon}{\sqrt{\gamma}}(\gamma - 1)\right\}$$

hen n is frequency of the note, r radius f the pipe, η viscosity of the gas & is a kinetic theory constant $\frac{k}{\eta C_v}$ k being ermal conductivity of the gas.

Partington and Shilling A diaphragm ttached to one end of a long tube was et in vibration by a triode valve oscilator of frequency 3000. A piston ~~was~~ ~~was f~~ closed the other end of the ube & the position of the piston could



be accurately read by a scale & vernie A stethescope established contact betwe the interior of the tube & the experimen ear. ~~&~~ The tube was surrounded with electric heating coils & a platinum resista thermometer noted the temp. of the gas. Di tance between successive positions of maximum resonance was observed. Thus $\frac{\lambda}{2}$ is known whence velocity is calculated The expt gave accurate values of v ~~at~~ up to temperatures as high as 1000°C.

Maxwell's Standard thermodynamical relations. (Saha 463)

The 1st law of thermodynamics shows that a quantity of heat dQ supp to a body is utilized to increase its internal nergy by du & to do external work dW.

$$\therefore \quad dQ = du + dW \qquad \underline{I}.$$

The 2nd law shows that when heat dQ supplied at temperature τ, the entropy s increased by $d\phi$ so that $dQ = \tau d\phi$.

$$d\phi = \frac{dQ}{\tau} \qquad \underline{II}.$$

From I $\quad dQ = \tau d\phi = du + dW = du + pdv$

i.e. $\quad du = \tau d\phi - pdv \qquad$ (i).

Let $\quad X = u - \tau\phi \qquad \underline{III}$.

$$dX = du - \tau d\phi - \phi d\tau.$$

$$= \tau d\phi - pdv - \tau d\phi - \phi d\tau$$

$$\therefore \quad d(u - \tau\phi) = -pdv - \phi d\tau \qquad (ii)$$

Let $\quad Y = u + pv \qquad \underline{IV}$

$$dY = du + pdv + vdp$$

$$= \tau d\phi - pdv + pdv + vdp$$

$$\therefore \quad d(u + pv) = \tau d\phi + vdp \qquad (iii)$$

Let $\quad Z = u - \tau\phi + pv \qquad \underline{V}$

$$dZ = \tau d\phi - pdv - \phi d\tau - \tau d\phi + pdv + vdp$$

$$= -\phi d\tau + vdp$$

i.e. $\quad d(u - \tau\phi + pv) = -\phi d\tau + vdp \qquad$ (iv)

Thus we have four relations

$$du = T\,d\varphi - p\,dv \qquad (i)$$

$$d(u - T\varphi) = -p\,dv - \varphi\,dT \qquad (ii)$$

$$d(u + pv) = T\,d\varphi + v\,dp \qquad (iii)$$

$$d(u - T\varphi + pv) = -\varphi\,dT + v\,dp \qquad (iv)$$

From (i) we have the isometric rate o
change of internal energy with entropy given by

$$\left(\frac{du}{d\varphi}\right)_v = T$$

Again, the ~~isothermal~~ isentropic rat
of change of internal energy with volume is given by

$$\left(\frac{du}{dv}\right)_\varphi = -p.$$

Now, if u be a function of x & y is
both x & y being variables,

$$\left(\frac{d}{dy}\right)_x \cdot \left(\frac{du}{dx}\right)_y = \left(\frac{d}{dx}\right)_y \cdot \left(\frac{du}{dy}\right)_x .$$

Using the above relation in (i)

$\left(\frac{d}{dv}\right)_\varphi \cdot \left(\frac{du}{d\varphi}\right)_v$ should be equal to $\left(\frac{d}{d\varphi}\right)_v \cdot \left(\frac{du}{dv}\right)_\varphi$.

e.g. if $u = \sin(xy+3)\,e^{x/y}$
~~both~~ L & R.H.S are equal to
$$e^{x/y}\left[\cos(xy+3)\left\{1 + \frac{2x^2}{y} - \frac{x^2}{y}\right\} - \sin(xy+3)\left\{\frac{2x}{y} + \frac{2x^3}{y^3} + xy\right\}\right]$$

ie. $$\left.\begin{aligned}\left(\frac{d\tau}{dv}\right)_\varphi &= -\left(\frac{dp}{d\varphi}\right)_v \\ &= -\tau\left(\frac{dp}{dQ}\right)_v\end{aligned}\right\} \quad (1)$$

The above is the 1st thermodynamical
ormula.

Now $\left(\frac{dp}{dQ}\right)_v$ the ~~variat~~ isometric vari-
tion of pressure with heat is always
ositive ∴ $\left(\frac{d\tau}{dv}\right)_\varphi$ i.e. the adiabatic
ariation of temperature with volume
negative. A substance cools on being
diabatically expanded.

Again the adiabatic rate of change
f temp. with volume is equal to the
roduct of temp. & the isometric ~~rat~~ rate
f change of pressure with heat supply.

From ii $\left(\frac{d\chi}{dv}\right)_\tau = -p$ & $\left(\frac{d\chi}{d\tau}\right)_v = -\varphi$

$$\left(\frac{d\chi}{d\tau}\right)_v \cdot \left(\frac{d\chi}{dv}\right)_\tau = -\left(\frac{dp}{d\tau}\right)_v$$

$$\left(\frac{d}{dv}\right)_\tau \cdot \left(\frac{d\chi}{d\tau}\right)_v = -\left(\frac{d\varphi}{dv}\right)_\tau$$

$$\left.\begin{aligned} \therefore \left(\frac{dp}{d\tau}\right)_v &= \left(\frac{d\varphi}{dv}\right)_\tau \\ \text{ie} \left(\frac{dQ}{dv}\right)_\tau &= \tau\left(\frac{dp}{d\tau}\right)_v \end{aligned}\right\} \qquad (2)$$

The above is <u>the 2nd thermodynamical formula</u>.

It shows that the isothermal variation of supply of heat with ~~temp~~ volume ~~i.e.~~ (e.g. in fusion & vapourization) is +ive since at constant vol pressure increases with temperature.

On page 189 B. A. Heat a formula for <u>rate of change of boiling point</u> with pressure was derived as

$$d\tau = \frac{\tau(v_2 - v_1)\,dp}{LJ} \quad \ldots \quad (a)$$

$$\text{ie} \quad \frac{L}{v_2 - v_1} = \tau\left(\frac{dp}{d\tau}\right) \quad (b)$$

L in (b) being in mechanical units. (b) is seen to be the same as (2) since heat L supplied to unit mass changes the volume ~~dv~~ by $dv = v_2 - v_1$.

Where L & $v_2 - v_1$ is +ive (i.e. ~~mo~~ in ost cases of boiling & fusion except e.g. in the melting of ice) $L/v_2 - v_1$ also +ive & hence dp/dT is +ive; ie ncrease of pressure raises the B.P or e F.P. In the melting of ice pressure ecreases the melting point.

Lord Kelvin determined exptly the epression of freezing point & found to agree with the value calculated from n (2). His values are:—

Increase of pres. dp	Exptal value dp	Calculated value.
8·1 atmos.	·0580°C	·0601°C
16·8	·1280°C	·1260°C.

Measuring $(dp/dT)_v$ for the boiling oint of water Lord Kelvin calculated latent heat of ~~vapour~~ steam & saw to be in very close agreement with a direct exptal value.

He found $\left(\frac{dp}{dT}\right)$ to be 27·12 m.m. of mercury.

$$L = T \times \left(\frac{dp}{dt}\right) \times v_2 - v_1$$

$$= \frac{373 \times 2{\cdot}712 \times 13{\cdot}6 \times g \times 1641}{J}$$

$$= \underline{539} \text{ calories}$$

Expts of Visser on the boiling poi of acetic acid also verified the formula.

On page 85 Prop. of Matter Ptons. No an expression for heat absorbed ~~for~~ when the area of ~~the~~ a film is increased: Work done dW by the film when area is increased by dA $= -S\,dA$ (S being surface tension) the –ive Sig Showing that work is actually done on the film. In the ~~gas~~ case of a ga $dW = p\,dv$. Hence eqn ② can be modified putting dA for dv & $-S$ for

Thus $\left(\frac{dQ}{dA}\right)_T = -T\left(\frac{dS}{dT}\right)_A$

Now dS/dT is negative say $-\beta$.

$\therefore dQ/dA = \beta T$. ~~If Cis~~ Thus we see that dQ is +ive; heat is absorbe by the film when its area is increas

If the increase is effected under adiabatic onditions, a corresponding cooling $d\tau$ kes place. If C is the thermal capa-ity of the film, $C d\tau = dQ$

$$\therefore d\tau = \tau\beta \frac{dA}{C}.$$

This eqn too has been verified by several bservers.

From iii viz $d(\chi) = d(u + pv) = T d\varphi + v dp$,

$$\left(\frac{d\chi}{d\varphi}\right)_p = \tau \ ; \left(\frac{d\chi}{dp}\right)_\varphi = v$$

$$\left.\begin{aligned} \therefore \left(\frac{d\tau}{dp}\right)_\varphi &= \left(\frac{dv}{d\varphi}\right)_p \\ \text{\& since } d\varphi = \frac{dQ}{\tau} \qquad \left(\frac{d\tau}{dp}\right)_\varphi &= \tau\left(\frac{dv}{dQ}\right)_p \end{aligned}\right\} (3)$$

The above is the <u>third thermodynamical</u> ormula.

$dQ = C_p d\tau$, & $\left(\frac{dv}{d\tau}\right) \times \frac{1}{v_0} = \alpha$ the coeff. of expn. v_0 being vol. at zero °C.

$$\therefore \frac{\alpha}{C_p} = \frac{dv}{dQ} \cdot \frac{1}{v_0}.$$

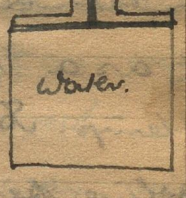
$$\therefore \left(\frac{d\tau}{dp}\right)_\varphi = T v_0 \times \frac{\alpha}{C_p}.$$

The eqn in the above form shows that

When α is +ive, i.e. the substance expan
on heating, then $\left(\frac{dT}{dp}\right)_{\phi}$ is also +ive. i.e.
the adiabatic increase of pressure rai
the temperature of the substance.

Joule verified the eqn in the Case of wa
by suddenly applying a pressure of
26·19 kgm to a vol. of water enclosed in
a vessel. At temp. 1·2°C (where α is −iv
he observed a fall of temp. ·0081°C; the
Calculated value at the same temp being
·0076. At 5·0°C (where α is +ive) a
rise of temp ·0044°C was observed,
the calculated value being ·0037°C.

Another verification is afforded b
the cooling due to adiabatic stretching
of a wire.



Work done pdv corresponds to Fdl F being force & dl the increase in length. & is −ive since work is done on the wire. ~~fo ∴ p~~

∴ Eqn $\left(\frac{dT}{dp}\right)_\phi = T\left(\frac{dv}{dQ}\right)_p$ becomes putting

F for p, & −dl for dv

$$\left(\frac{dT}{dF}\right)_\phi = -T\left(\frac{dl}{dQ}\right)_p$$

Now ~~if~~ β coefft of expansion $= \frac{1}{l}\cdot\frac{\delta l}{\delta T}$

& if ϖ is mass per unit length, C_p sp. heat,

$\varpi l C_p\, dT = dQ$

$$\therefore dT = dF \times -T.\frac{\beta l\, dT}{\varpi l c_p\, dT}$$

$$= dF \times -\frac{T\beta}{\varpi C_p}$$

Hence when the tension is suddenly creased by dF, the temperature falls β is +ive & in the case of rubber here β is −ive, the temp. rises. The expt as performed with German Silver wire sing the wire itself ~~as the thermometric~~ ~~balance~~ & another thin wire wound round as a thermocouple to measure the change temp. Haga's expts showed that the mean oling per kgm ·00813 °C, the calculated alue being ·00810. For rubber β is −ive

∴ Sudden stretching has a heating effe

From iv viz $d(Z) = -\varphi\, dT + v\,dp$

$$\left(\frac{dZ}{dT}\right)_p = -\varphi \;;\; \left(\frac{dZ}{dp}\right)_T = v$$

$$\left.\begin{aligned} \therefore\ \left(\frac{d\varphi}{dp}\right)_T &= -\left(\frac{dv}{dT}\right)_\varphi \\ \left(\frac{dQ}{dp}\right)_T &= -T\left(\frac{dv}{dT}\right)_\varphi \end{aligned}\right\} \qquad (4).$$

The above is the <u>fourth thermodynam</u> formula. Since adiabatically vol. increases with temp. i.e. $\frac{dv}{dT}$ is +ive, ~~th~~ $\frac{dQ}{dp}$ is −ive, the isothermal variat of heat supply with pressure is negative i.e. If the pressure is increased, heat has tobe abstracted from the body in order to keep the temperature cons

(in rubber $\frac{dl}{dT}$ & in water bet. 0 & 4° $\frac{dv}{dT}$ are −ive)

The above eq<u>ns</u> can be derived in a <u>more purely</u> <u>mathematical way</u>, wi arbitrary assumptions ~~A~~ X, Y, Z.

Of the four quantities p, v, τ, φ,
a if any two are independent variables
nd are known, the other two can be
etermined since they are dependent on
ese. Let x, y, be independent variables

$$du = \tau\, d\varphi - p\, dv$$

$$= \tau \frac{d\varphi}{dx} \cdot dx + \tau \frac{d\varphi}{dy} \cdot dy - p \frac{dv}{dx} \cdot dx - p \frac{dv}{dy} \cdot dy.$$

$$\left(\frac{du}{dx}\right)_y \cancel{=}$$

$$\left(\frac{du}{dx}\right)_y = \tau \frac{d\varphi}{dx} - p \frac{dv}{dx}$$

$$\left(\frac{du}{dy}\right)_x = \tau \frac{d\varphi}{dy} - p \frac{dv}{dy}.$$

$$\left(\frac{d}{dy}\right)_x \cdot \left(\frac{du}{dx}\right)_y = \left(\frac{d}{dx}\right)_y \cdot \left(\frac{du}{dy}\right)_x$$

i.e. $\frac{d\tau}{dy} \cdot \frac{d\varphi}{dx} + \tau \frac{d^2\varphi}{dx\,dy} - \frac{dp}{dy} \cdot \frac{dv}{dx} - p \frac{d^2v}{dx\,dy}$

$$= \frac{d\tau}{dx} \cdot \frac{d\varphi}{dy} + \tau \frac{d^2\varphi}{dx\,dy} - \frac{dp}{dx} \cdot \frac{dv}{dy} - p \frac{d^2v}{dx\,dy}$$

i.e. $\frac{d\tau}{dy} \cdot \frac{d\varphi}{dx} - \frac{dp}{dy} \cdot \frac{dv}{dx}$

$$= \frac{d\tau}{dx} \cdot \frac{d\varphi}{dy} - \frac{dp}{dx} \cdot \frac{dv}{dy}. \quad \underline{I}.$$

Of the four quantities p, v, τ, φ, we shall take any two as x & y, ~~&~~ there are 6 possible groups

(1) pv, (2) $p\tau$, (3) $p\varphi$

(4) $v\tau$ (5) $v\varphi$ (6) $\tau\varphi$.

Taken in the order 5, 4, 3, 2, 1, 6 they give 6 eqns 4 of which are identical with those derived above.

1) $x = v$; $y = \varphi$

$$\therefore \frac{dv}{dx} = \frac{d\varphi}{dy} = 1 ; \quad \frac{dv}{dy} = \frac{d\varphi}{dx} = 0.$$

$$\therefore -\left(\frac{dp}{d\varphi}\right)_v = \left(\frac{d\tau}{dv}\right)_\varphi \qquad (1)$$

2) $x = v$, $y = \tau$

$$\therefore \frac{dv}{dx} = \frac{d\tau}{dy} = 1 ; \quad \frac{dv}{dy} = \frac{d\tau}{dx} = 0$$

$$\therefore \left(\frac{d\varphi}{dv}\right)_\tau = \left(\frac{dp}{d\tau}\right)_v \qquad (2)$$

(3) $x = p$, $y = \varphi$;

$$\frac{dp}{dx} = \frac{d\varphi}{dy} = 1 ; \quad \frac{dp}{dy} = \frac{d\varphi}{dx} = 0.$$

$$\therefore \left(\frac{d\tau}{dp}\right)_\varphi = \left(\frac{dv}{d\varphi}\right)_p \qquad (3)$$

(4) $x = p \qquad y = \tau.$

$$\frac{dp}{dx} = \frac{d\tau}{dy} = 1 \; ; \; \frac{d\tau}{dx} = \frac{dp}{dy} = 0.$$

$$\left(\frac{d\varphi}{dp}\right)_\tau = -\left(\frac{dv}{d\tau}\right)_p \qquad ④$$

) $x = p, \qquad y = v.$

$$\frac{dp}{dx} = \frac{dv}{dy} = 1 \; ; \; \frac{dp}{dy} = \frac{dv}{dx} = 0.$$

$$\left(\frac{d\tau}{dp}\right)_v \left(\frac{d\varphi}{dv}\right)_p - \left(\frac{d\tau}{dv}\right)_p \left(\frac{d\varphi}{dp}\right)_v = 1 \qquad ⑤$$

) $x = \tau \qquad y = \varphi$

$$\frac{d\tau}{dx} = \frac{d\varphi}{dy} = 1 \; ; \; \frac{d\tau}{dy} = \frac{d\varphi}{dx} = 0.$$

$$\left(\frac{dp}{d\tau}\right)_\varphi \left(\frac{dv}{d\varphi}\right)_\tau - \left(\frac{dp}{d\varphi}\right)_\varphi \left(\frac{dv}{d\tau}\right)_\varphi = 1 \qquad ⑥$$

Applications of the above eqns.

Variation of internal energy

hen the vol. changes at constant mperature. $\left(\frac{du}{dv}\right)_\tau$.

The second eqn $\left(\frac{d\varphi}{dv}\right)_\tau = \left(\frac{dp}{d\tau}\right)_v$

Now $\quad T\,d\varphi = du + p\,dv$

$$\therefore d\varphi = \frac{1}{\tau}(du + p\,dv)$$

$$\left(\frac{d\varphi}{dv}\right)_\tau = \frac{1}{\tau}\left(\frac{du}{dv} + p\right)$$

$$\therefore \left(\frac{du}{dv}\right)_\tau = \tau\left(\frac{d\varphi}{dv}\right)_\tau - p$$

$$\therefore \left(\frac{du}{dv}\right)_\tau = \tau\left(\frac{dp}{d\tau}\right)_v - p.$$

The eqn can be applied to three particular cases

1) Expansion of a perfect gas

$$\left(\frac{dp}{d\tau}\right)_v = \frac{R}{v} \quad \text{Since} \quad Pv = R\tau$$

$$\& \therefore \left(\frac{du}{dv}\right)_\tau = \tau\frac{R}{v} - p = 0.$$

In a perfect gas isothermal expansion neither consumes or gives out energy. The molecules can ∴ be supposed to be beyon the range of mutual attractions.

It will be remembered that Joule te the validity of this result in the case o an actual gas & saw no fall of temp w the gas expanded freely due to his appara ot being sufficiently sensitive. He wrongly oncluded that there are no intermolecular ttractions in actual gases.

2) Actual gases obeying Van der Waals eqn

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

$$\left(\frac{dp}{dT}\right)_v = \frac{R}{v-b} \quad \& \therefore \left(\frac{du}{dv}\right)_T = \frac{RT}{v-b} - p$$

i.e. $\left(\frac{du}{dv}\right)_T = \frac{a}{v^2}$ which is always +ive.

$= 2\cdot73 \times 10^3$ for oxygen.

i.e. in actual gases internal nergy increases with isothermal expanion. To keep the temp. constant heat as to be supplied from outside. ~~H~~ ence we conclude that in actual gases ere is intermolecular attraction, which o, however, very small ~~small~~ as is een from the eqn for a is a small uantity & v in the case of gas is arge. ..

3) Solids and liquids.

$$\left(\frac{du}{dv}\right)_T = T\left(\frac{dp}{dT}\right)_v - p$$

$$\therefore = -T\cdot\left(\frac{dp}{dv}\right)_T \cdot \left(\frac{dv}{dT}\right)_p - p$$

for $\left(\frac{dp}{dT}\right)_v = \left(\frac{d\varphi}{dv}\right)_T = \left(\frac{dp}{dv}\right)_T \cdot \left(\frac{d\varphi}{dp}\right)_T = -\left(\frac{dp}{dv}\right)_T \cdot \left(\frac{dv}{dT}\right.$

Now $v_0 \times \left(\frac{dp}{dv}\right)_T = k_T$ the isothermal ~~elast~~ bulk modulus $v\left(\frac{dv}{dT}\right)_p \times \frac{1}{v_0}$ is the α_p the Coefft of vol. expansion at Constant pressure

$$\therefore \left(\frac{du}{dv}\right)_T = T\,k_T\,\alpha_p - p.$$

Which in the case of bra

at N.T.P $= 273 \times 3.5 \times 10^{11} \times 5.67 \times 10^{-5} - 1.013 \times$

$= (273 \times 3.5 \times 5.67 - 1.013) \times 10^{6}$ i

$= 5.418 \times 10^{9}$ dynes / cm^2.

The value is nearly 2 million times that in gases.

This large value of the intermolec attraction accounts for the definite shap and volume in the case of solids & definite vol. in the case of liquids.

Specific heat at Constant pressure.

The fourthe eqn was modified by itkowsky to measure sp. heats at various ressures and temperatures.

$$\left(\frac{d\varphi}{dp}\right)_\tau = -\left(\frac{dv}{d\tau}\right)_p$$ & Since $d\varphi = \frac{dQ}{\tau}$

$$\left(\frac{dQ}{dp}\right)_\tau = -\tau\left(\frac{dv}{d\tau}\right)_p$$ ~~Now $\left(\frac{d}{d\tau}\right)_p \left(\frac{dQ}{dp}\right)_\tau = \left(\frac{d}{dp}\right)_\tau \left(\frac{dQ}{d\tau}\right)_v$~~

Now $\left(\frac{d}{d\tau}\right)_p \cdot \left(\frac{dQ}{dp}\right)_\tau = \left(\frac{d}{dp}\right)_\tau \cdot \left(\frac{dQ}{d\tau}\right)_p$ & $\left(\frac{dQ}{d\tau}\right)_p = C_p$

$$\therefore \left(\frac{d}{dp}\right)_\tau C_p = -\tau\left(\frac{d^2v}{d\tau^2}\right)_p$$

If C_P C_1 be the ~~press~~ values of C_p t pressures P atmos. & 1 atmosp.

$$\int_{C_1}^{C_P} d(C_p) = \int_1^P -\tau\left(\frac{d^2v}{d\tau^2}\right)_p \cdot dp.$$

$$C_P - C_1 = \int_1^P -\tau\left(\frac{d^2v}{d\tau^2}\right)_p dp.$$

From Amagat's & Andrews Curves e see that pv is not equal to p_0v_0 hen the pressure is high.

We may write $pv = \eta p_0 v_0$

where η is a function of temp., press &

$$= \eta_0 p_0 v_0 (1 + \alpha\theta)$$

where η_0 is Const. θ is temp. in °C,

& α is mean vol. expansion at pressure p

when temp. is raised from 0 to θ.

α is ∴ a function of temp.

$$\theta = T - 273 \therefore d\theta/dT = 1$$

~~&~~

$$v = \frac{\eta_0 p_0 v_0}{p}(1 + \alpha\theta) = A(1 + \alpha\theta)$$

$$\left(\frac{dv}{dT}\right)_p = A\left(\alpha + \theta\frac{d\alpha}{dT}\right)$$

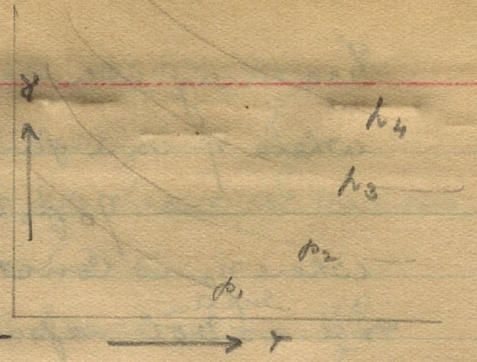
$$\left(\frac{d^2v}{dT^2}\right)_p = A\left(\frac{d\alpha}{dT} + \theta\frac{d^2\alpha}{dT^2} + \frac{d\alpha}{dT}\right)$$

$$= A\left(\theta\frac{d^2\alpha}{dT^2} + 2\frac{d\alpha}{dT}\right)$$

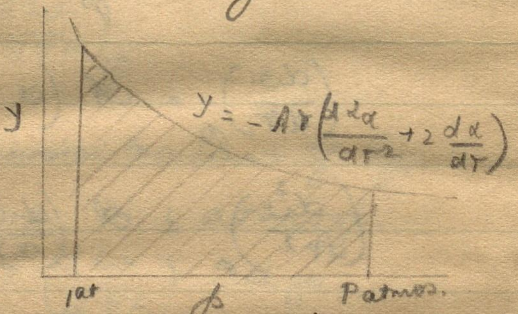
$$C_p - C_1 = \int_1^p -AT\left(\theta\frac{d^2\alpha}{dT^2} + 2\frac{d\alpha}{dT}\right)d$$

Expts of Regnault gave values of α for different values of temp θ and

t different pressures.
urves can be drawn
onnecting α & T, each
urve corresponding to
particular value of pres-
ure p.



From each curve the value of the
unction $Y = -AT\left(\frac{d^2\alpha}{dT^2} + 2\frac{d\alpha}{dT}\right)$ can be
omputed for any given value of temp.
Another curve is drawn taking Y on the
-axis & the corres-
onding pressure
n the y-axis. The
rea of the ~~curve~~ space
ncluded between
e curve, the X-axis & the ordinates
= 1 atmos. $p = P$ atmos.

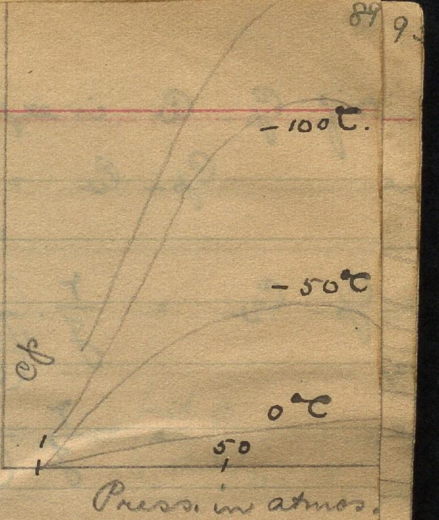


gives $\int_1^P Y\,dp$

which is $= \int_1^P -AT\left(\frac{d^2\alpha}{dT^2} + 2\frac{d\alpha}{dT}\right)dp$

$= C_p - C_1$

Knowing C_v, C_p can be calculated. The curves connecting C_p & P at different temp. are shown in the diagram. At high temp. C_p is practically const. but, at ~~hi~~ low temp. C_p rises with increase of pressure.



Expressions for $C_p - C_v$

$$C_p - C_v = \tau\left(\frac{d\varphi}{d\tau}\right)_p - \tau\left(\frac{d\varphi}{d\tau}\right)_v$$

$$= \tau\left(\frac{d\varphi}{dv}\right)_p\left(\frac{dv}{d\tau}\right)_p - \tau\left(\frac{d\varphi}{dp}\right)_v\left(\frac{dp}{d\tau}\right)_v$$

$$= \tau\left(\frac{d\varphi}{dv}\right)_p\left(\frac{dv}{d\tau}\right)_p\left(\frac{dp}{d\tau}\right)_v\left(\frac{d\tau}{dp}\right)_v$$

$$- \tau\left(\frac{d\varphi}{dp}\right)_v \cdot \left(\frac{d\varphi}{d\tau}\right)_v\left(\frac{dv}{d\tau}\right)_p\left(\frac{d\tau}{dv}\right)_p$$

$$= \tau\left(\frac{dv}{d\tau}\right)_p \cdot \left(\frac{dp}{d\tau}\right)_v \left\{\left(\frac{d\varphi}{dv}\right)_p \cdot \left(\frac{d\tau}{dp}\right)_v - \left(\frac{d\varphi}{dp}\right)_v \cdot \left(\frac{d\tau}{dv}\right)\right.$$

$$= \tau\left(\frac{dv}{d\tau}\right)_p \cdot \left(\frac{dp}{d\tau}\right)_v \qquad \text{by } 5^{\text{th}} \text{ rel}$$

n if $C_p - C_v$ is expressed in Calories

$$C_p - C_v = \frac{\tau}{J}\left(\frac{dv}{d\tau}\right)_p \cdot \left(\frac{dp}{d\tau}\right)_v \qquad \underline{(A.)}$$

$$C_p - C_v = \frac{\tau}{J} \cdot \frac{\left(\frac{dp}{d\tau}\right)_v^2}{\left(\frac{dp}{d\tau}\right)_v \cdot \left(\frac{d\tau}{dv}\right)_p}$$

$$= -\frac{\tau}{J}\,\frac{(dp/d\tau)_v^2}{(d\varphi/dv)_\tau \times (dp/d\varphi)_\tau}$$

$$= -\frac{\tau}{J} \cdot \left(\frac{dp}{d\tau}\right)_v^2 \cdot \left(\frac{dv}{dp}\right)_\tau \qquad \underline{\underline{(B)}}$$

$pv = \eta\, p_0 v_0$ where η is a variable

$p\,dv + v\,dp = p_0 v_0\, d\eta.$

$$\left(\frac{dv}{dp}\right)_\tau = \frac{p_0 v_0}{p} \cdot \left(\frac{d\eta}{dp}\right)_\tau - \frac{v}{p}$$

$$\therefore\ C_p - C_v = -\frac{\tau}{Jp}\left\{p_0 v_0 \left(\frac{d\eta}{dp}\right)_\tau - v\right\}\left(\frac{dp}{d\tau}\right)_v^2 \cdot \underline{(C)}$$

$$C_p - C_v = \frac{\tau}{J}\,\frac{(dv/d\tau)_p^2}{\left(\frac{dv}{d\tau}\right)_p \cdot \left(\frac{d\tau}{dp}\right)_v}$$

$$= \frac{\tau}{J} \cdot \frac{\left(\frac{dv}{d\tau}\right)_p^2}{-\left(\frac{d\varphi}{dp}\right)_\tau \times \left(\frac{dv}{d\varphi}\right)_\tau}$$

$$= -\frac{\tau}{J}\,\frac{\left(\frac{dv}{d\tau}\right)_p^2}{\left(\frac{dv}{dp}\right)_\tau}$$

$$= -\frac{\tau}{J}\cdot\left(\frac{dv}{d\tau}\right)_p^2\cdot\left(\frac{dp}{dv}\right)_\tau$$

$$= \frac{\tau}{J}\cdot\left\{\frac{1}{v_0}\cdot\left(\frac{dv}{d\tau}\right)_p\right\}^2 v_0^2 \times \left(\frac{-dp}{dv/v_0}\right)_\tau \cdot$$

$$= \frac{\tau}{J}\, v_0\, \alpha^2 k_\tau \qquad (D)$$

α being volume coefft of expa

k_τ the isothermal bulk modulu

& Since in the case of solids $\alpha = 3$
λ being linear coefft,

$$C_p - C_v = 9\frac{\tau}{J}\, v_0\, \lambda^2 k_\tau \qquad (E)$$

Eqn $C_p - C_v = \frac{R}{J}$ (Meyer's Eqn) is a particular form of these general eqns A to E. when $pv = R\tau$ i.e. gas pe

$$\left(dv/d\tau\right)_p = \frac{R}{p} \quad \& \quad \left(\frac{dp}{d\tau}\right)_p = \frac{R}{v}$$

$$\therefore C_p - C_v = \frac{\tau}{J}\,\frac{R}{p}\cdot\frac{R}{v} = \frac{R^2\tau}{JR\tau} = \frac{R}{J}.$$

(by Eqn A

Again to apply C, η, t when the as is perfect, $\frac{d\eta}{dp} = 0$

$$\therefore \quad C_p - C_v = \frac{\tau v}{Jp} \cdot \frac{R^2}{v^2} = \frac{R}{J}.$$

$C_p - C_v$ for solids and liquids.

Eqns C & D enable us to find $C_p - C_v$. or solids & liquids & since C_p can e exptly determined, ~~C_p can~~ C_v can e calculated.

Thus for mercury

$$C_p - C_v = \frac{\tau}{J} v_0 . \alpha^2 K \tau$$

$$= \frac{273}{4.2 \times 10^7} \times \frac{1}{13.6} \times 1.81 \times 10^{-8} \times \frac{10^6}{3.9 \times 10^{-6}}$$

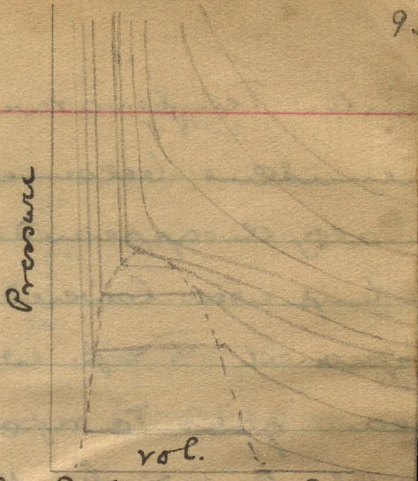
$$= \cdot 0041 \text{ Cal.}$$

Dulong & Petit's law is found to be ery accurate when C_v is substituted or the usual exptal value C_p.

Atomic wt × C_v is a Constant.

Continuity of State.

Andrew's experiments on compressi-



Andrews — CO_2

bility of gases, and the isothermal curves obtained by him (1876) & the more extended experiments of Amagat (1884) are described in B. A. Notes. The curves show a critical point above which any amount of pressure is unable to liquefy the gas.

To determine the critical constants T_c, P_c, V_c several methods have been employed

1) From Andrew's curves. The method is applicable only to gases like CO_2 for which the curve has actually been draw

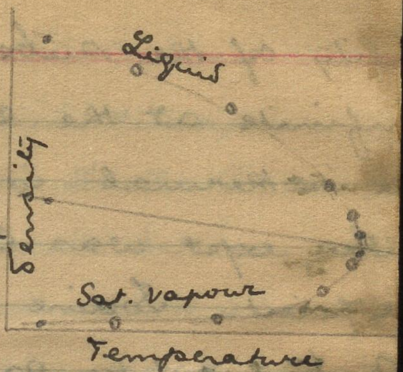
2) Caignard de la Tour's expt.

~~The~~ equal masses of liquid and saturated vapour were enclosed in the bulb, & the pressure was noted by the gas in the narrow

ube. Temperature was raised till the
eniscus becoming flatter & flatter
nally disappeared. Temp. & pres. were noted. Then
e temp was lowered till the meniscus again
ppeared. T. & p. were again noted. The
ean gives T_c & p_c. V_c cannot be accu-
ately known by this method, for any
light deviation of temp. from T_c ~~&~~
anges the volume by a large amount.
, dney Young ~~James~~ adjusted by trial to have
e meniscus disappear just when it is
t the top of the tube & thus measured V_c.

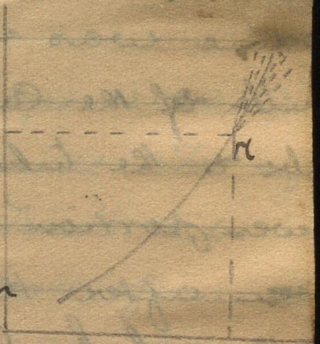
3) Cailletet & Mathias — Law of recti-
near diameters. If the density of
liquid (ρ_l) at its least possible pressure
~~of its~~ the density of its saturated va-
our (ρ_v) be plotted as ordinates & the
rresponding temperatures as abscissae,
en a curve roughly parabolic is ob-
ined. The mean $\frac{1}{2}(\rho_l + \rho_v)$ is found to
strictly a st. line. The point where

the st. line meets the [illegible] [illegible] parabolic curve gives T_c & $\frac{1}{V_c}$. The graph shown here is for ~~nitro~~ nitrogen.



4) Cailletet & Colardeau

* made expts on water and drew the steam line. It was found that when different quantities of the liquid were taken, the steam line though identical up to a point M showed divergences after that point. Coordinates of M gives T_c & P_c.

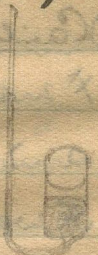


State of matter near the critical point.

* A natural deduction from Cagniard De la Tour's expt, that above the critical point all the substance is gas, & cannot be liquefied unless by mere application of pressure, without lowering temperature. Also the compressi-

lity of the substance $\left(\frac{dv}{dp}\right)$ is almost nfinite at the critical point since e isothermal is practically horizontal.

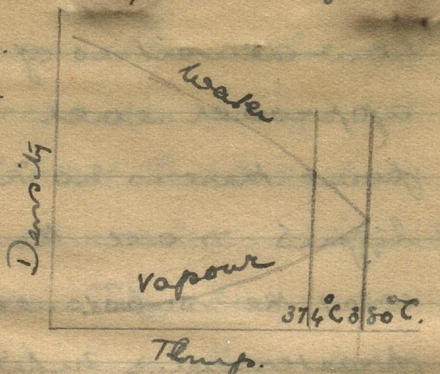
An expt was conducted to elucidate e point. Iodine can dissolve in liquid O_2 but not in gaseous CO_2. Some odine was introduced into the ulb of the Caigniard de la Tour's be & the tube was cooled. ~~A~~ The wer portion alone was coloured ven after the meniscus disappeared. the whole CO_2 is gas, we should expect e iodine to be deposited. Hence even fter the critical point, we may surmise, liquid & gaseous states con- inue.



Andrews' interpretation of the expt. as different. He said that as the ubstance approaches T_c the physical nd chemical properties of liquid & aturated & vapour become more and more alike. Andrews' curves show how densities of liquid & vapour approach each other. At the Critical point there is no distinction between gas liquid & all the argument ~~&~~ about what the substance is is "verba, voces, praeteraque nihil."

Callendar's recent expts (1928) ~~to~~ show a different result. He ~~rep~~ used a Caignard de la Tour's tube of quartz & found ~~that~~ both from th appearance of mirage & from th displacement of glass beads of varying densities that the densities of liquid & vapour at Critical point are not equal. Due to the extreme compressibility the upper layers increase the densities of the lower layers.

He also repeated the total hea expts of ~~R~~ Regnault and ~~found~~ Drew graph Connecting density & temperature or water & steam.



t the Critical point 74°C densities of ater & steam do ot coincide; they o so only at 380°C.

ence substances ~~can exist~~ are either as liquid r as gases at temperatures near t e T_C. At 374°C latent heat of steam hich according to Regnault should be ero is actually 7.24 cal.

But how does the meniscus dis- ppear? The vapour & liquid can ix in all proportions, & so the urface tension effect completely isappears.

Equations of State.

The first modification of the gas qn $pv = RT$ was made by Vander Waals

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

The term $\frac{a}{v^2}$ was introduced to correct for the ~~m~~ diminution in actual pressure due to the attraction of the neighbouring molecules on a molecule which is about to impinge on the wall. The force is $\propto$ the product of the masses of the attracting and attracted molecules i.e. is inversely $\propto$ to the sq. of the ~~vo~~ specific volume.

The term b was introduced to correct for the dimensions of the molecules & as proved in Kinetic theory (Cf notes Page 24) $b = v \times \frac{\sigma}{2\lambda}$.

Methods of determining a & b.

1) Elimination method.

Determine p & v at three different temperature ~~& them~~ as far removed from each other as possible, & hence from the 3 eqns solve for a, b, R.

2) Constant volume coefft.

$$\alpha_v = \frac{1}{p_0} \times \left(\frac{dp}{dt}\right)$$

$$p = \frac{R\tau}{v-b} - \frac{a}{v^2} \quad \therefore \quad \frac{dp}{d\tau} = \frac{R}{v-b}$$

$$\& \quad \alpha = \left(\frac{dp}{d\tau}\right)\frac{1}{p_0} \quad \therefore \quad \frac{R}{v-b} = \alpha p_0$$

ie $b = v - \dfrac{R}{\alpha p_0}$

Again $\alpha p_0 = \dfrac{R}{v-b} \quad \therefore \quad \dfrac{a}{v^2} = \dfrac{R\tau_0}{v-b} - p_0$

$$= \tau\alpha p_0 - p_0$$

$$\therefore \quad a = v^2 \cancel{\alpha} p_0 (\tau_0\alpha - 1)$$

Thus a & b can be calculated.

3) Constant pressure Coeff^t

The method of proceedure is

e same.

4) Isothermal Slope.

$$p = \frac{R\tau}{v-b} - \frac{a}{v^2}$$

$$\therefore \left(\frac{dp}{dv}\right)_\tau = -\frac{R\tau}{(v-b)^2} + \frac{2a}{v^3}$$

Knowing $\left(\frac{dp}{dv}\right)_\tau$ for two values of v, a & b can be calculated.

(5) From the value of the critical Const

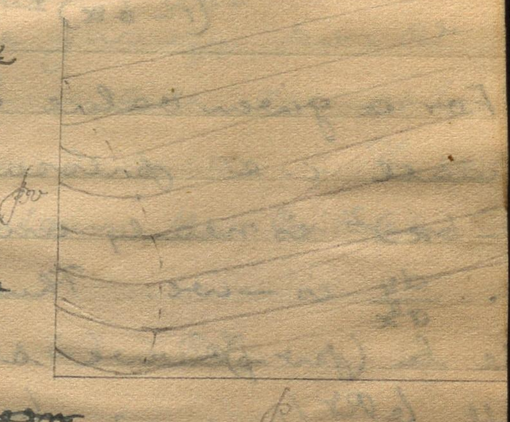
i.e. $v_c = 3b$; $p_c = \frac{a}{27b^2}$ & $T_c = \frac{\cancel{27R}\,8a}{27R}$

However, since v_c cannot be known accurately the values of p_c & T_c alone should be utilized.

6) Joule Kelvin Inversion The temper-ature of inversion is $T = \frac{2a}{Rb}$. ∴ The ratio $\frac{a}{b}$ can be known.

Merits of the Eqn

1) Explains the Shape of Amagat's Curves.



The curves show the variation of pv with p, ~~the eqn~~ which is also the variation of p with $\frac{1}{v}$ since to a first approximation pv is const.

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

$$\text{ie } \left(pv + \frac{a}{v}\right)\left(1 - \frac{b}{v}\right) = RT.$$

Putting pv as y & $\frac{1}{v}$ as x

$$(y + ax)(1 - bx) = RT.$$

$$(1 - bx)(dy + a\,dx) + (y + ax) \times -b\,dx = 0$$

ie $dx\{b(y + ax) - a(1 - bx)\} = (1 - bx)\,dy$

$$\therefore \frac{dy}{dx} = b\,\frac{y + ax}{1 - bx} - a.$$

$$= \frac{bRT}{(1 - bx)^2} - a$$

For a given value of T, when x is mall i.e. pressure is small, ~~when~~ $-bx)^2$ is nearly unity & $a > \frac{bRT}{(1-bx)^2}$. $\therefore \frac{dy}{dx}$ is -ive. Thus at first he ~~to~~ (pv-p)curve slopes downward, ill $bRT/(1-bx)^2$ becomes equal to a hen the curve is horizontal & finally, e slope becomes +ive & the curve oes up.

Again the value of x for which e ~~curve~~ slope is zero is given by

$1 - bx = \sqrt{\frac{bRT}{a}}$ ie $x = \frac{1}{b}\left\{1 - \sqrt{\frac{bRT}{a}}\right\}$

Thus as T increases x becomes smaller and smaller. The horizontal part of the curve approaches the y-a more & more & finally disappears.

2) Calculation of Critical Constants.

At the critical point compressibility is infinite, & the curve has a point of inflection. ~~$\frac{dx}{dx}$~~ $\frac{dp}{dv}$ & $\frac{d^2p}{dv^2}$ should both be zero. The gas eqn $pv = RT$ gives $\frac{dp}{dv} = -\frac{p}{v}$ which cannot be zero except when v is ∞. ∴ The gas eqn fails to explain the critical state.

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

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \qquad (1)$$

$$\frac{dp}{dv} = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}$$

which is zero when $\frac{2a}{v^3} = \frac{RT}{(v-b)^2}$ (

$$\frac{d^2p}{dv^2} = \frac{2RT}{(v-b)^3} + \frac{6a}{v^4}$$

Which is zero when $\frac{3a}{v^4} = \frac{RT}{(v-b)^3}$. (3)

rom (1), (2), & (3) we get

$$v_c = 3b \; ; \; T_c = \frac{8a}{27Rb}$$

$$p_c = \frac{a}{27b^2}.$$

) <ins></ins>Theory of Corresponding States

iz that gases equally removed from ritical point behave similarly s proved by Van der Waal's eqn.

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

Let $v = \alpha v_c$; $p = \beta p_c$ & $T = \gamma T_c$.

$$\left(\beta p_c + \frac{a}{\alpha^2 v_c^2}\right)\left(\alpha v_c - b\right) = R\gamma T_c.$$

$$e \left(\beta \times \frac{a}{27b^2} + \frac{a}{\alpha^2 \cdot 9b^2}\right)\left(\alpha \times 3b - b\right) = \gamma R . \frac{8a}{27Rb}$$

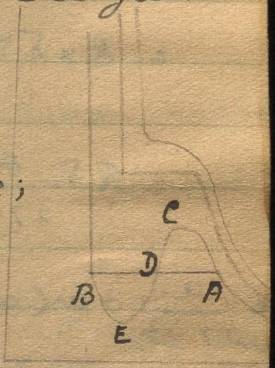
$$e \left(a\beta + \frac{3a}{\alpha^2}\right)\left(3\alpha - 1\right) = \frac{8\gamma Ra}{R}$$

ie $\left(\beta + \frac{3}{\alpha^2}\right)(3\alpha - 1) = 8\gamma$

This eqn is independent of a., b, R the the Constants of the gas & ∴ proves the theory of corresponding states.

4) Horizontal vapour pressure line.

The horizontal vapour pressure line on the reduced isothermal can be shown to be the same for all gas. Let v_3, v_1 be the sp. volumes at A & B of the reduced isothermal $v_3 = \alpha v_c$; $v_1 = \beta v_c$; $p = \gamma p_c$ & $T = \delta T_c$.



The eqn to the horizontal line can be shown to be the same for all gas. By the II law of thermodynamics ~~work done~~ by taking a substance 1st along the St. line AB, & then back along the Curve ACDEB, work done $= Q_1 \times \frac{T_1 - T_2}{T_1} = 0$ since the temperature is the same throughout the cycle.

$$\therefore\ p(v_3 - v_1) = \int_{v_1}^{v_3} p\,dv$$

$$= \int_{v_1}^{v_3} \left\{ \frac{R\tau}{v-b} + \frac{a}{v^2} \right\} dv$$

$$= \Big[R\tau \log(v-b) - \frac{a}{v} \Big]_{v_1}^{v_3}$$

$$= R\tau \log \frac{v_3 - b}{v_1 - b} - a \left(\frac{1}{v_3} - \frac{1}{v_1} \right)$$

$$= R \times \delta \tau_c \log \frac{\alpha v_c - b}{\beta v_c - b} - a \left(\frac{1}{\alpha v_c} - \frac{1}{\beta v_c} \right)$$

$$= R\delta . \frac{8a}{27Rb} \log \frac{3\alpha b - b}{3\beta b - b} - \frac{a}{3b} \left(\frac{1}{\alpha} - \frac{1}{\beta} \right)$$

e $\frac{a}{27b^2}\, 3b(\alpha - \beta)$

$$= R\delta \frac{8a}{27Rb} \log \frac{3\alpha - 1}{3\beta - 1} - \frac{a}{3b} \left(\frac{1}{\alpha} - \frac{1}{\beta} \right)$$

$$(\alpha - \beta)\, \frac{a}{9b} = \frac{8a}{27b}\, \delta\, \frac{3\alpha - 1}{3\beta - 1} - \frac{a}{3b} \left(\frac{1}{\alpha} - \frac{1}{\beta} \right)$$

ie $$\frac{\alpha - \beta}{3} = \frac{8}{9}\, \delta\, \frac{3\alpha - 1}{3\beta - 1} - \left(\frac{1}{\alpha} - \frac{1}{\beta} \right)$$

This eqn is independent of the constants of the gas & ∴ shows that the horizontal vapour pressure line on the reduced isothermal is the same for all gases.

Defects of van der Waals's eqn.

① a & b are not constant at all temperatures. The following table refers to argon

157	1.90×10^6	61
183	1.735×10^6	56
213	1.600×10^6	48
233	1.530×10^6	45

2) Critical Coefft

$\frac{RT_c}{p_c v_1}$ which should be unity is the gas is perfect & should be ~~$\frac{R\times 8a}{27Rb\times 3}$~~ $\frac{R\times 8a\times 27b^2}{27Rb\times 3b\times a} = 2.66$ for a gas obeying van der Waals is actually greater than 2.66. The values of the Critical Coefft are He 3.27, H 3.276, Ne 3.249, N 3.412, Ar 3.424, CO_2 3.4 SO_2 3.62, pentane 3.76, ethyl alcohol 3.81, acetic acid 4.99.

3) Boyle point T_B is that temp. at which for a given pressure

4) Lastly the actual value of v_c is nearly b & not 3b as vander Waals eqn requires.

Modifications of the Gas Eqn

1) Dieterici To make the critical coefft nearly 3.7, the following modification was introduced

$$p \cancel{= \frac{RT}{v}} \left(p + \frac{a}{v^{5/3}}\right)(v-b) = RT.$$

$$p = \frac{RT}{v-b} - \frac{a}{v^{5/3}} \qquad 1)$$

$$\frac{dp}{dv} = -\frac{RT}{(v-b)^2} + \frac{5}{3}\,\frac{a}{v^{8/3}}$$

$$\frac{d^2p}{dv^2} = \frac{2RT}{(v-b)^3} - \frac{5}{3}\cdot\frac{8}{3}\cdot\frac{a}{v^{11/3}}$$

At the critical point, $\frac{dp}{dv}$ & d^2p/dv^2 are both zero.

$$\frac{5}{3}\frac{a}{v^{8/3}} = \frac{RT}{(v-b)^2} \qquad 2)$$

$$\& \quad \frac{5}{3}\cdot\frac{8}{3}\frac{a}{v^{11/3}} = \frac{2RT}{(v-b)^3} \qquad 3)$$

From 1) 2) & 3)

$$v_c = 4b$$

$$T_c = \frac{15a}{16R\,(4b)^{2/3}}$$

$$p_c = \frac{a}{4\,(4b)^{5/3}}$$

Critical Coefft $\frac{RT_c}{p_c v_c} = 3{\cdot}75$ which agrees more closely with the observed values. But $v = 4b$ according to abo whe whereas actually $v = 2b$, & Vander Waa gives $v = 3b$.

2) Amagat proposed

$$\left\{p + \frac{a}{f(v)}\right\}(v-b) = RT.$$

3) Berthelot ~~f~~ mostly ~~from~~ basing himself on observed values, & partly

lso supporting himself on theory proposed $\left\{p + \frac{a}{v^2 T}\right\}(v-b) = RT$; or he argued that the temperature lso affects intermolecular attraction. rom the above he derived

$$pv = RT\left\{1 + \frac{9}{128}\cdot\frac{\pi}{\theta}(1 - 6\theta^2)\right\}.$$

where $\pi = p/p_c$ & $\theta = T/T_c$.

This eqn is found to ~~satisfy~~ agree best with the nown behaviour of most gases over irly wide ranges & hence has been ften applied ~~in~~ for reduction of ermometer readings to the perfect as scale & for other measurements ith gases.

4) Clausius introduced three constants c, β & b.

$$\left\{p + \frac{c}{T(v+\beta)^2}\right\}(v-b) = RT.$$

$$p = \frac{RT}{v-b} - \frac{c}{T(v+\beta)^2}.$$

$$\frac{dp}{dv} = \frac{-R\tau}{(v-b)^2} + \frac{2c}{\tau(v+\beta)^3} \qquad 2)$$

$$\frac{d^2p}{dv^2} = \frac{2R\tau}{(v-b)^3} - \frac{6c}{\tau(v+\beta)^4} \qquad 3)$$

At the critical point, equating 2) & (3) to zero, we get

$$v_c = 2\beta + 3b$$

$$\tau_c = \sqrt{\frac{8}{27}\,\frac{c}{R(b+\beta)}}$$

$$p_c = \sqrt{\frac{Rc}{216(b+\beta)^3}}$$

The critical coefft $\frac{R\tau_c}{p_c v_c} = \frac{8(\beta+b)}{3(\beta+b)-}$
Which is > 2.66.

But the value of v_c is also > 3b which is at variance with expt.

In a later form Clausius introdu
a function of temp. $\varphi = \frac{R\tau^2}{c}$

$$\frac{p}{R\tau} = \frac{1}{v-b} - \frac{c}{R\tau^2(v+\beta)^2}$$

$$\therefore \frac{p}{R\tau} = \frac{1}{v-b} - \frac{1}{\varphi(v+\beta)^2}.$$

& he got $v_c = 3b + 2\beta$,

$$p = \frac{R\tau_c}{8(\beta + b)} \quad \& \quad \tau_c = \frac{8}{27(b+\beta)}$$

5) Diatrecit (improved form)

$$p = \frac{RT}{v-b} e^{-\frac{a}{RTv}}$$ (See Kinetic Theory 63)

When a & b are mall this form reduces itself to Van der Waals.

$$p = \frac{RT}{v-b}\left(1 - \frac{a}{RTv}\right)$$ Since a is small

$$= \frac{RT}{v-b} - \frac{a}{v^2 - vb}$$

$$= \frac{RT}{v-b} - \frac{a}{v^2}$$ Since b is small.

This eqn gives $v_c = 2b$ & Critical Coefft 3.695.

cf Saha 223

5) Saha & Bose

$$p = -\frac{RT}{2b} \log\left(\frac{V-2b}{V}\right) e^{-\frac{a}{RTV}}.$$

This also reduces to Van der Waals' when a & b are small.

$$p = \frac{RT}{2b} \times \frac{2b}{v}\left(1 - \frac{a}{RTv}\right)$$

$$= \frac{RT}{v} - \frac{a}{v^2}$$

$$\text{ie} \left(p + \frac{a}{v^2}\right)(v - b) = RT \text{ nearly.}$$

The above eqn gives Critical Coefft 3.53 which is very nearly the ~~ta~~ average of all gases. Al $v_c = 2b$.

The final conclusion however i that it is futile to look for an eqn wh satisfies all gases. For such an eqn can exist only if the structure of gases are similar. In actua gases the ~~conditions~~ hypothesis of elastic spheres at finite distances is far from true, & ~~to~~ the ~~behaviour~~ critical coeff varies from gas to gas according to the molecular associations, & the molecular structure of each particu gas.

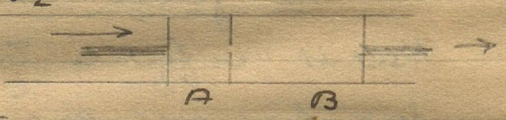
An eqn which is true for individual gases & is derived from virial theorem is.

$$\left\{p + \frac{a(T)}{v^2}\right\}\left\{v - b\,e^{-\frac{a}{RT}}\right\} = RT.$$

(Saha 474)

Joule Thomson effect is the ~~cooling~~ change of temp. produced when a gas is passed through an orifice on the two sides of which a difference of temperature is maintained.

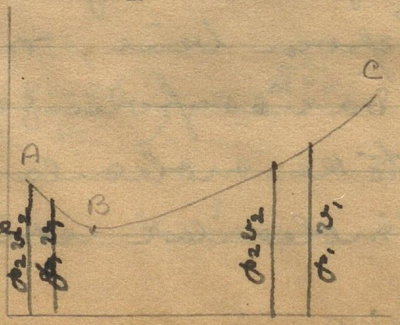
If p_1, v_1, u_1, & p_2, v_2, u_2 be the pressure, & sp. vol., & internal energy per gm. ~~of~~ ~~on~~ of the gas on the two sides, A & B,



$$u_1 + p_1 v_1 = u_2 + p_2 v_2.$$

$$\therefore u_2 - u_1 = p_1 v_1 - p_2 v_2.$$

When $p_1 v_1 = p_2 v_2$ i.e. the state of gas is represented by the horizontal portion of the



($pv - p$) curve,

$u_1 = u_2$.

But $u_1 = ~~p~~\ P_1 + K_1$ & $u_2 = P_2 + K_2$ where P & K are the potential & kinetic energy. Since $p_2 < p_1$, $v_1 > v_2$, i.e. the molecules in B are at greate distances from each other & ∴ $P_2 >$ ∴ $K_2 < K_1$ Hence the energy of motio of the molecules & ∴ the temperature i less ~~in~~ in B than in A. The J. K. effect here is one of cooling.

2) When $p_1 v_1 < p_2 v_2$ i.e. the state of gas is represented by the portion AB of the curve, & $u_1 > u_2$; $K_1 + P_1 > K_2$ But $P_2 > P_1$ ∴ ~~The differ~~ K_2 is muc more below K_1 than in the former case The ~~cool~~ effect is again one of coolin & the amount of cooling is greater than that of case (1)

3) When $p_1 v_1 > p_2 v_2$, i.e. the state of the gas is represented by the portion

BC of the Curve. $u_2 > u_1$

ie $K_2 + P_2 > K_1 + P_1$ ∴ $K_2 - K_1 > P_1 - P_2$

But ~~p~~ $P_1 - P_2$ is a negative quantity.

$K_2 - K_1$ may be negative, zero or positive.

The effect may be cooling or heating or either according to the state of the gas.

The principle of J. K. Cooling effect as used by Linde to liquefy per-anent gases.

The following table gives the cooling roduced when the difference of pressure one atmosphere.

Gas	J. K. effect per atmos.
air	·208
CO_2	1·005
O	·253
N	·249
H_2	−·039

For two gases He & H_2 at ordinary mperatures the J. K. effect is one of ~~heat~~ heating.

Explanation from Maxwell's relations

For the J. K. effect, the condition is

$u + pv$ = Constant.

$\therefore du + p\,dv + v\,dp = 0$

but $du = T\,d\phi - p\,dv$

$\therefore$ $\cancel{T\frac{d\phi}{d}}$ Substituting

$$T\,d\phi + v\,dp = 0$$

ie $$T\left(\frac{d\phi}{dT}\right)_p dT + T\left(\frac{d\phi}{dp}\right)_T dp + v\,dp = 0$$

ie $$C_p\,dT - T\left(\frac{dv}{dT}\right)_p dp + v\,dp = 0$$

ie $$C_p\cdot\left(\frac{dT}{dp}\right)_i = T\left(\frac{dv}{dT}\right)_p - v$$

the subscript i stands for $u + pv$

$$\therefore \left(\frac{dT}{dp}\right)_i = \frac{1}{C_p}\left\{T\left(\frac{dv}{dT}\right)_p - v\right\}$$

This eqn establishes the existence of the J. K. effect & gives its magnitude when the change in pressure is small.

The differential change in temperature

is given by $dT = \frac{1}{C_p}\left\{ T\left(\frac{dv}{dT}\right)_p - v \right\} dp$

$= \delta \, dp$

When the difference in ~~large~~ pressures

s large $\int_{T_1}^{T_2} dT = \int_{p_1}^{p_2} \delta \, dp.$

& δ not being

constant, an integration alone can

ive $(T_2 - T_1)$.

J. K. effect ~~the~~ as due to deviation

f actual gases from Boyle's law &

oule's law

Boyle's law is pv is a constant

t. ∴ $\frac{d}{dp}(pv) = 0$.

Joule's law ~~sta~~ is that when a gas

xpands freely its internal energy is

~~stra~~ not changed. $\left(\frac{du}{dp}\right)_T = 0$. This

s what Joule sought to examine by

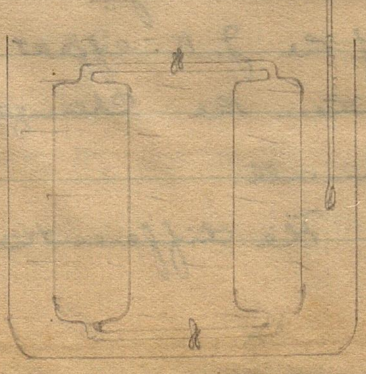
is expt. of free expansion between

wo chambers.

$$\left(\frac{dT}{dp}\right)_i = \frac{1}{C_p}\left\{ T\left(\frac{dv}{dT}\right)_p - v \right\}$$

$$= \frac{1}{C_p}\left\{ -T\left(\frac{d\varphi}{dp}\right)_T - v \right\}$$

by 4th eqn



but $T\,d\phi = du + p\,dv$

$$\therefore \left(\frac{dT}{dp}\right)_i = \frac{1}{C_p}\left\{-T\left(\frac{du}{dp}\right)_T - \left(p\left(\frac{dv}{dp}\right)_T + v\right)\right\}$$

$$= \frac{1}{C_p}\left\{-\left(\frac{du}{dp}\right)_T - \frac{d}{dp}(pv)\right\}$$

The J. K effect is zero if both $\frac{du}{dp} = 0$ & $\frac{d}{dp}(pv) = 0$. Since ~~the gas~~ in the behaviour of actual gases there are divergences from both Joule's & Boyle laws, a heating or cooling is produce which is the resultant of the two divergences. ~~In the porous plug expt~~ ~~As in the gas passes from a higher to a lower pressure, $\left(\frac{du}{dp}\right)$ is negative~~ $\left(\frac{du}{dp}\right)$ is intrinsically negative. ∴ The fir ~~second~~ term within the bracket is positive. $\frac{dT}{dp}$ is +ive ~~acco~~ or zero, or −ive according as $\cancel{\left(\frac{du}{dp}\right)_T}$ $\left[\frac{d(pv)}{dp}\right]_T$ is $\lesseqgtr \left(\frac{du}{dp}\right)_T$

1) At the min point $\frac{d(pv)}{dp}$ is zero & ∴ $< \left(\frac{du}{dp}\right)_T$ ∴ $\left(\frac{dT}{dp}\right)$ is +ive —

An increase of pressure causes heating;

nd a diminution of pressure ~~to~~ as in

e porous plug expt causes cooling.

2) In the portion AB of the curve,

$\frac{d(pv)}{dp}$ is −ive & ∴ < $\frac{du}{dp}$. The case

s similar to (1)

3) In the portion BC $\frac{d(pv)}{dp}$ is +ive,

& may be $\lesseqgtr$ $\frac{du}{dp}$ & hence the effect

ay be cooling, heating or neither.

Calculation of J. K. effect.

1) For a perfect gas

$$\left(\frac{dT}{dp}\right)_i = \frac{1}{C_p}\left\{T\left(\frac{dv}{dT}\right)_p - v\right\}$$

$$= \frac{1}{C_p}\left(\frac{RT}{p} - v\right) = \frac{1}{C_p}(v - v) = 0.$$

∴ In a perfect gas dT/dp is zero;

the smaller the cooling, the more

perfect the gas. In mos hydrogen, not only

s there no cooling; there is actually

heating. "C'est plus que parfait'

2) For a gas obeying Van der Waals'

Resultant external work done by

the gas $= p_2v_2 - p_1v_1$

∴ Resultant internal work done by the gas $= u_1 - u_2 = \int_{v_1}^{v_2} \frac{a}{v^2}\,dv$

$= \frac{a}{v_1} - \frac{a}{v_2}$

∴ Total work done by the gas

$= p_2v_2 - p_1v_1 + \frac{a}{v_1} - \frac{a}{v_2}$.

$$pv = \frac{R\tau}{\left(1+\frac{a}{pv^2}\right)(1-bp)}$$

$$= R\tau - \frac{R\tau a}{pv^2} + R\tau bp$$

$$= R\tau - \frac{a}{R\tau}p + bp$$

$$\therefore p_2v_2 - p_1v_1 = -\frac{a}{R\tau}(p_2-p_1) + b(p_2-p$$

Since $\left(\frac{a}{v_1} - \frac{a}{v_2}\right)$ is a small quantity, we may put $v = \frac{R\tau}{p}$

$$\therefore \frac{a}{v_1} - \frac{a}{v_2} = \cancel{\frac{p}{R\tau}}\cancel{\frac{1}{p_1}}\frac{a}{R\tau}(p_1 - p_2$$

∴ Resultant ~~externa~~ work

$$= \left(\frac{2a}{R\tau} - b\right)(p_1 - p_2).$$

ince $p_1 - p_2$ is +ive, if $\frac{2a}{R}$ work is one by the gas or on it according as $\frac{2a}{RT} - b$ is +ive or negative. In the former case, the gas cools & in the latter t gets heated.

At ~~low~~ low temperatures $\frac{2a}{RT}$ is large ∴ the cooling too is great. But as mp. rises, the cooling becomes maller & smaller.

Also for gases like hydrogen for hich a is very small, the ~~cooling~~ erm $\frac{2a}{RT}$ is $<$ b even at ~~small~~ ordinary temperatures. Hence their anomalous behaviour.

If the cooling is dT due to a difference p of pressure, $C_p \, dT$ is energy absorbed rom the gas

$$\therefore C_p \, dT = \left(\frac{2a}{RT} - b\right) dp$$

This eqn enables us to calculate dT.

For oxygen at 0°C,

$$\left(\frac{dT}{dp}\right)_i = \frac{1}{7.03 \times 4.18 \times 10^7}\left\{\frac{2 \times 1.36 \times 10^6 \times 1.01 \times 10^6}{8.3 \times 10^7 \times 273} - 32.0\right\}$$

$$= \frac{89}{7\cdot 03 \times 4\cdot 18 \times 10^7}$$ degrees / dyne cm^2.

= ·3 degrees for press $\frac{1\,kgm}{cm}$

The calculated & observed values are as f

Gas	Calculated value	Observed value
H_2	−·17	·03
O_2	·30	·313
CO_2	·74	1·31
Air	·28	·27

Temp of J. K. Inversion

For a gas obeying Vander Waals the temp. of J. K. inversion is given by

$\frac{2a}{RT} = b$ ie $T_i = \cancel{bR}\,\frac{2a}{Rb}$.

$$\frac{T_i}{T_c} = 8a\,\frac{2a}{Rb} \Big/ \frac{8a}{27Rb} = \frac{27}{4}.$$

If T_c is known T_i can be calculated & viceversa.

Corrections for a gas thermometer.

Saha 4

The eqn for the Joule Kelvin effect is $T\left(\frac{dv}{dT}\right)_p = C_p\left(\frac{dT}{dp}\right)_i + v$. This being a standard thermodynamical eqn, holds good whatever be the substance, provided T is measured on the thermodynamic scale,

$C_p = \frac{dQ}{d\tau}$.

If the ~~ten~~ same temp. measured with gas thermometer reads θ, ~~& ($C_p' = \frac{dQ}{d\theta}$~~

e can find the relation between θ & τ as ollows. Let $C_p' = \frac{dQ}{d\theta}$ (i.e. ~~cp~~ sp. heat measured on the gas scale).

$$C_p = \left(\frac{dQ}{d\tau}\right)_i = \frac{dQ}{d\theta}\cdot\left(\frac{d\theta}{d\tau}\right)_i = C_p'\left(\frac{d\theta}{d\tau}\right)_i$$

$$C_p\left(\frac{d\tau}{dp}\right)_i = C_p'\cdot\frac{d\theta}{d\tau}\cdot\frac{d\tau}{d\theta}\cdot\left(\frac{d\theta}{dp}\right)_i$$

$$= C_p'\,\frac{d\theta}{dp}.$$

$$\left(\frac{dv}{d\tau}\right)_p = \left(\frac{dv}{d\theta}\right)_p\left(\frac{d\theta}{d\tau}\right)_p$$

$$\tau\left(\frac{dv}{d\theta}\right)_p\cdot\frac{d\theta}{d\tau} = C_p'\left(\frac{d\theta}{dp}\right)_i + v$$

ie $$\int_{\tau_1}^{\tau_2}\frac{d\tau}{\tau} = \int_{\theta_1}^{\theta_2}\frac{\left(\frac{dv}{d\theta}\right)_p d\theta}{C_p'\left(\frac{d\theta}{dp}\right)_i + v}$$

The quantities on the right hand ide are all measured on the gas scale and the integration is theoretically possible. When θ_1 & θ_2 are the melting point ~~& the~~ of ice & b. p. of water, let the value of the integral be x. $\therefore \log T_2 - \log T_1 = x$

ie $\log_e (T_1+100)/T_1 = x$ ie $1 + \frac{100}{T_1} = e^x$

$\therefore T_1 = \frac{100}{1-e^x}$. The eqn thus gives the value on the standard scale of the m. p. of i

Any other temp T corresponding to a gas thermometer reading θ can hence be calcul

But $\left(\frac{d\theta}{d\theta}\right)_p$ & $\left(\frac{d\theta}{dp}\right)_i$ are not constants & sufficient data is not available to determine the dependence of $\frac{d\theta}{dp}$ on θ. The correction is $\therefore$ is not very practicab

Supposing however $\frac{dv}{d\theta}$ & $\frac{d\theta}{dp}$ constants, putting $\frac{d\theta}{dp} = \mu$

$$\int_{\cancel{T_1}}^{\cancel{T_2}} \frac{dT}{T} = \int_{\cancel{\theta_1}}^{\cancel{\theta_2}} \frac{dv}{C_p'\mu + v}$$

ie $\log T = \log(C_p'\mu + v) + \log a$

$$T = a\,(C_p'\mu + v)$$

$T_0 = a(C_p'\mu + v_0)$ & $T_{100} = a(C_p'\mu + v_{100})$

$$\therefore \frac{T_0}{100} = \frac{a(C_p'\mu + v_0)}{a(v_{100} - v_0)}$$

$$i.e.\ T_0 = \frac{1}{\frac{v_{100}-v_0}{100\,v_0}} \times \left(C_p'\mu + v_0\right) \times \frac{1}{v_0}$$

$$= \frac{1}{\alpha}\left(C_p'\mu + v_0\right) \times \frac{1}{v_0}$$

$$= \frac{1}{\alpha}\left\{1 + \frac{C_p'\mu}{v_0}\right\}$$

$\frac{1}{\alpha}$ is the zero (centigrade) of the gas cale ∴ the correction to be applied get the zero (centigrade) of the thermodynamic cale is $+\frac{1}{\alpha}\,\frac{C_p'\mu}{v_0}$.

For hydrogen $\frac{1}{\alpha}\cdot\frac{C_p'\mu}{v_0} = -\cdot 13$

$\frac{1}{\alpha}$ i.e. $\theta_0 = 273\cdot 13$

∴ The thermodynamic ~~zero~~ temp $T_0 = 273$.

For CO_2 $\theta_0 = 269\cdot 5$; Correction is $4\cdot 4$

∴ $T_0 = 273\cdot 9$.

Radiation

Radiation is one of the three modes f exchanging heat and is the commonest. ts properties are exactly the same as those f light propagation, and any theory applied light corpuscular theory of Newton, Fresnel's elastic solid wave theory, Maxwell's electromagne theory, or Planck's quantum theory can with equal success be applied to heat radiation. Heat is radiated approximately along st. lin & casts geometrical shadows; its high veloci may be gauged from ~~of~~ the instantaneous cooling felt when a cloud comes across the sun. The charring that can be caused by a lens shows that heat rays are focusse like light rays. Intensity of heat obeys the inverse sq. law & ~~radiation~~ heat rays are reflected, refracted, diffracted, & polarized by the same means & according to the same laws as light waves.

Continuity of Spectrum. Heat waves like light waves are but a portion of the long series of electromagnetic radiations. The smallest known wavelengths are of Cosmic rays $\lambda =$ one X u. (X u being 10^{-3} A°u.) Next come γ rays of λ nearly ·06 A°u. X rays

ave a wavelength near 12 A°U. After
-rays Ultraviolet extends upto 4000A°U.
he visible spectrum lies between 4000
& 8000A°U. The infrared or heat waves
xtend to ·4 m.m. And lastly there
re the Hertzian waves which in the
Short wave region have λ between ·4 Cm
& 1 Cm. Short wave broadcast has λ between
Cm & 1 metre & long wave broadcast
above f. 1 metre & extending upto any length.

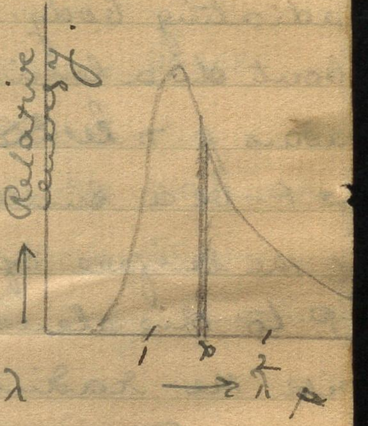
Prevost's theory of exchanges, Newton's law
f cooling, radiometers etc B. A. Notes
ages 129 – 153.

Emissive power E_s is the total radiant
nergy per unit time per unit area of
urface of the radiating body

Monochromatic emissive power — If
e radiation from a source be dispersed
to a spectrum & its ~~intensity~~ energy be measured
t different parts (by a thermopile), it will be
een that energy depends on the wavelength

in a certain definite manner as show

by the curve. The monochromatic emissive power e_λ at any given wavelength λ may be defined by saying that the energy emitted by the spectral range λ to $\lambda + d\lambda$ per unit area per unit time is ~~$\propto$~~ $e_\lambda d\lambda$. Thus, since the ordina of the curve is ~~$\propto$~~ e_λ, the area of the shaded strip is $e_\lambda d\lambda$.



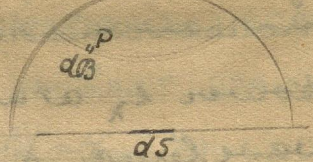
E_s the total emissive power

$$= \int_0^\infty e_\lambda d\lambda$$

Intensity of radiation i_s from a surfac ~~ds~~ at any given temperature is the energy radiated per unit of its area per unit solid angle in a direction normal to i the surface.

The relation between i_s & E_s can be deduced as follows

Let dS be a small surface element of a
adiating body. Describe
bout dS a hemisphere of
adius ρ & let ~~BD~~ dB located
t P be a small element



f the surface of this hemisphere, the radius
ρ to this element making an angle θ
ith the radius ON which is normal
dS. The energy incident on dB
er unit time is ~~x~~ the product of
s, the surface cosine $dS \cos\theta$,
he solid angle $\frac{dB}{\rho^2}$.

$$dQ = i_s\, dS \cos\theta \cdot \frac{dB}{\rho^2}.$$

Assuming that the radiation is symmetrical
with respect to ON,
total energy incident p.s. on the
rea $\rho\, d\theta \times 2\pi\rho \sin\theta$ generated
y the revolution of dB about ON

$$dQ = i_s\, dS \cos\theta \times \frac{2\pi\rho^2 \sin\theta\, d\theta}{\rho^2}$$

Hence energy incident on the whole
emisphere $= \int_0^{\pi/2} i_s\, dS \cos\theta \times 2\pi \sin\theta\, d\theta$

$$= 2\pi\, i_s\, dS.\left[\frac{-\cos 2\theta}{2}\right]_0^{\pi/2}$$

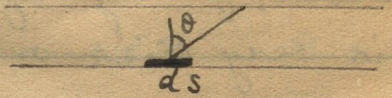
$$= \pi\, i_s\, dS.$$

But total incident energy $= E_s\, dS$

$\therefore \quad E_s = \pi\, i_s.$

Density of radiation is the radiant energy per ~~sq~~ c.c. of the medium. Its value in terms of E_s may be deduce as follows.

Energy radiated in time dt from the surface through an annular space on a hemisphere about dS the normal to which is inc at θ to the Surface normal to dS is



$dQ =$ ~~$i_\lambda d\lambda$~~ $i_s\, dS \cos\theta \times 2\pi \sin\theta\, d\theta \times d$

If dt is the time reqd for the energy to reach a wall h above dS, $dt = \frac{h}{c\cos}$ c being the velocity of radiation.

$\therefore dQ = i_s\, dS \times 2\pi \sin\theta\, d\theta \times \frac{h}{c}.$

$\therefore$ Energy of radiation per unit volume due to radiations at inclination $\theta = 2\pi\, i_s \frac{\sin\theta}{c}$

Energy density (the energy per unit ol, due to radiations at all inclination, & due to both direct & reflected radiations)

$$= 2\int_0^{\pi/2} 2\pi i_s \frac{\sin\theta\, d\theta}{c}$$

$$\psi = \frac{4\pi i_s}{c} = \frac{4}{c}E_s \qquad \therefore E_s = \frac{c\psi}{4}$$

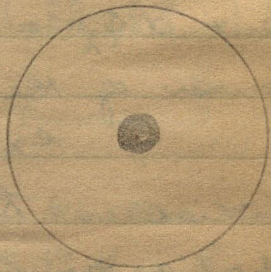
Absorptivity In general radiation falling upon a surface is partly bsorbed, partly reflected, & unless the ody is very thick or very opaque, is partly ransmitted. Absorptivity A of a surface is efined as the ratio of energy absorbed that incident per unit area per unit ime. Reflectivity R & Transmissivity T re also similarly defined.

R + T + A is evidently unity.

All the ~~eq~~ quantities are pure numerics, ess than unity for any actual body, & ary greatly with the wavelength of the ncident energy, & to a lesser extent ith the temperature of the body.

A total absorber, one for which A is unity, R & T zero is called a black body.

At a given temperature the quotient obtained by dividing the emissive pow by the absorptivity of any body is the same for all bodies & is equal to the emissive power of a black body at the same temperature. The above law, derived by Kirchoff in 1859 is known a Kirchoff's law.



Let a body of absorptivity a_λ for limits between λ & $\lambda + d\lambda$ be placed within a perfectly black enclosure & let the~~m~~ enclosure & the body be in thermal equilibrium. If dQ_λ be energy emitted ~~out~~ by the enclosure per unit time, $a_\lambda \, dQ_\lambda$ is absorbed by the body & $(1-a_\lambda) \, dQ_\lambda$ is reflected or transmitted to the enclos

Further if e_λ be emissive power of e body, total energy incident on the nclosure from ~~A~~ the body

$= e_\lambda + (1 - a_\lambda)\, dQ_\lambda$; all this is absorbed

~~Q~~ Energy emitted by the enclosure

$= dQ_\lambda$

By the theory of exchanges of Prevost, the two quantities should be equal

$\therefore \; e_\lambda - a_\lambda \, dQ_\lambda = 0$

ie $e_\lambda / a_\lambda = dQ_\lambda$

But $dQ_\lambda = E_\lambda$ the emissive power of the black body

$\therefore \; e_\lambda / a_\lambda = E_\lambda$.

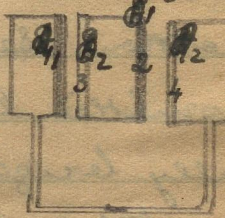
Which is Kirchoff's law.

Applications & verifications

A Coloured China when heated & xamined in a dark room is seen to e very bright in its Coloured portions ~~those ex~~ portions Further instead of xhibiting their natural colours, they xhibit the complementary Colours.

Thus a red flower on the china appear
greenish yellow & a green leaf appear
reddish yellow. What it most absorb
that it most emits when it's temp. is
high enough. A piece of red glass
heated to 1000° & examined in a dark
room appears a ~~red~~ green predomin

A qualitative ~~expt~~ proof is afforded by
Ritchie's expt (first conducted in 1833)

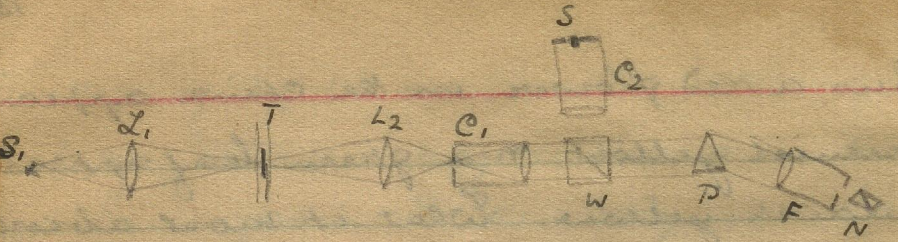


Let E_1 A_1, E_2 A_2 be the emissive power & absorptivity of the black surfaces 1, 2 & 3, 4 resply.

Since the liquid column in the connect tube is not displaced, ~~A_1 E~~ $E_1 A_2 = E_2 A_1$

ie $\frac{E_2}{A_2} = \frac{E_1}{A_1} = E_1$ since the absorptive ~~power~~ of a black body is unity.

Pfluger's Expt quantitatively verified Kirchoff's law in the case of the ordinary & ex. rays of tourmaline. Light from a source S, is condensed by L, to a



very thin tourmaline crystal T from hich both ord. & ex. rays emerge, are ondensed by L_2, collimated by C_1 & falls on a Lummer Brodhum Spectro- hotometer. It consists of a cube W t in two along a diagonal & the t portion semisilvered to have the ransmitted light ~~from~~ S & reflected light qually bright. Then it falls on a prism to a telescope after which it is analysed y a nicol. A standard source S is sed ~~then~~ Fe for comparison.

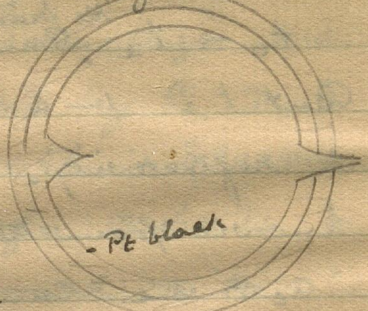
First T is removed & S, compared ith ~~S~~ S_1 for both ord. & ex.; Next S is removed & T maintained at some high temp & its missive power for Or & ex. Eo, Ee ompared with S. Lastly, both S & T (T being at the former temp) ~~are~~

compared with S, If I be emissive power of S, the three expts to determine I_o, I_e, E_o E_e, $I_o t_o + E_o$, $I_e t_e + E_e$. for any particular wavelength ∴ t_o & t_e the transmissivity can be calculated ~~the trans~~ But $t = 1 - a - r$, a being absorptivity r reflectivity. ~~R as~~ r_o & r_e can be known from the refractive indices μ_o & μ ∴ a_o & a_e can be calculated. Pfluger found $\frac{a_e}{a_o} = \cdot 650$, & $\frac{E_e}{E_o} = \cdot 641$. These are very nearly equal & hence Kirchoff's law is verified

Kirchoff's law holds good only for temp. radiation, ~~i.e.~~ & not for other sources of radiation say by electric discharge in gases, chemical action in flames the action of short wavelengths on fluoresce & phosphorescent screens etc.

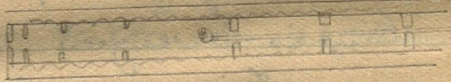
Black body for exptal purposes depends on the principle that radiation within an ~~closed~~ enclosure is black.

If a small hole be opened on the side, the merging radiation is black; & if the ole is of finite size, a small correction as to be made; ~~for~~ & the lack of blackness an be found. Fery's lack body utilizes his principle directly. e can see that it is also a perfect absorber.



Black body due to Fery.

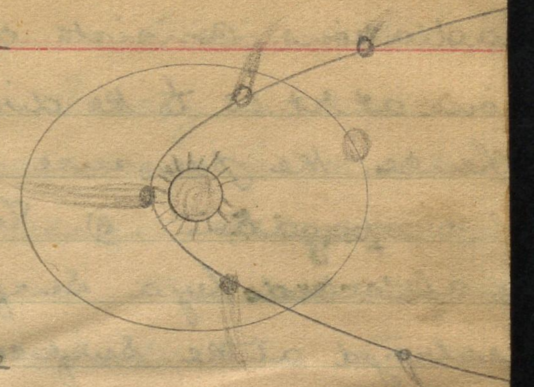
n Wien's black body metal cylinder eated by electric oils & the apperture imited by diaphragms s used. Its temp. is measured by a hermoelement.



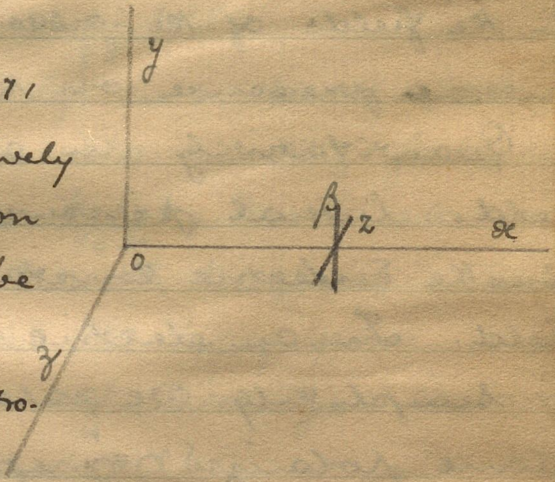
Black body due to Wien

Pressure exerted by radiation

The existence of such a pressure had already been ~~predicted~~ deduced by Kepler from the fact that comets' tails are always irected away from the Sun. The path



they trace is a parabola with the sun at ~~one~~ the ~~of~~ the focus, but the tails are always on the line joining the Sun to the Comet.



Maxwell in 1871 proved Conclusively that a radiation pressure is to be expected on the basis of the electro-magnetic theory of light. Qualitatively the line of argume
is as follows 1) Lines of electric or magne-
tic. force may be Supposed to be under
Stress longitudinally & to repel
each other laterally, this repulsion
Causing a lateral pressure 2) Accor-
ding to the e.m. theory light & therma

adiations consists of el. + mag. vibra-
ions at rt. ∠s to the direction of propagation,
hence the pressure is in the direction
f propagation. 3) When radiant energy
s absorbed by a surface, these fields are
estroyed at the surface & the lateral pressure
n the fields of the oncoming waves pro-
uces a pressure on the surface.

Quantitatively in a static electric
ield, lateral pressure = $\frac{kF^2}{8\pi}$ where
k is the dielectric constant, F is the
ield. In an electric wave, which
r simplicity we shall assume to be
lane polarized & represented by
$\frac{d^2 Z}{dt^2} = \frac{c^2}{\mu k}\frac{d^2 Z}{dx^2}$, Z is the electric
ector, the max. value of which is
F_0. The average lateral pressure $= \frac{kF_0^2}{16\pi}$.
lly in a magnetic field represented by
$\frac{d^2\beta}{dt^2} = \frac{c^2}{\mu k}\frac{d^2\beta}{dx^2}$, lateral pressure
$= \frac{\mu H_0^2}{16\pi}$. ∴ Total pressure on the
urface $p = (kF_0^2 + \mu H_0^2)\frac{1}{16\pi}$.

This can be shown to be equal to the energy density ψ. Energy in vol ($S\,dl$) area of section S & length dl $= \frac{1}{2} QV$ Q being charge, & V potentia

$Q = \sigma S$ where σ is the Maxwell displa
ment & $= \frac{kF}{4\pi}$. $V = F\,dl$.

$\therefore$ Energy $= \frac{kF^2 S\,dl}{8\pi}$

$\therefore$ Energy density in a static field $= \frac{kF^2}{8\pi}$. In the S.H. moving field, average density $= \frac{kF_0^2}{16\pi}$ due to electric wave & $\frac{kH_0^2}{16\pi}$ due to magnetic wave the sum of the two being ψ.

$\therefore p = \psi$. cf Richtmyer 203

Pressure & intensity

Intensity is the energy incident on uni
area p.s. & equal to the energy in a cylinder of area 1 sq cm & length c $= 3 \times 10^{10}$ cm. $\therefore$ Intensity $= \psi c$

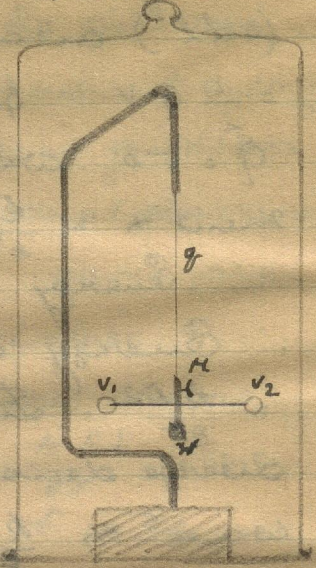
$$\therefore p = \frac{\text{Intensity}}{c} = \frac{I}{c}$$

On a perfectly reflecting surface, ψ is $\frac{2I}{c}$ $\therefore p = \frac{2I}{c}$.

Pressure due to sunlight $= \dfrac{\cdot 137 \times 10^{7}}{3 \times 10^{10}}$

$= 4{\cdot}567 \times 10^{-5}$ dynes/cm².

Experimental proof



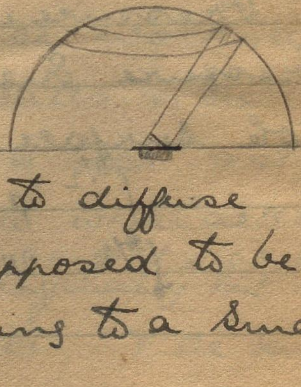
ey Lebedew, Nicholls & Hull,
aha etc.
Two thin vanes are attached
the arms of a glass cross,
a steadying wt W to the
end of the central rod.
he arrangement is suspended
y a fine quartz fibre
ithin an evacuated bell-jar.
When radiation falls on v_1, a
wist on the fibre is produced which
an be measured by a spot of light
reflected by a mirror attached to the cross.
we have $pal = \mu\theta$ p being pressure,
a area of the vane, l distance of the
vane from the centre of the cross, μ the
orsional couple. To find I the vanes
re replaced by thick blackened copper

discs & the rise in temp p.s. noted.
$IS = M\sigma t$, ~~Sf~~ where I is intensity S is area of the disc, M its mass, σ its specific heat & t rise in temp. p.s. as noted by a thermoelement.

In noting the value of θ the followin sources of error have to be taken into account 1) radiometer action due to the unequal heating on the two sides of the vane 2) Convection currents, 3) rocket action, due to heated air molecules rebounding from the surface. 2 & 3 are made small by evacuating the bell-jar & 1) is made small by choosing very thin vanes.

Radiation pressure

for diffuse radiation



The density ψ if due to diffuse radiation, may be supposed to be due to radiation streaming to a small

rea S from all over the surface of a
hemisphere which has S at its Centre.
he Quota of density supplied by an
nnular ~~ring~~ space at ∠lar deviation θ from
he surface normal is $\psi \times \frac{d\omega}{2\pi}$
where $d\omega = 2\pi\rho \sin\theta \times \rho\, d\theta / \rho^2$
$= 2\pi \sin\theta\, d\theta$ ~~/ρ2~~.

~~Pressure~~ Force due to small element
n the ~~surface~~ annular space is $\varphi\, S \cos\theta$ φ being
quota of surface energy supplied by
his element, ~~f~~for S cos θ is the area normal
o the radiation. The ~~normal co~~ vertical
component of this force is $S\varphi \cos^2\theta$.

Summing up for the whole surface
f the ring ~~to~~ Force = $S\psi \frac{d\omega}{2\pi} \cos^2\theta$
∴ Pressure = $\psi \frac{d\omega}{2\pi} \cos^2\theta$
Pressure due to radiation from the
whole surface of the hemisphere

$$= \int^{\pi/2} \psi \frac{d\omega}{2\pi} \cos^2\theta$$

$$= \int_0^{\pi/2} \psi .\ \cos^2\theta \sin\theta\, d\theta$$

$$= \frac{\psi}{3}$$

It may be noted that black body radiation (i. e. radiation within an ~~perfectly bl~~ ~~en~~ enclosure) is simila to a perfect gas. In both there is a great velocity at random in all directions; both exert pressure $\frac{\psi}{3}$ in one case & $\frac{1}{3}\rho v^2$ in the other, & in both the energy per unit volume increases with temperature.

Boltzman's proof of Stefan's law.

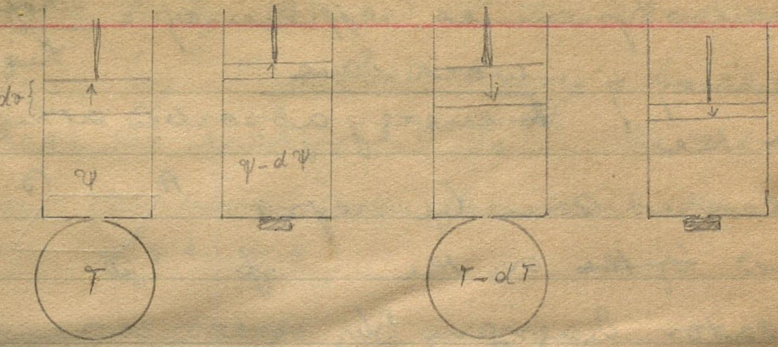
From the analogy between ~~radia~~ black body radiation & a perfect gas, Boltzman was led to consider a Carnot's cycle worked by what he called an ether engine. It consists of a cylinder C in which works a smooth piston. The walls & the piston are impervious to heat, & at the base there is a small hole which acts as an ideal black body. The body is in perfect vacuum. Originally let p be the pressure, v the ~~of~~ vol., T the temp.

ψ the energy density within the Cylinder.
et the Cylinder be ~~placed~~ closed with
perfectly reflecting Cap, ~~so that~~ which
an be removed when needed.

Let the Cylinder be taken through
he four following processes

1) Let it be placed above ~~a~~ the Small
ole of an enclosure at T° k, & let the
eflecting Cap be removed. The piston
drawn up Slowly so that the process
isothermal & the necessary energy is
rawn from the enclosure. If the increase
n vol. be dv, the energy drawn in
o do external work against pressure
is $p\,dv$, & energy drawn to given energy
ensity ψ to the new vol. dv created is
$\psi\,dv$. But $p = \frac{1}{3}\psi$ ∴ Total
energy absorbed $= \frac{4}{3}\psi$

2) The reflecting Cap is now put on,
he cylinder is thermally isolated, & the
iston is further allowed to rise, taking



the necessary energy from the radiations within itself, till the temp. falls to $T - dT$ & the energy density to $\psi - d\psi$.

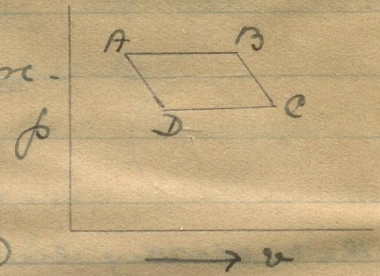
3) The cylinder is now placed on an enclosure at temp. $T - dT$ & the reflecting cap removed. The piston is allowed to come down, reducing the vol. by dv, transferring energy to the enclosure, & thus keeping the process isothermal.

4) Lastly, the cap is put on, a further deminution of vol. is caused, so that the temp. rises to T, energy density to ψ, & vol reduces to v.

The cycle has been completed, ~~and~~ it is also reversible. Hence by II Law thermodynamics efficiency = $\dfrac{\text{difference of temp.}}{\text{higher temp.}}$

fficiency $\eta = \dfrac{\text{work done}}{\text{~~a~~ energy absorbed at higher temp.}}$

Now the rocesses can be represented by ~~the~~ on the ndicator diagram by e sides of a ~~▱gm~~ quadrilateral ABCD



hich when δv becomes sufficiently mall reduces to a ▱gm.

Work done = area of the ▱gm = AB × ertical height = $dv \times dp = dv \times \frac{1}{3} d\psi$.

$$\therefore \frac{dv \times \frac{1}{3} d\psi}{\frac{4}{3}\psi\, dv} = \frac{d\tau}{\tau} \quad \text{i.e.} \quad \frac{d\psi}{\psi} = 4\frac{d\tau}{\tau}$$

ntegrating $\log\psi = 4\log\tau + \log a$

$$\psi = a\tau^4$$

Since the ~~a~~ emissive power E a small hole on the side of the linder is given by $E = \dfrac{c\psi}{4}$,

$$E = \frac{ca}{4}\tau^4$$
$$= \sigma\tau^4.$$

For a body which approximates to

a black body placed in an atmosphere at T_0, by Prevost's theory, since it also receives energy σT_0^4, the net radiation per unit area per unit time

$$= \sigma(T^4 - T_0^4).$$

<u>Alternative proofs.</u> ①

A cylinder whose walls are perfectly reflecting & impervious to heat is fitted with a piston also reflecting & impervious, moving in the cylinder without friction. The base of the cylinder is a black body A at temp. T. For simplicity the area of section is assumed to be unity. Let ψ be the energy density, x the vol, & p the radiation pressure.

Suppose the temp. of the black body is increased by dT. In order keep the energy density constant the piston will have to move outwards by a distance dx

If φ be the entropy, $\tau\, d\varphi$ is the energy upplied which is equal to the sum of e increase du of internal energy & the work one by the radiation pressure viz $p\,dx$

$$\tau\, d\varphi = du + p\,dx$$

$$= d(x\psi) + \frac{1}{3}\psi\, dx$$

$$= \psi\, dx + x\, d\psi.$$

$$= \frac{4}{3}\psi\, dx + x\, d\psi.$$

$$\left(\frac{d\varphi}{dx}\right)_\psi = \frac{4\psi}{3\tau} \quad \& \left(\frac{d\varphi}{d\psi}\right)_x = \frac{x}{\tau}$$

ut $\tau\left(\frac{d}{dx}\right)_\psi \cdot \left(\frac{d\varphi}{d\psi}\right)_x = \left(\frac{d}{d\psi}\right)_x \cdot \left(\frac{d\varphi}{dx}\right)_\psi$

ie $\frac{1}{\tau} = \frac{4}{3} \cdot \frac{\tau - \psi \cdot \frac{d\tau}{d\psi}}{\tau^2}$

ie $\tau = \frac{4}{3}\left(\tau - \psi\frac{d\tau}{d\psi}\right)$

ie $\frac{d\tau}{\tau}\ \frac{\tau}{\cancel{3}} = \frac{4}{3}\psi\frac{d\tau}{d\psi}$ ie $\frac{d\psi}{\psi} = 4\frac{d\tau}{\tau}$

Hence .... (ut supra)

2) On page 83 it was shown that

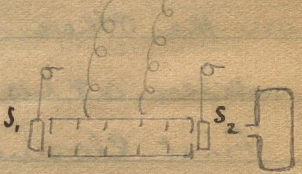
$$\left(\frac{du}{dv}\right)_\tau = \tau\left(\frac{dp}{d\tau}\right)_v - p.$$

$$\text{Now } \left(\frac{du}{dv}\right)_T = \psi \, ; \quad \left(\frac{dp}{dT}\right) = \frac{1}{3}\frac{d\psi}{dT}$$

$$\therefore \quad \psi = \frac{1}{3}T\frac{d\psi}{dT} - \frac{1}{3}\psi$$

$$\text{i.e.} \quad \frac{d\psi}{\psi} = 4\frac{dT}{T} \ldots$$

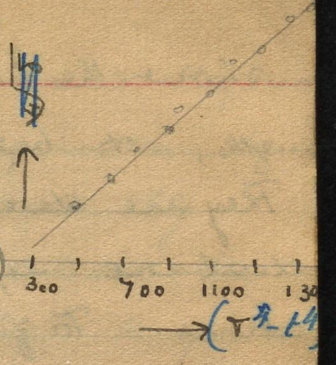
Verification of Stefan Boltzmann's law. By Lummer & Pringsheim.



An extensive measurement of radiation for temperatures of the radiating body ranging between 200°C & 1300°C was made by Lummer & Pringheim The black body which a spherical enclos Coated inside by platinum black & provided with a small orifice is placed in the heater which for ~~low~~ temp. up to 900°C is a liquid Sodium nitrate bath, & above 900°C is a double-walled gas furnace. The temp. of the ~~furnace~~ black body is measured by a thermoelement. The radiation is measur y a Lummer & Kurlbaum bolometer. t is protected at both ends by water cooled hutters, ~~& the deflectio~~ which may be removed hen desired. The difference in radiant energy eceived in ~~both~~ the two ends is ∝ the deflection in the galvanometer. One one side of he bolometer is the high temp. radiator, on the other side a standard radiator f water at its B.P.

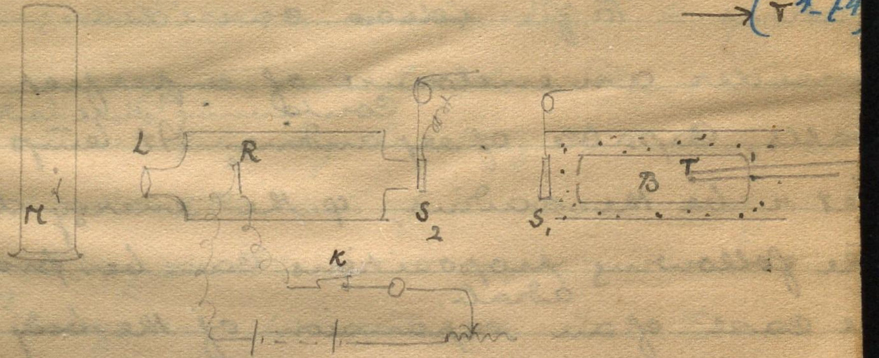
First closing shutter S_1 & opening S_2, e deflection d_1 was noted. By Stefan's aw $d_1 = a\,(373^4 - 290^4)$ where a is Const, 290 temp. of the water used to ool the shutter. Next S_1 was opened, S_2 closed & the inverse sq. law verified by placing the bolometer at various istances from the heater. Lastly, eeping the bolometer at a fixed distance, maintaining the temp. of the heater at ifferent steady values, δ was found out n each case. Plotting δ & $(T^4 - 290^4)$

an approximate St. line graph was obtained.



Accurate determination of σ

Coblentz (1920) & Kussmann (1924)

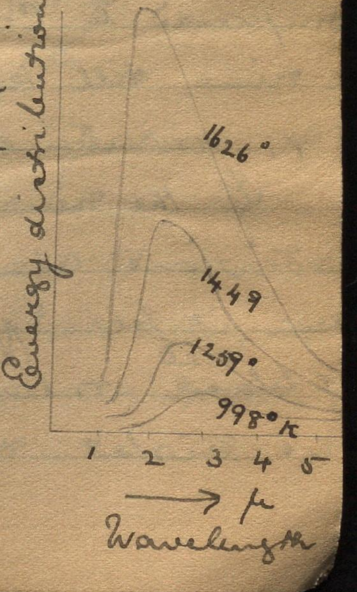


Radiation from a black body B falls on a strip R & is measured by a Boy's radio-micrometer M Cf Saha Page 576.

Wein's Displacement laws.

The energy corresponding to different wavelengths in the Spectrum of a black body or full radiation is a quantity characteristic of the temp.

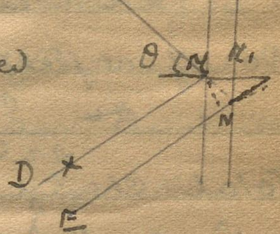
Wein's two laws derived from classical theory



n show the Relations between temp. & wave-
ength, & between temp. and energy.
They are derived by a consideration of
diabatic expansion of black body ra-
iations. To fix ~~ideas~~ our ideas, let us
onsider an enclosure of ~~a~~ perfect reflecting
alls, Capable of expanding containing full radiation. At temp T
et r be the radius, φ the energy density.
he following propositions can be proved in
e case of an adiab. expansion of the ~~body~~ enclosure
1) Full radiations remain full after an
diabatic expansion. Let the walls move
utwards with a velocity u (small
ompared to C the radiation velocity) for
time till temp. falls to T_1, & density
ψ_1 & radius increases to r_1.
If the new radiations be not the black
adiation~~s~~ characteristic of temp. T_1, let
~~them~~ it be different, say having more
of ~~black~~ red & less of violet. Two bodies
ne violet & another red, if introduced

within the enclosure will be at differen temperatures; a Carnot's engine can be worked between the two. Again by adiabatically compressing the body, ~~the~~ two bodies are once more at diff. temp. & more energy is available. Thus work is done simply by heating & cooling a body, without the aid of a second body — which is impossible

2) Change in wavelength due to a receding reflector.



Let a wave be reflected from a reflector at M in the direction MD & let MD = λ. If D is the position of a crest, M is the position of the ~~succ~~ next crest, but within the time taken by the first crest to travel D, the reflector has moved back to M_1, & so reflection of the 2nd crest takes place at M_1 & ∴ the ~~wav~~ change in wavelength

Due to recession of the reflector

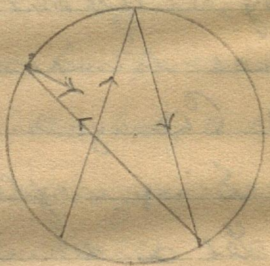
$= (M_1E_2 + MM_1) - MD$

$= 2e\cos\theta$ e being the distance through which ~~of~~ the reflector has moved.

$\frac{e}{\lambda} = \frac{u}{c}$ ∴ $e = \frac{u}{c}\lambda$

∴ Change in wavelength $= \frac{2u\cos\theta}{c}\lambda$.

) Relation between change in wavelength
& change in radius.



~~Path~~ Distance travelled
etween successive reflec-
ions $= 2r\cos\theta$

∴ No. of reflections p.s.

$= \cancel{2u}\ \frac{c}{2r\cos\theta}$

∴ Total change in wavelength p.s. $= \frac{2u\cos\theta\lambda}{c} \times \frac{c}{2r\cos\theta}$

$d\lambda = \frac{u\lambda}{r}$

But $u = dr$ the increase in radius p.s.

$\frac{d\lambda}{\lambda} = \frac{dr}{r}$ ie $\log\frac{\lambda}{r} =$ Const.

ie $\frac{\lambda}{r}$ is a Const.

4) Relation between change in wavelength
& change in temp.

Since the change is adiabatic

$du + dw = 0$ u & w being energy & work resply, $du = d\left(\frac{4}{3}\pi r^3 \psi\right)$

$$dw = p\,dv = \frac{\psi}{3}\,dv = \frac{\psi}{3}\,d\left(\frac{4}{3}\pi r^3\right)$$

$$\therefore \frac{4}{3}\pi \frac{\psi}{3} \times 3r^2\,dr + \psi \times \frac{4}{3}\pi 3r^2\,dr + \frac{4}{3}\pi r^3\,d\psi = 0$$

ie $\psi\,dr + 3\psi\,dr + r\,d\psi = 0$

ie $4\frac{dr}{r} + \frac{d\psi}{\psi} = 0$

ie ψr^4 is a Constant.

But ψ/T^4 is a Const. & λ/r is a Const

$\therefore$ λT is a Const.

The above law states that if a black body radiation at a particular temperature T_1 be altered by an adiabatic change to some other temp. T_2, then a wavelength λ_1 in the radiation at T_1 corresponds to a wavelength λ_2 in the radiation at temp. T_2, the relation between the two being given by $\lambda_1 T_1 = \lambda_2 T_2$

The laws shows why the max. points at high temp. are displaced towards the left in the $(E_\lambda - \lambda)$ curve.

5) Relation between monochromatic
missive power & wave length.

Since ψr^4 is a Const & $\frac{\lambda}{r}$ also a
onst, $\psi \lambda^4 = k$ ie $\psi = k/\lambda^4$

$d\psi = \left(-4k/\lambda^5\right) d\lambda$

But $d\psi = \frac{4}{C} E_\lambda \, d\lambda$

E_λ being monochromatic emissive power.

$\therefore \frac{4}{C} E_\lambda = \frac{4k}{\lambda^5}$ ie $E_\lambda \lambda^5$ = a Const.

) Relation between E_λ & T

ince λT is a const

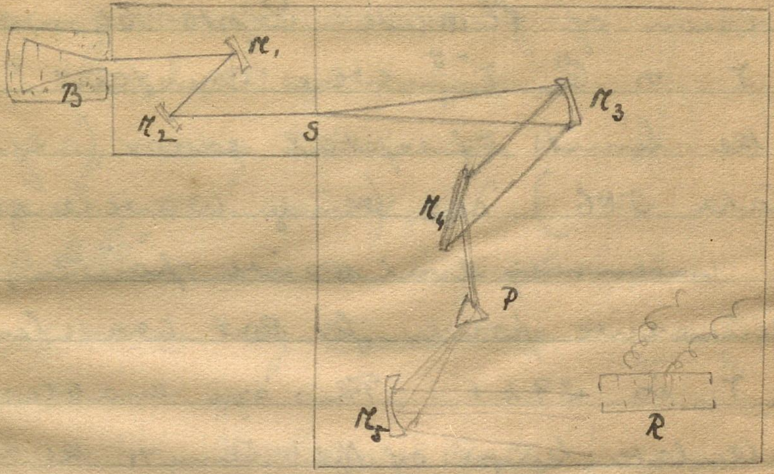
$\frac{E_\lambda}{T^5}$ is a Const ie $E_\lambda T^{-5}$ = a Const.

The above is Wien's 2nd displacement
aw and states that the monochromatic
missive power for corresponding wave-
engths is directly ∝ to the fifth power of
e temperature.

It shows why the max. points rise
ery rapidly along the energy axis.

Lummer & Pringsheim's Verification

Monochromatic emissive power for
mp. ranging from 600 to 1600 was measured

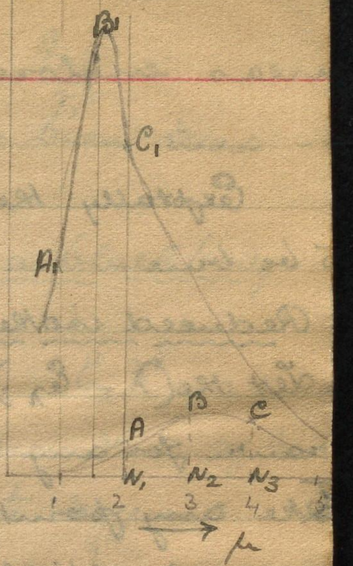


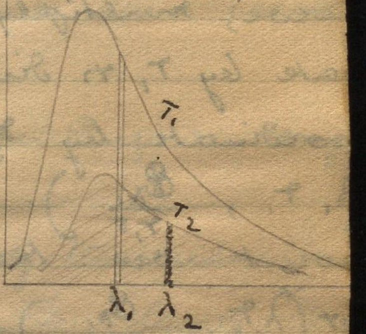
by Lummer & Pringsheim. They used a fluorite prism which has a strong absorptivity for $\lambda = 6\,\mu$. The range of wavelengths ∴ extended from $\cdot 7\,\mu$ (red) to $6\,\mu$. Radiation from a black body B falls on M_1, M_2, is focussed to slit S, is collimated by M_3, reflected by M_4, disperse by P, & any desired wavelength is made to fall on the radiometer, by suitably inclining M_5 ~~of~~ at the focus of which R is placed. All the mirrors are metallic or are silvered on the front face. The

nergy distribution has tobe corrected for
e dispersion of fluorite. Expts showed
hat $\lambda_m T$ & $E_m T^{-5}$ were constant
ithin the limits of exptal error (cf.
able Saha 586) λ_m being wavelength
or max. ~~intensity~~ emissive power,
& E_m emissive power for that wavelength.

$\lambda_m T$ is ·2941. This eqn enables
s to calculate temps of the sun & the moon.
n solar spectrum max. energy is for ·4680 A°u.
e $4{\cdot}68 \times 10^{-5}$ Cm. $\therefore T = \frac{\cdot 2941}{4{\cdot}68 \times 10^{-5}}$
$= 6284°$ k. $= 6011°$ C.
& hence for the moon max. energy is
t 14 μ, ie $1{\cdot}4 \times 10^{-3}$ Cm, $T = \frac{\cdot 2941}{1{\cdot}4 \times 10^{-3}}$
$= 210°$ k $= -63°$C. These values agree with those obtained from other sources

Wien's laws enable us to
find the isocurve at any temp. if the
isocurve at some other temp. is known.
eg let ABC be the curve for temp
300°k. Let wavelengths for A,B,C be 2, 3 & 4 μ
At 1200°C, the corresponding pts have





wave lengths, 1½ & 2, μ, & their y coordinates are $AN_1{}^4$, $BN_2{}^4$, $CN_3{}^4$ resp'ly. Thus by using Wien's two laws any number of pts on the 1200° isocurve can be found.

Verification by Computation of area.

According to ~~St~~ Stefan Boltzmann law the area enclosed between ~~an isocurve~~ isotherm of temp T_1 & the λ-axis should be ∝ to the 4th power of T_1.

The same can be derived from ~~the~~ Wien's law

$$E_{\lambda_1} T_1^{-5} = E_{\lambda_2} T_2^{-5} \quad \text{ie} \quad E_{\lambda_1} = \left(\frac{T_1}{T_2}\right)^5 E_{\lambda_2}.$$

$$\lambda_1 T_1 = \lambda_2 T_2 \quad \text{ie} \; d\lambda_1 = \left(\frac{T_2}{T_1}\right) d\lambda_2$$

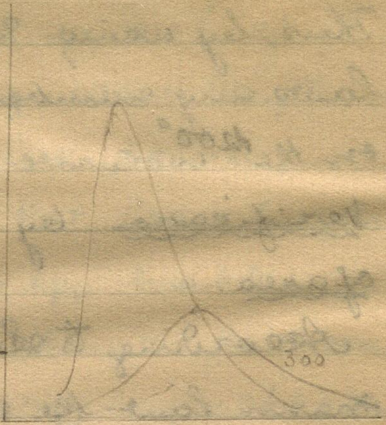
$$\therefore E_{\lambda_1} d\lambda_1 = \left(\frac{T_1}{T_2}\right)^4 E_{\lambda_2} d\lambda_2.$$

This equation gives the ratio of the two strips at λ_1 & λ_2. Integrating

$$S_1/T_1{}^4 = S_2/T_2{}^4$$ S_1 & S_2 being

areas enclosed between the curve & the - axis

Exptally the above result has been shown o be true.



Reduced isotherm.

Let the $(\lambda - E_\lambda)$ curve be rawn for any temp ~~A~~ T_1 ake any point on the urve, multiply its x- coordi- ate by T_1 & divide its y oordinate by ~~T~~ T_1^5. Plot the point $(\lambda_1 T_1 , \frac{E_{\lambda_1}}{T_1^5})$. Similarly for every oint on the T_1 isotherm, a corresponding t $(\lambda_1 T_1 , \frac{E_{\lambda_1}}{T_1^5})$ is obtained. When these oints are joined together a curve is obtained hich is called the reduced isotherm.

By Wien's laws the reduced isotherm hould be the same for all temperatures. f an isotherm at T_2 be drawn, & pts $(\lambda_2 T_2 , \frac{E_{\lambda_2}}{T_2^5})$ are plotted, the pts will lie n the same curve as before since by

Wien's laws $\lambda_1 T_1 = \lambda_2 T_2$; $\frac{E_{T_1}}{T_1^5} = \frac{E_{T_2}}{T_2^5}$.

This result has also been seen to hold true in all cases.

Distribution of energy in a black body Spectrum.

Combining Wien's two laws, $E_\lambda \lambda^5$ is a cons But this Constant is not independent of temperature, since the isotherms at different temps. are all different. Hence Wien wrote

$$E_\lambda \lambda^5 = f(\lambda T)$$

for (λT) is a Constant depending on temp

$$\therefore E_\lambda = \lambda^{-5} f(\lambda T).$$

Wien at the suggestion of Michaelson applied Maxwell's distribution laws to the problem of find $f(\lambda T)$, & made two assumptions

1) Molecules emit waves ∝ to the velocity $\lambda \propto c$ or

$$c^2 = \varphi(\lambda)$$

2) The energy radiated within the range λ to $\lambda + d\lambda$ is ∝ first to the no. of molec

aving velocity between c & c+dc & due

the value of λ.

$$E_\lambda\, d\lambda \quad \propto N \;\&\; \propto \eta(\lambda)$$

where $N = \frac{4}{\alpha^3\sqrt{\pi}}\, c^2 e^{-c^2/\alpha^2}\, dc.$

$$\therefore E_\lambda\, d\lambda = k\, c^2 e^{-c^2/\alpha^2}\, dc\, \eta(\lambda)$$

$$= k\left\{\varphi(\lambda)\,\eta(\lambda)\,\frac{\varphi'(\lambda)}{2\sqrt{\varphi(\lambda)}}\right\} e^{-c^2/\alpha^2} \times d\lambda$$

$$= k\, F(\lambda)\, e^{-c^2/\alpha^2}\, d\lambda$$

ie $E_\lambda = k\, F(\lambda)\, e^{-\frac{ac^2}{T}}$ ~~Since $\alpha^2 \propto$~~

Since α^2 is proportional to T.

Comparing this with

$$E_\lambda \quad \propto k\, \lambda^{-5} f(\lambda T)$$

Wien assumed $F(\lambda)$ to be λ^{-5}

& $f(\lambda T)$ to be $e^{-\frac{a}{\lambda T}}$

Hence

$$E_\lambda = \underline{k\, \lambda^{-5}\, e^{-\frac{a}{\lambda T}}}$$

Merits :— 1) When λ is ∞

$$E_\lambda = k\frac{1}{\infty^5\, e^{\frac{a}{\infty}}} = \frac{k}{\infty^5} = 0$$

2) When λ = 0

$$E_\lambda = k.\left(\frac{1}{\lambda}\right)^5 \frac{1}{e^\infty} = k\frac{\infty^5}{e^\infty} = k\frac{x^5}{e^x} \quad x \to \infty$$

By successive differentiations

$k\frac{5x^4}{e^x}$; $\frac{20x^3}{e^x}$; $\frac{60x^2}{e^x}$; $\frac{120x}{e^x}$; $\frac{120}{e^x}$

The last quantity is evidently zero

$\therefore E_\lambda \; (Lt \; \lambda \to 0) = 0$

Both these facts are borne out by Lummer & Pringsheim's Curves

3) The general shape of the curve agrees very well with that got exptly in the visible portion of the spectrum.

Defect When $T = \infty$

$E_\lambda = k\lambda^{-5} e^0 = k\lambda^{-5}$; the total radiation is ∴ a finite quantity which cannot be. At infinite temperature the radiation too should be infinite.

<u>Degrees of freedom</u> The separate and independent quantities necessary & sufficient to determine the position and configuration of a body are known as its degrees of freedom. A block sliding in a groove has one degree, a disc sliding on ice has 3, a billiard ball has 5. (cf Ritchmyer 226)

he ~~g~~ degrees of freedom are additive. f there are N molecules in a volume of space each with n degrees of freedom, he total number of degrees of freedom s Nn. The number of degrees of reedom is the number of independent erms necessary to express the kinetic nergy of the system as a function f ~~the temp~~ its coordinates. The theorem f equipartition of energy states that ach degree of freedom has on ~~an~~ the average exactly the same amount of kinetic nergy, as has, on the average, a degree f freedom in any other group. If the verage kinetic energy of the molecules a given volume be $\overline{E_x}$ due to motion the x direction, $\overline{E_y}$ due to motion in e y direction & $\overline{E_z}$ due to motion in e z direction $\overline{E_x} = \overline{E_y} = \overline{E_z} = \overline{E}$

$\overline{E}$ being a constant dependent on temp. Diatomic molecules have not only ~~rotatory~~, translatory but rotatory & vibratory energy as well. Kinetic energy associat with each degree of freedom of vibratory motion ~~energy~~ is also $\bar{E}$. Now, the time average of K. E. = the time average of potential energy. ∴ Total energy associated with a degree of freedom of vibratory motion is $2\bar{E}$]

Now $p = \frac{1}{3} n m \overline{c^2}$

$\bar{E}_k = \frac{1}{2} m \overline{c^2}$ $\bar{E}_k$ being the averg kinetic energy of a molecule due to translatory motion

$$\therefore \bar{E}_k = \frac{1}{2} \cdot \frac{3p}{n} = \frac{3}{2} \frac{R_u T}{V_m n}$$

$$= \frac{3}{2} \frac{R_u}{N_0} T$$

$$= \frac{3}{2} k T$$

Where n = No of mol. per CC

Loschmidt number 2.705×10^{19}

R_u = gas Const. 8.315×10^{7} ergs per ° per m

V_m = Vol of one gm molecule

22.4 litres at N. T. P.

N_0 = No of molecules per mole

Avogadro number 6.06×10^{23}

k is Boltzmann's Constant $\frac{R_u}{N_0}$

$= 1{\cdot}372 \times 10^{-16}$ ergs per degree.

Since the molecule has 3 degrees of reedom, ~~kenergy~~ the average K. E. per degree of freedom is $E = \frac{1}{2} kT$.

Raleigh Jeans Law.

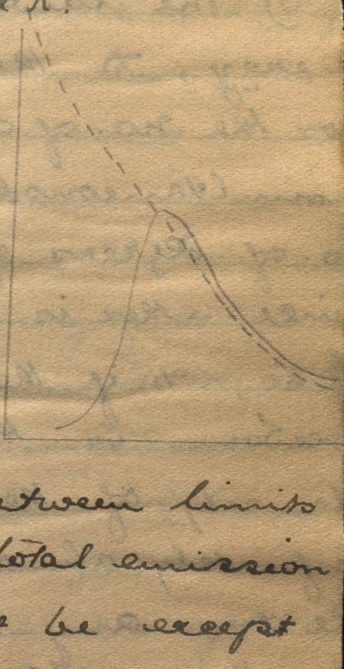
Any vibrating system s capable of a great many modes of ibration. Thus an organ pipe can ibrate in its fundamental & in a reat many overtones. Each mode of ibration constitutes a degree of freedom. he same may be said about the ther vibrations in an enclosure. Raleigh & Jeans have shown applying e principle of sound waves that the number of degrees of freedom per unit volume of ether, associated ith vibrations lying within the wavelength range λ to $\lambda + d\lambda$ is

$$\frac{8\pi d\lambda}{\lambda^4}.$$

Kinetic energy associated with each degree of freedom is $\frac{1}{2} kT$ & since there is an equal amount of P.E, total energy per degree of freedom $= kT$

$\therefore$ Energy density of the enclosure for the wave length range λ to $\lambda + d\lambda$

$$\psi_\lambda \, d\lambda = 8\pi kT \lambda^{-4} \, d\lambda.$$



The $(\lambda - E_\lambda)$ curve in accordance with this eqn coincides with the Lummer Pringsheim exptal curves at large wave lengths; but when λ is small, E_λ is infinitely great.

Integrating $\lambda^{-4} \delta\lambda$ between limits zero & infinity, we get total emission to be infinity, which cannot be except if the temperature be infinite.

These futile attempts to formulate the exact law led to the discovery of a new theo

The Quantum Theory.

Circumstances that led to its inception.

1) Wien's law, derived rigidly on the Principles of classical mechanics was found not to hold good at high temperatures.

2) Raleigh Jeans' law was likewise seen not to tally with exptal results.

3) The law of equipartition of energy, & the formula $d\phi = 8\pi\frac{d\lambda}{\lambda^4}$ for the no. of degrees of freedom cannot simultaneously be correct. The total no. of degrees of freedom should be infinite, since ether is a continuous medium. If so, & if the energy per degree of freedom is the same, the energy density of the ether should be vastly — infinitely almost — greater than that of the ~~in~~ any solid body within the enclosure for the solid body being of atomic structure can have only a finite no. of degrees of freedom. This, however, is impossible.

The density of energy in the ~~medium~~ ether cannot be infinite, nor ~~of~~ that in the body zero. Is then ether really continuou

4) Photoelectric phenomena investiga by Larmor, & codified by Einstein, gave the important Einstein equation

$$E = (\nu - \nu_0)\, a$$

E being ~~intensity of the~~ kinetic energy of the emitted electron just when leaving the surface, ν frequency of the incident beam, ν_0 a constant ~~for~~ peculiar to each substance, a a un versal constant. Supposing the classi theory to hold good, viz enery of a light beam is uniformly distributed on the wave surface, the energy incident per unit solid ∠ is $\frac{Q}{4\pi}$ (Q being total emission of the source) $\frac{aQ}{4\pi}$ is absorbed by unit area of the surface, $AaQ/4\pi$ is absorbed by the whole surface. Two facts follow: 1) electron begin to be emitted only after all have acqui necessary K.E $(E) = h(\nu - \nu_0)$ 2) The nergy is independent of the frequency of he incident beam. But expts show o time lag, & they prove that E is dependent on frequency.

5) Corpuscular radiations of all kinds re beyond the power of classical theory explain.

Hence Planck introduced in 1900 he Quantum Concept. Radiations are tomic or discontinuous in structure. ach atom of light called the photon keeps ts energy content intact, & there is no fractional radiation or transference; ut radiation or absorption of heat or light akes place only by integral multiples of very small amount (ε) called a quantum. xchange of energy is not possible in ractions of a quantum.

ε is taken $\propto$ to frequency $\varepsilon = h\nu$.

$\therefore$ The dimensions of the universal constant h is $\frac{\varepsilon}{\nu} = \frac{\text{energy}}{\text{frequency}} = \text{energy} \times \text{time}$

$= m l^2 t^{-1} = m l t^{-1} \times l$

= moment of momentum.

(Cf Ritchmyer Pages 244 – 259)

Consider a system containing a large number (N) of degrees of freedom, to which the eqn $n = n_0 e^{-\varepsilon/\mathcal{E}_0}$ applies where n is the no. of degrees having energy ε, $\mathcal{E}_0$ is the most probable energy. Let energy be distributed among the several degrees in multiples of ε.

$$N = n_0 + n_1 + n_2 + \ldots$$

$$= n_0 + n_0 e^{-\varepsilon/\mathcal{E}_0} + n_0 e^{-2\varepsilon/\mathcal{E}_0} + \ldots$$

$$= n_0 (1 + x + x^2 + \ldots) \qquad x \text{ being } e^{-\varepsilon/\mathcal{E}}$$

$$= \frac{n_0}{1-x}$$

Total energy content of all degrees of freedom together

$W = n_0 \times 0 + n_1 \times \varepsilon + n_2 \times 2\varepsilon$

$= 0 + n_0 x\, \varepsilon + n_0 x^2 \times 2\varepsilon + \ldots\ldots$

$= n_0 x \varepsilon\, (1 + 2x + 3x^2 + \ldots\ldots)$

$= \dfrac{n_0 x \varepsilon}{(1-x)^2}.$

The average energy per degree of freedom $\bar{U} = \dfrac{W}{N} = \dfrac{x\varepsilon}{1-x} = \dfrac{\varepsilon}{\frac{1}{x} - 1}$

$= \dfrac{\varepsilon}{e^{\varepsilon/\varepsilon_0} - 1}.$ According to kinetic heory value of ~~d~~ $\bar{U}$ is obtained only when

$= 0$ $\quad f(\varepsilon)/F(\varepsilon)$ $\quad \varepsilon \to 0$ is $\dfrac{0}{0}$

$f'(\varepsilon)/F'(\varepsilon)$ $\quad \varepsilon \to 0$ is $\dfrac{1}{e^{\varepsilon/\varepsilon_0} \times \frac{1}{\varepsilon_0}} = \varepsilon_0$

Thus ε_0 is got to be the mean energy per degree of freedom.

We shall assume the eqn $\bar{U} = \dfrac{\varepsilon}{e^{\varepsilon/\varepsilon_0} - 1}$ to be of general validity in any system.

Let us consider an enclosure which contains radiation in equilibrium with the walls of the enclosure. The walls are absorbing radiations of all frequencies by means of a system of "atomic oscillators." It is reasonable to assume that radiation within a frequency range ν to $\nu + d\nu$ must be in equilibrium irrespective of the presence in the system of other frequencies, with the group of oscillators whose frequencies cover the same range ν to $\nu + d\nu$.

Now the no. of degrees of freedom per unit volume in the wavelength range λ to $\lambda + d\lambda$ $= \frac{8\pi}{\lambda^4} d\lambda$.

Hence total radiant energy per unit volume ~~in t~~ in the range λ to $\lambda + d\lambda$

$$\text{is} \quad \psi_\lambda d\lambda = \frac{8\pi}{\lambda^4} \frac{\varepsilon}{e^{\varepsilon/\varepsilon_0'} - 1} \cdot d\lambda. \quad * \text{①}$$

Now $\varepsilon_0 = k_0 T$ (taking both kinetic &

potential energy into account).

According to classical mechanics and quipartition of energy, ε should be n infinitesimal quantity. But when $\varepsilon = 0$,

$$\psi_\lambda d\lambda = 8\pi k_0 T \lambda^{-4} d\lambda. \quad ②$$

hich is Raleigh Jeans formula in complete disagreement with exptal results. omething wrong some where.

$$\psi_\lambda d\lambda = 8\pi\lambda^{-4}\cdot\frac{\varepsilon}{e^{\varepsilon/k_0T}-1}\,d\lambda \qquad 3)$$

by Wien's displacement laws

$$\psi_\lambda d\lambda = C_1\,\lambda^{-5} f(\lambda T)\,d\lambda. \qquad 4)$$

Eqn 3 has λ^{-4} where 4) has λ^{-5}. & 3 has $\left\{\varepsilon/e^{\varepsilon/k_0T}-1\right\}$ a function f T where 4 has a function of λT.

Both these differences disappear if n 3 instead of making $\varepsilon = 0$, we put $= h\nu = \frac{hc}{\lambda}$ i.e $\propto 1/\lambda$.

$$\psi_\lambda d\lambda = 8\pi c h\,\lambda^{-5}\,\frac{1}{e^{ch/\lambda k_0T}-1}\,d\lambda. \qquad 5)$$

$$\text{or}\quad \psi_\nu d\nu = 8\pi h\frac{\nu^3}{c^3}\cdot\frac{1}{e^{h\nu/k_0T}-1}\,d\cancel{\lambda} \qquad 6)$$

5) & 6) are two identical forms of ~~Wien~~ Planck's eqn for distribution of energy.

1) The eqn reduces to Wien's form

$$E_\lambda = c_1 \lambda^{-5} e^{-c_2/\lambda\tau}.$$

(5) is the same as

$$E_\lambda = 2\pi c^2 h \lambda^{-5} \frac{1}{e^{+ch/\lambda k_0 \tau} - 1} \qquad (7$$

ie

$$= c_1 \lambda^{-5} \frac{1}{e^{+c_2/\lambda\tau} - 1}$$

$$= c_1 \lambda^{-5} e^{-c_2/\lambda\tau}$$

Since when λ is small, $e^{c/\lambda\tau}$ is great compared to 1 & ∴ $e^{c_2/\lambda\tau} - 1 = e^{c_2/\lambda\tau}$ (nearly).

2) For ~~infinitely~~ very large wave lengths the eqn reduces to Jeans form

$$E_\lambda \to \psi_\lambda = 8\pi k_0 \tau \lambda^{-5} d\lambda.$$

For (5) ~~is the~~ can be expanded as follows

$$\psi_\lambda = 8\pi c h \lambda^{-5} \frac{1}{\left\{1 + \frac{ch}{\lambda k_0 \tau} + \cdots\right\} - 1}$$

& since λ is very large, & ∴ higher powers of $\frac{ch}{\lambda k_0 \tau}$ can be neglected,

$$\psi_\lambda = 8\pi ch \lambda^{-5} \cdot \frac{\lambda k_0 \tau}{ch}$$

$$= 8\pi k_0 \tau \lambda^{-5}.$$

3) A particular forms of Wien's first displacement law viz $\lambda_m \tau$ is constant, n be deduced from (5)

& E_λ is max. when ψ_λ is max.

ie when $\lambda^5 \left(e^{ch/\lambda k_0 \tau} - 1\right)$ is min.

e when the 1st differential of the above e expn is zero.

ie $\lambda^5 e^{ch/\lambda k_0 \tau} \times \frac{ch}{\lambda^2 k_0 \tau}$

$$= \left(e^{ch/\lambda k_0 \tau} - 1\right) \times 5\lambda^4$$

ie $e^{ch/\lambda k_0 \tau} \times \frac{ch}{k_0 \tau} = 5\lambda \left(e^{ch/\lambda k_0 \tau} - 1\right)$

ie $e^{ch/\lambda k_0 \tau} \left(1 - \frac{ch}{5 k_0 \tau \lambda}\right) = 1$

which condition is satisfied either if

$\lambda = \infty$ i.e. $\frac{ch}{\lambda k_0 \tau} = 0$

or if $\frac{ch}{5 k_0 \theta \lambda} = \cdot 993$, $\frac{ch}{k_0 \theta \lambda} = 4\cdot 965$.

$$\therefore \lambda_m \theta = \frac{ch}{k_0 \times 4\cdot 965}$$ which is a Constant.

4) Stefan's fourth power law can be derive

from eqn 6

$$\psi_\nu \, d\nu = 8\pi h \frac{\nu^3}{c^3} \frac{1}{e^{h\nu/k_0\theta} - 1} \, d\nu$$

$$E_\lambda \, d\lambda = \frac{2\pi h \nu^3}{c^2} \cdot \frac{1}{e^{h\nu/k_0\theta} - 1} \, d\nu$$

$$= a\nu^3 \cdot \frac{1}{e^{b\nu} - 1} \, d\nu$$ a being $\frac{2\pi h}{c^2}$ & $b = \frac{h\nu}{k_0\theta}$.

$$\therefore E_s = a\int_0^\infty \nu^3 \frac{1}{e^{b\nu} - 1} \, d\nu$$

$$= a\left\{\int_0^\infty \nu^3 \cdot e^{-b\nu} \, d\nu + \int_0^\infty \nu^3 e^{-2b\nu} \, d\nu + \cdots\right.$$

$$= a \cdot \frac{6}{b^4} + \frac{6}{(2b)^4} + \frac{6}{(3b)^4} + \cdots$$

$$= \frac{6a}{b^4} \cdot \left\{\frac{1}{1^4} + \frac{1}{2^4} + \cdots\right\} = 1\cdot 082 \times \frac{6a}{b^4}$$

$$= 1\cdot 082 \times \frac{12 \cdot \pi h}{c^2} \cdot \frac{k_0^4}{h^4} \cdot \theta^4 = \left\{\frac{1\cdot 082 \times 12\pi k_0^4}{c^2 h^3}\right\}$$

σ i ch 993 ch 4·965.

Sacrifice consists of the vi

These sacrifices

intentions, those by

the sacrifice of thanksg

The ~~sacr~~ sacrifice a

redemption.

Let us consider this

1. Christ offered himself

2) Christ offered himsel

3) It is a true sacrifice

Christ gave his pr

he said, "My Body shal

shall be shed for th

a

ee decrea

a being $\frac{2\pi h}{c^2}$

$= \frac{h a}{k_0 r}$.

$dr + \ldots$

$62 \times \frac{6a}{64}$

$\frac{+ 2\pi k_0^4}{c^2 k^3}\}$

and the victim are by
rer and the best for every act
ed to be the best for every act
ty, there is he is a true
and Man, the same reasons apply-
and yet the willingness of
two fold better and real

e of the Mass is a true
crafice of all ~~tims~~ times.

---

powers
(3) A p
replacem
be ded
& E_λ i
ie
ie when
exp^n
ie λ^5
ch
ie e
e
ie e
which Co
$-1)$
$\lambda = \infty$ ... $\overline{\lambda k_0 T}$ $= 0$

ie $\mathcal{E}_s \propto T^4$

$$\sigma = \frac{1.082 \times 12\pi k_0^4}{c^2 h^3} = 5.72 \times 10^{-5} \text{ ergs} \quad \underline{\text{I}}$$

s Wien's Constant $A = \lambda_m T \left(= \frac{ch}{k_0 \times 4.965} \right) = .2884 \quad \underline{\text{II}}$

From the above eqns h & k_0
can be solved for

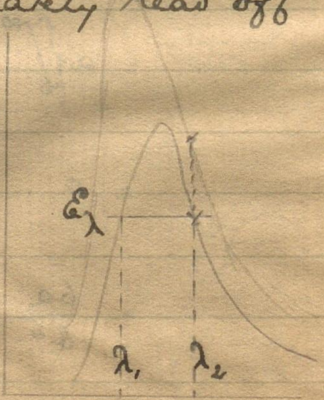
$$k = 7.914 \times 10^{-16} \quad \& \quad h = 6.57 \times 10^{-27}.$$

Verification of Planck's law.

The method shows that $\frac{ch}{k_0} = 4.965 \times \lambda_m T$ is strictly a constant. (Saha §97)

In the isothermal method, λ_m is found at various temps. & the eqn verified. But λ_m is not accurately read off from the curve.

Hence Paschen employed e method of equal ordinates. f the intercepts of the curve y a horizontal line are at λ_1, λ_2, by Wien's Law



$$\lambda = \frac{c_1}{\lambda_1^5} e^{-c_2/\lambda_1 T} = \frac{c_1}{\lambda_2^5} \cdot e^{-c_2/\lambda_2 T}.$$

$$\therefore C_2 = 5T.\frac{\lambda_1\lambda_2}{\lambda_2-\lambda_1}.\left\{\log\lambda_2 - \log\lambda_1\right\}$$

If the range of exp'ts is such that Wiens law cannot be assumed, then C_2 by Planck's law is given by

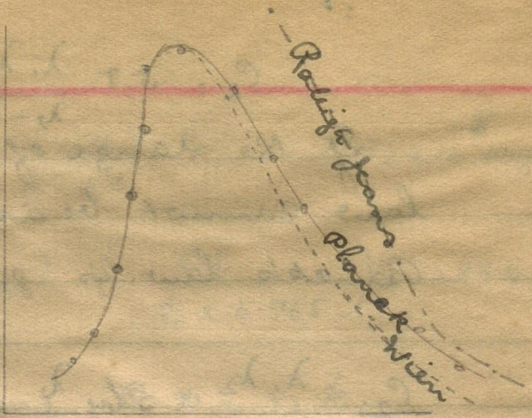
$$\frac{C_2}{T}.\frac{\lambda_1\lambda_2}{\lambda_2-\lambda_1} = 5\log\frac{\lambda_2}{\lambda_1} - \log\left\{\left(1-e^{-\frac{C_2}{\lambda_2 T}}\right)\div\left(1-e^{-\frac{C_2}{\lambda_1 T}}\right)\right.$$

An approximate value is substituted on the right hand side & method of successive approximations is employed. C_2 was seen to very nearly constant.

Isochromatic method i.e. showing the constancy of C_2 from two values of temperature & E_λ for which λ is the same is preferable, since in the isothermal method comparison is made at two different wavelengths & the absorption effects of the apparatus are not the same for all wavelength

Expressions |||r to the one above are obtained.

The Superiority of
Planck's law above
he other two is
llustrated by the
djoining ($E_\lambda - \lambda$) curve.
The ⊙s show the
bserved values of Coblentz. A continuous curve drawn in accordance
ith Planck's law passes through nearly
ll of them.



Radiation Pyrometers. Radiation pyrometry
in general more widely employed than gas
yrometry & electrical pyrometry. For the
olume of gases becomes far too large
arge at high temperatures; & as for
lectrical pyrometry, whether based on
hermoelectric e.m.f. or on resistance,
 higher limit is imposed by the melting
oint of the metal.

Radiation pyrometers have no
igher limit; & they are extremely handy.

There are, besides, other advantages, viz the pyrometers has not to be in contact with the furnace or the planet; nor have they to reach the temp. of the hot body.

But the one disadvantage is that the radiation laws hold good only for perfectly black bodies. But actual bodies ar never "black".; The error, however, cannot be great since at high temps. most bodies are full radiators. The error is always negative; the radiat~~or~~ measures that ~~the~~ temp. which the body would have had if it had been ~~a~~ perfectly black, i.e. a temp. lower than the actual temp. of the body.

Radiation pyrometers are of two kinds – (1) total radiation pyr. ~~&~~ or (2) Spectra or optical pyr.

. Total radiation Pyrometers are based on Stefan's ~~law~~ fourth power law.

A common type due to Fery is describe

below. Radiation from

he hot body falls on a

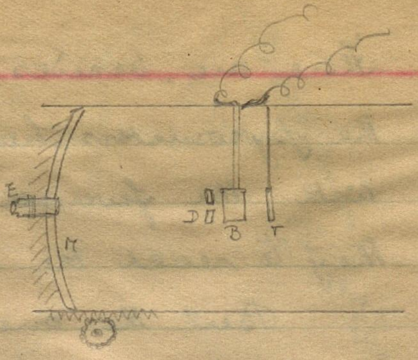
oncave metallic mirror

is reflected to a diagphragm

through which it passes

the bolometer B. ~~The diaphr~~

& B are placed at the



ocus of M. The other side of B is protected

y a tongue T which is kept at a constant

mp, by a current of water.

M can be moved ⊥r to its plane by a

ack & pinion arrangement. Two slightly

nclined mirrors attached to the diagphragm

~~fixed~~ enable exact focussing, for at the

osition of exact focus, the mirrors when

viewed through an eyepiece fixed to a central

rifice of M, should appear continuous.

The deflection in the millivoltmeter

attached to the bolometer ~~shown~~ is should

e proportional to the difference of radiation

n the two sides.

$\theta = a(T^4 - T_0^4)$ where θ is deflection, T & T_0 temps. of the hot body & the tongue.

But actually, due to 1) thermoelectric e.m.f. not been exactly $\propto$ to diff. of temp. 2) stray reflections & 3) Conduction of heat through the leads, the above eqn is has to be replaced by

$\theta = a(T^b - T_0^b)$ b being a Constant varying between 3.8 & 4.2, which has to be determined by Calibration.

The readings are unaffected by the dista of the body from the instrument, for when the distance is doubled, though ~~the~~ intensit of radiation is made $\frac{1}{4}$, the area of the image also is reduced to $\frac{1}{4}$, so that intensity per unit area of the diaphragm is unaltered. Thus, provided the image is of larger area than the orifice of the diaphragm, the ~~intensity~~ total energy falling on the bolometer is unaffected by distance.

For very high temps. a rotating sector is placed in front of the instrument. If is the observed temp, T_A the ctual temp, θ the ∠ of the ector, $\left(\frac{T_A}{T}\right)^4 = \frac{2\pi}{2\pi - \theta}$.

<u>Optical Pyrometers.</u> If E_{λ_1}, E_{λ_2} be e emissive power at two temps. T_1 & T_2, rresponding to the same wavelength λ, then by Wien's law

$$E_{\lambda_1} = C_1 \lambda^{-5} e^{-c_2/\lambda T_1}$$

$$E_{\lambda_2} = C_1 \lambda^{-5} e^{-c_2/\lambda T_2}$$

$$\therefore \quad \frac{E_{\lambda_1}}{E_{\lambda_2}} = e^{c_2/\lambda T_2 - C_1/\lambda T_1}$$

$$\text{ie} \quad \frac{c_2}{\lambda}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \log\left(\frac{E_{\lambda_1}}{E_{\lambda_2}}\right)$$

Hence if $E_{\lambda_1}/E_{\lambda_2}$ be known, T_2 can e calculated from T_1

There~~disay~~ are two types — one in which e intensity of the standard source is varied ntil ~~the~~ it matches the ~~incid~~ radiation of nknown temp; — the other in which the

~~amount~~ fraction (falling on the instrument) of the light from the standard is varied.

1) The disappearing filament type.

An ordinary telescope having a heated filament in place of the crosswire is employed. The filament is connected to the a ~~an~~ battery, rheostat & ammeter. The filamen & the image of the given source at known temp T are [illegible] viewed simultaneously & the current adjusted till the two are indistinguishable from each other. If i_1 is the current, R the ~~fil~~ resistance of the filam E_{λ_1} the emissive power of the ~~source~~ given radiator, $E_{\lambda_1} \propto i_1^2 R$.

The radiator at temp. T_1 is replaced by the ~~an~~other at the unknown temp T_2. If i_2 is the current required to match the filament to this radiator, E_{λ_2} its emissive power, $E_{\lambda_2} \propto i_2^2 R$.

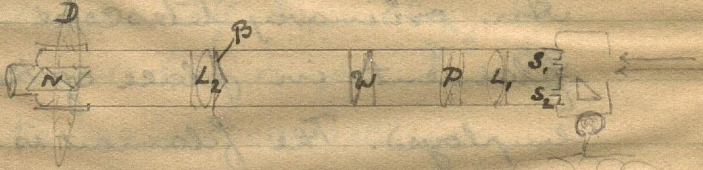
$\therefore E_{\lambda_1}/E_{\lambda_2} = (i_1/i_2)^2.$

Hence t_2 can be calculated.

The images are viewed through a red lass R. At times a prism also is employed.

The <u>polarizing type</u>.

The standard
ource reflected
rom a rt. ∠d



rism ~~passes~~ illuminates a slit S_2 the radiation at temp. t_1 illuminates nother slit S_1. The rays are collimated by a ens L_1, dispersed by a direct vision pectroscope P, polarized by a Wollaston's prism W, the images brought to touch ach other (for comparison) by a biprism B, focussed by a lens L_2, & viewed through he nicol N. Eight images are produced, f which all except two are cut off. These wo are due to the two slits; ~~and~~ they are olarized in orthogonal planes and form wo halves of a ⊙. If at ∠ zero the

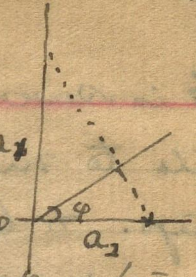


image of S_1 is completely dark, & at ∠φ S_1 & S_2 are of equal intensity, then $a_2 \cos\varphi = a_1 \sin\varphi$ where a_1 & a_2 are amplitudes of the two vibrations ie $E_{\lambda_2} \cos^2\varphi = E_{\lambda_1} \sin^2\varphi$.

If the slit ~~S_2~~ S_1 is now illumined by the second source of which the emissive power is E'_{λ_1}, & if φ' is the ∠ of the nico which gives equal intensity for S_1 & S_2,

$$E_{\lambda_2} \cos^2\varphi' = E'_{\lambda_1} \sin^2\varphi'$$

$$\therefore E_{\lambda_1} \tan^2\varphi = E'_{\lambda_1} \tan^2\varphi'$$

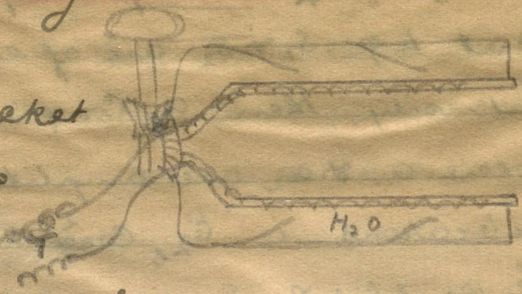
Hence T_1 & T_1' can be compared.

The Solar Constant cf B.A. notes.

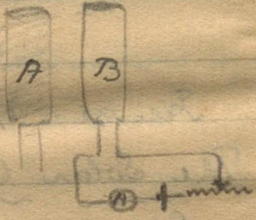
All modern methods for determination of the solar constant are improvements on of the mercury heliometer.

The instrument used in Washington observatory is a water stirred pyrohelio-meter. It consists of a vessel shaped conically, coated inside with black, which receives radiation through a diaphra

It is surrounded by oils to measure emp. & by a jacket f water which is onstantly rotated y an electric motor.



An electrical method is sometimes mployed. A platinum strip A coated with amp black received the solar radiation; & another B is heated by known current. The urrent is adjusted to have oth A & B at the same emp.



Correction for atmospheric absorption an be made as follows.

If i_0 be energy incident on unit layer, $i_0 a$ is that transmitted (a being ransmission coeff^{t}. $i_0 a^2$ is that transmitted from the 2nd layer ...

∴ If x be the thickness, So the

incident energy, S the energy received by the earth is $S = S_0 a^x$

If t be thickness at zenith ∠ zero, thickness at zenith ∠ z_1 is $\frac{t}{\cos z_1}$

$$\therefore S_1 = S_0 \cdot a^{t/\cos z_1}$$
$$= S_0 \, a^{t \sec z_1}$$

S_2 (at zenith ∠ z_2) $= S_0 \, a^{t \sec z_2}$.

From these two eqns t & S_0 can be eliminated since z at say 10 A. M is $\frac{90 \times 2}{6} = 30^\circ$, at 11 A. M is 15° S at these hours can be exptly determ

Temperature of the Sun

Can be calculated from the Solar Constant as explained in B. A. notes. The f^n $\lambda_m T = B$ can also be used. Both methods give values ranging from 5700 to 6000. In the latter an assumption is made that the Sun is a black body — which is not strictly true

Heat. Barton - Sound.

Thermodynamic potential.

The function $F = U - \tau\varphi$ was named by Helmholtz the characteristic $f^{\underline{n}}$ & by Gibbs as the thermodynamic potential at constant ~~pressure~~ volume.

Gibbs also called $\psi = U - \tau\varphi + pv$ the thermodynamic potential at constant pressure.

Many of the physical constants of a substance can be expressed in terms of these F or ψ.

$$dF = du - \tau d\varphi - \varphi d\tau$$

$$= -\varphi d\tau - p dv$$

$$\left(\frac{dF}{d\tau}\right)_v = -\varphi \quad ; \quad \left(\frac{dF}{dp}\right)_\tau = -p.$$

Internal energy $u = F + \tau\varphi = F - \tau\left(\frac{dF}{d\tau}\right)_v$

$$C_v = \tau\left(\frac{d\varphi}{d\tau}\right)_v = -\tau\left(\frac{d^2F}{d\tau^2}\right)_v$$

$$C_p - C_v = -\tau\,\frac{(d\varphi/dv)_\tau^2}{(dp/dv)_\tau} = -\tau\,\frac{\left(\frac{d^2F}{d\tau\,dv}\right)_\tau^2}{\left(\frac{d^2F}{dv^2}\right)_\tau}$$

$$C_p = C_v + C_p - C_v$$

$$\gamma = C_p / C_v \quad \text{etc.}$$

Pressure coefft $\alpha_p = \frac{1}{p}\left(\frac{dp}{dT}\right)_v = \frac{1}{p}\frac{\left(\frac{d^2F}{dv\,dT}\right)}{dp/dv}$

Isothermal elasticity $k_T = -v\left(\frac{dp}{dv}\right)_T = -v\,\frac{d^2F}{dv^2}$.

$$d\Psi = v\,dp - \varphi\,dT$$

$$\left(\frac{d\Psi}{dp}\right)_T = v \quad ; \left(\frac{dF}{dT}\right)_p = -\varphi .$$

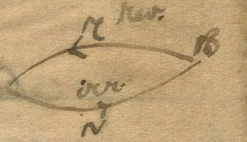
$$U = \psi + T\left(\frac{d\psi}{dT}\right)_p - p\left(\frac{d\psi}{dp}\right)_T$$

$$C_p = -T\left(\frac{d^2\psi}{dT^2}\right)_p \quad \text{etc.}$$

Conditions for the stability of any system.

For a complete cyclic change $\int_0 \frac{dQ}{T} = 0$ if the change is reversible; but if it is not, due to loss of heat by friction etc which are irrecoverable, $\int_0 \frac{dQ}{T}$ is −ive.

Consider a cycle made up of two portions ANB & BMA, the former of which is irreversib



while the latter is reversible.

The whole cycle is ∴ irreversible

ie $\int_{ANB} \frac{dQ}{\theta} + \int_{BMA} \frac{dQ}{\theta} < 0.$

But $\int_{BMA} dQ/\theta = \phi_A - \phi_B.$

$\therefore \int_{ANB} \frac{dQ}{\cancel{d}\theta} < \phi_B - \phi_A$ ~~$< dQ$~~

ie $\frac{dQ}{\theta}$ for an irreversible change is $< d\phi$ & for an reversible change $dQ/\theta = d\phi$

ie for irreversible change ~~d~~ $\theta d\phi > dQ$

reversible change $\theta d\phi = dQ.$

If the <u>system</u> is <u>isolated</u>

$dQ = 0$

For irreversible changes, $\theta d\phi > 0$ ie is +ive Hence $d\phi$ is +ive since θ is always +ive

Hence the statement of Clausius that the entropy of the universe always tends to a maximum; for the universe is an isolated irreversible system. ~~The~~ Such a system is not stable until the entropy becomes a maximum.

For reversible changes $\tau d\varphi = 0$ ie $d\varphi = 0$. The system is always stable.

If the system is not isolated, i.e. it is communicating,

$$dQ \neq 0$$ ~~&~~

For reversible changes $\tau d\varphi = dQ$ 1)

For irreversible changes $\tau d\varphi > dQ$. (2)

Now $F = U - \tau\varphi$

$$dF = dU - \tau d\varphi - \varphi d\tau$$

$$= \overset{dQ}{\cancel{\tau d\varphi}} - p\,dv - \tau d\varphi - \varphi d\tau$$

$$dF + p\,dv + \varphi d\tau = \cancel{\tau d\varphi}\, dQ - \tau d\varphi$$

Since for irr. system $dQ - \tau d\varphi$ is −ive,

$dF < -p\,dv - \varphi d\tau$ 3)

For a reversible system, $dQ - \tau d\varphi = 0$

$dF = -p\,dv - \varphi d\tau$. 4)

$$A = \psi = U - \tau\varphi + pv$$

$$d\psi = dQ - p\,dv - \tau d\varphi - \varphi d\tau + p\,dv + v\,dp$$

$$= (dQ - \tau d\varphi) + v\,dp - \varphi d\tau.$$

$$d\psi - (v\,dp - \varphi d\tau) = dQ - \tau d\varphi.$$

Hence for an irreversible

System, $d\psi < v\,dp - \phi\,dT$ 5)

& for a reversible system $d\psi = v\,dp - \phi\,dT$. (6)

From 2) we see that when v & T are constant dF ie $dv = dT = 0$,

$dF < 0$ ie dF is –ve.

Hence condition for the stability of a non isolated system is that F is a minimum. F is like the potential energy of a body which always tends to be a minimum. Hence the term thermodynamic potential at constant volume.

Illrly when p & T are constant, the system is stable only when ψ is minimum. Hence the name th. pot. at constant pressure.

Application to triple point

If a system consists of individuals at different potentials of masses m_1, m_2 … whose potentials per unit mass at const. vol. are F_1, F_2 … & at constant pressure are ψ_1, ψ_2 … the total potential of the system at constant ~~pres.~~ vol $\mathcal{F} = m_1 F_1 + m_2 F_2 \dots$

& at Const. pres. $\psi = m_1 \psi_1 + m_2 \psi_2 + \dots$

Consider a system of total mass unity of which m is vapour & $(1-m)$ liquid. If ψ_1, ψ_2, ψ_3 represent potentials ~~of the sy~~ per unit mass in solid, liquid & gaseous states, the total potential of the system

$$\psi = \psi_3 m + \psi_2 (1-m)$$

$$\therefore d\psi = (\psi_3 - \psi_2)\, dm.$$

Now $d\psi$ is always -ive since the system is communicating

1) If $\psi_3 > \psi_2$, dm should be -ive. ie only condensation is possible.

2) If $\psi_3 < \psi_2$ dm should be +ive ie. only vaporization is possible.

If $\psi_3 = \psi_2$, dm may be +ive or -ive. This gives the case of equilibrium between g vapour and liquid

$\therefore$ $\psi_3 = \psi_2$ is the eq^n^ to the steam line.

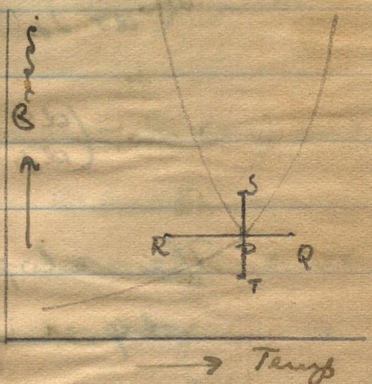
|||rly eqn.. to the ice line is $\psi_2 = \psi_1$

& to the hoar frost line is $\psi_1 = \psi_3$.

Since the eqns are $\psi_1 = \psi_3$ 1) $\psi_1 = \psi_2$ 2) & $\psi_2 = \psi_3$ 3)

it can be shown that the three lines are concurrent. 1) & 2) meet at a point where $\psi_3 = \psi_2$ which is evidently a point on 3)

Nature of the substance on all sides of the triple point P can be deduced.



Due to passage of the substance from P to Q at constant pressure

$$d\psi = \left(\frac{d\psi_3}{d\tau}\right)_p d\tau - \left(\frac{d\psi_2}{d\tau}\right)_p d\tau$$

$$= -(\varphi_3 - \varphi_2)\, d\tau. \quad \text{\& since } \frac{dQ}{\tau} = \frac{L}{\tau} = d\varphi$$

$$= -\frac{L}{\tau}\, d\tau.$$

Change from P to Q is increase in temp; $d\tau$ is +ive, ie $d\psi$ or $\psi_3 - \psi_2$ is −ive

∴ Only vapourization is possible ∴ The Substance at Q is in the ~~liquid~~ vapour state.

At the point R (which has dT -ive) $\psi_3 - \psi_2$ is +ive ∴ only Condensation is possible. The substance is in the liquid or solid state.

To find the slope of the Curves.

$$\left(\frac{d\psi}{dT}\right)_p = -\varphi \; ; \; \left(\frac{d\psi}{dp}\right)_T = v$$

$$\therefore -\left(\frac{d\varphi}{dp}\right)_T = \left(\frac{dv}{dT}\right)_p .$$

The slope of the Curve $\frac{dp}{dT} = -\frac{d\varphi}{dv}$.

~~$d\varphi =$~~ If ${}_1L_2$ denote latent heat for Conversion from solid to liquid, ${}_1L_3$ for sublimation, ${}_2L_3$ for ~~boil~~ vapourization,

For the steam line, $d\varphi = {}_2L_3/T$

$dv = (v_3 - v_2)$

$$\therefore dp/dT = \frac{{}_2L_3}{T(v_3 - v_2)} .$$

IIIrly for the ice line $\frac{dp}{dT} = \frac{{}_1L_2}{T(v_2 - v_1}$

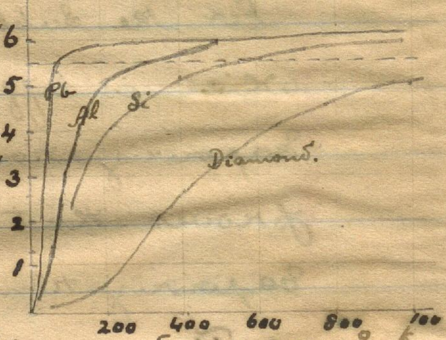
But $v_2 < v_1$ ∴ The slope is –ive while for most other substances $v_2 > v_1$ & ∴ the slope of the fusion line is +ive.

For the Sublimation line $\frac{dp}{dT} = \frac{L_3}{T(v_3 - v_1)}$ which is different from that of the Vapourization line & ∴ incidentally proves that ~~Stea~~ Sublimation line & Vapourization line are not continuous.

Theory of Specific heats.

More than a century ago Dulong and Petit postulated the empirical law that the product of the sp. heat by at. wt $C_p \cdot M$ is a constant. If instead of C_p we put C_v the product is more nearly const. It is called the atomic heat C_v. ‡

When subjected to accurate expts the law was found unsatisfactory especially at low temp. e.g. for lead C_v remains sensibly constant till about 300 K, below which it falls ~~to~~ very rapidly tending towards zero at 0°K. Aluminium falls below the normal value at a higher temp. For certain substances like beryllium, Boron, Silicon, Carbon the atomic heat even at ordinary temps is very low. If the temp. be sufficiently raised C_v reaches 6. Thus for diamond at 2000° K C_v is over a 6, but at 200°K it is only ·7.



The graph shows variation of C_v with temp. for 4 typical substances. The curves for most other substances are comprised between those of Al & Pb.

Experimentally only C_p can be found out; C_v can be calculated since $C_p - C_v$ is known.

$$C_p - C_v = 9 \cdot \frac{V_0 T}{J} \lambda^2 k_T = 9 \cdot \frac{A T}{J \rho} \lambda^2 k_T$$

For diamond $A = 12$; $\rho = 3{\cdot}51$ gm/cm³

$\lambda = 1{\cdot}32 \times 10^{-6}$ per deg. & $k_T = \frac{10^{12}}{{\cdot}16}$ dynes/cm²

$$C_p - C_v = \frac{9 \times 12 \times 1{\cdot}32^2 \times 10^{-12} \times 10^{12}}{{\cdot}16 \times 4{\cdot}2 \times 10^7 \times 3{\cdot}57} \times T$$

$$= 8{\cdot}0 \times 10^{-6}\, T.$$

However $C_p - C_v$ cannot always be directly calculated as above since λ & k_T at ~~so~~ very high & very low temps. have not been determined for various substances.

Gruneisens law says that λ is proportional to C_p ie $\lambda = a C_p$. Also $\frac{k_T}{\rho}$ is sensibly const. $= b$ $\therefore C_p - C_v = \frac{9 K T a^2 C_p^2 b}{J}\, T$

$= A C_p^2 T$ where A is a const. which can be ~~con~~ determined for each substance. Hence knowing C_p at any temp. C_v can be calculated.

Classical theory of Dulong & Petit's law.

According to the kinetic theory, each atom executes vibrations about a position of equilibrium, & the energy is partly potential & partly kinetic, the two amounts being equal. If we consider a monatomic solid within a gas enclosure

& at ~~this~~ both being at temp. T, then by the law of equipartition of energy, the kin. energy per degree of freedom of the the solid atom should be the same as per degree of freedom of the gas atom & it is equal to $\frac{1}{2} k_0 T$. The no. of degrees of freedom of the atom due to its vibratory motion is 3 & ∴ total ~~potential~~ kin. energy $= \frac{3}{2} k_0 T$. There being an equal amount of P.E. total average energy $= 3 k_0 T$.

Energy E per gm. atom ~~molecule~~ $= 3 k_0 N T$

$= 3RT$

But sp. heat $C_v = \frac{dE}{dT} = 3R$

$$= \frac{3 \times 8 \cdot 315 \times 10^7}{4 \cdot 18 \times 10^7} = 5 \cdot 959 \text{ Cal}$$

This is ~~to~~ a first approximation the Dulong & Petit value.

The theory however gives no explanation about the temp. variation of C_v.

Einstein's theory. No further advance was possible until in 1907 Einstein applied the quantum theory.

He made two important assumptions 1) that the atoms of a monatomic solid vibrate with a characteristic frequency ν which is the same for all atoms of that solid & which is determined by the nature of the substance & not on temp. 2) that the energy per degree of freedom of the atom is given by Planck's formula

$$\bar{E} = \frac{h\nu}{e^{h\nu/k_0T} - 1}$$

An atom having 3 degrees of freedom & there being N atoms in a gm atom, Energy per gm atom

$$E = 3Nh\nu \Big/ e^{h\nu/k_0T} - 1$$

The atomic heat

$$C_v = \frac{dE}{dT} = -3Nh\nu \frac{1}{(e^{h\nu/k_0T} - 1)^2} e^{\frac{h\nu}{k_0T}} \cdot -\frac{h\nu}{k_0T^2}$$

$$= 3Nk_0 x^2 \frac{e^x}{(e^x - 1)^2}$$ x being $\frac{h\nu}{k_0T}$

$$= 3R\left\{\frac{x^2 e^x}{(e^x - 1)^2}\right\}$$

The function within the double bracket is called the Einstein function of x, $\mathcal{E}(x)$

1) When T is very small, x becomes very large, ∴ $(e^x - 1)$ very nearly $= e^x$

$\therefore \mathcal{E}(x) = \frac{x^2}{e^x}$

In the limit $x \to \infty$, $\mathcal{E}(x) \to \frac{2x}{e^x} \to \frac{2}{e^x} \to 0$

ie $C_v = 0$ at $T = 0$

which is borne out by expts.

2) When T is very high, x is small

$$\mathcal{E}(x) = \frac{x^2 e^x}{(1+x+\dots-1)^2} = e^x = 1+x+\dots$$
$$= 1 \text{ nearly}$$

$C_v = 3R$ which is the constant value predicted by the classical theory.

But on accurate computation the Einstein formula gives too low a value for C_v at low temp. The a observed) values are all higher.

3) Characteristic temp. Θ_H is that temp at which $x = 1$ ie $\Theta_H = \frac{h\nu}{k_0}$

At Θ_H, $C_v = 3R.\frac{e}{(e-1)^2} = 3R.\frac{2.72}{1.72^2}$

$$C_v = 3R \times \cdot 921 = 5 \cdot 96 \times \cdot 921$$

$$= 5 \cdot 49$$

Θ_H for any substance can be read from (C_v-T) graph since it is the abscissa of the pt. whose ordinate is 5·49.

It can be shown that at temps equally remote from Θ_H all substances have the same C_v – & Dulong & Petit's law is perfectly observed. At a temp say φ times Θ_H, $x = \frac{1}{\varphi}$

$$C_v = 3R \left\{ \frac{1}{\varphi^2} \frac{e^{1/\varphi}}{(e^{1/\varphi} - 1)^2} \right\}$$

Thus the atomic heat of Pb at 39°k = that of diamond at 738°k.

Characteristic temps. & frequencies (Einstein)

Substance	Θ_H °k	ν sec^{-1}
Pb	78	$1 \cdot 61 \times 10^{12}$
Al	307	$6 \cdot 42 \times 10^{12}$
Si	561	$11 \cdot 9 \times 10^{12}$
C (Diamond)	1475	$30 \cdot 8 \times 10^{12}$

4) Characteristic frequency gives a 4th test of the law

Assuming the Einstein eqn as the fundamental underlying concepts we may compute the characteristic frequency with which the atoms of the solid vibrate.

$\frac{h\nu}{k_0 \theta_H} = 1$ ∴ $\nu = \frac{\theta_H k_0}{h}$

But θ_H is that temp. at which $C_e = 5.47$ & can be found from the graphs ∴ ν is calculated

For lead $\nu = \frac{78 \times 1.372 \times 10^{-16}}{6.56 \times 10^{-27}} = 1.61 \times 10^{12}$

For crystals ν can be found by the method of Restrahlen ~~which~~ (Cf Notes on Light Page)

$$\left(\frac{d\tau}{dv}\right)_\phi = -\left(\frac{dp}{d\phi}\right)_v \qquad \left(\frac{d\tau}{dp}\right)_\phi \left(\frac{d\phi}{dv}\right)_p - \left(\frac{d\tau}{dv}\right)_p \left(\frac{d\phi}{dp}\right)_v = 1$$

$$\left(\frac{d\phi}{dv}\right)_\tau = \left(\frac{dp}{d\tau}\right)_v \qquad \left(\frac{dp}{d\tau}\right)_\phi \left(\frac{dv}{d\phi}\right)_\tau - \left(\frac{dp}{d\phi}\right)_\tau \left(\frac{dv}{d\tau}\right)_\phi = 1$$

$$\left(\frac{d\tau}{dp}\right)_\phi = \left(\frac{dv}{d\phi}\right)_p \qquad \left(\frac{d\tau}{dp}\right)_i = \frac{1}{c_p}\left\{\tau\left(\frac{dv}{d\tau}\right)_p - v\right\}$$

$$\left(\frac{d\phi}{dp}\right)_\tau = -\left(\frac{dv}{d\tau}\right)_p \qquad \int_{\tau_1}^{\tau_2}\frac{d\tau}{\tau} = \int^{p_2}$$ [illegible]