PART A: HEAT AND THERMODYNAMICS

CHAPTER I. REVIEW OF MATHEMATICS

a) Introduction:

The science of Heat deals with the changes in the properties of matter with the transfer of heat. It is an experimental science and the data obtained are represented by empirical laws, many of which can be justified a posteriori by theory. Thermodynamics on the other hand is a purely mathematical discipline. The laws governing the transformation of energy through work and heat are derived from three basic postulates, and important relations are obtained between the properties of "systems in thermal equilibrium." If the "system" of Thermodynamics is then identified with the "quantity of matter" dealt with in Heat one obtains rigorous relations between the empirical quantities. In order to distinguish carefully between these two categories of truths we shall denote the empirical relations by $\sim$ and the deductions from postulates by $=$.

However these two sciences, even taken together, do not give a complete picture. Most of the empirical laws do not follow from thermodynamics, and the irreversibility of thermal processes seems to violate the more basic laws of mechanics. The fact is that thermodynamics would be an empty discipline, with no application in nature, were not matter composed of a myriad of molecules, or at least a large number of degrees of freedom. The basis of both the empirical laws of Heat and the postulates of Thermodynamics are found in Statistical Mechanics, and furthermore the latter gives a concrete picture of the abstractions of thermodynamics, such as entropy and energy.

It is therefore deemed valuable to include some Statistical Mechanics with an introductory course in Heat and Thermodynamics, although it is separated in a second part of the course because the methods are so different. This can, of course, only be done at the expense of some aspects of the latter which are normally included. We shall limit ourselves to pure substances and, with one exception, to work done by hydrostatic pressure. The exception is the chapter on magnetism which is introduced because the ordering and disordering of dipole orientations give such a clear illustration of changes of entropy. This eliminates many interesting applications, such as chemical equilibrium and the laws of dilute solutions, but it is felt that these can readily be learnt when needed and are easily forgotten when not used, whereas the principles of Statistical Mechanics when once learnt remain permanently a part of one's visualization of thermodynamic processes.

The student of thermodynamics is perforce assumed to be familiar with partial differentiation, and with all sorts of changes of dependent and independent variables separately. However, in Thermodynamics the dependent and independent variables are frequently partially interchanged, and this is confusing. There is no way to avoid this and the only solution is constant care in the mathematical manipulations.

The necessary formulae are few and are reviewed in the following sections of this chapter.

b) Partial Derivatives:

Let z (x,y) be a known function of two independent variables x and y. The *differential* of z is given by

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad (Ib1)$$

where the functions

$$A = \left(\frac{\partial z}{\partial x}\right)_y, \quad B = \left(\frac{\partial z}{\partial y}\right)_x \qquad (Ib2)$$

are the *partial derivatives* of z, the subscript on the parenthesis indicating that that variable is held constant in the differentiation with respect to x and y.

It is frequently necessary to change the independent variables from x and y to two new variables u and v. Let x and y be known functions of u and v so that

$$dx = \left(\frac{\partial x}{\partial u}\right)_v du + \left(\frac{\partial x}{\partial v}\right)_u dv$$

$$dy = \left(\frac{\partial y}{\partial u}\right)_v du + \left(\frac{\partial y}{\partial v}\right)_u dv$$

Substituting in (Ib1) one obtains

$$dz = \left[\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial u}\right)_v + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial u}\right)_v\right] du$$
$$+ \left[\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial v}\right)_u + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial v}\right)_u\right] dv$$

from which one may conclude that

$$\left(\frac{\partial z}{\partial u}\right)_v = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial u}\right)_v + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial u}\right)_v \qquad (Ib3)$$

$\frac{V}{M} = v$ = specific vol $\frac{cm^3}{gm}$ } differentiate by problem

$\frac{V}{n} = \omega = cm^3/mole$

$pV = nRT$

$\frac{pV}{n} = RT = pv$

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{\left(\frac{\partial x}{\partial z}\right)_y}$$

$$\left(\frac{\partial z}{\partial z}\right)_y \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial t}\right)_y \cdots = 1$$

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

note

recip equa

and a similar equation in which u and v are interchanged. This is the fundamental relation for transforming partial derivatives. It reduces to two simpler forms which are of constant application and deserve to be remembered.

Let $v = y$

so that only one variable is being changed. Obviously

$$\left(\frac{\partial y}{\partial u}\right)_y = 0$$

so that (I b 3) becomes

$$\left(\frac{\partial z}{\partial u}\right)_y = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial u}\right)_y$$

or

$$\left(\frac{\partial u}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial u}\right)_y = 1 \qquad \text{(I b 4)}$$

This may be called the "chain" relation because it can be shortened or extended by removing or adding "links." Thus

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y = 1 \qquad \text{(I b 5)}$$

$$\left(\frac{\partial w}{\partial u}\right)_y \left(\frac{\partial u}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial w}\right)_y = 1$$

The characteristic of the chain relation is that the same variable is held constant in each partial derivative.

Let $v = z$

so that one of the new independent variables is the old dependent variable. (I b 3) then becomes

$$0 = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial u}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial u}\right)_z$$

Now let $u = y$

so that

$$0 = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x$$

and using (Ib5)

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \qquad \text{(Ib6)}$$

This may be called the "cyclic" relation because the variables x, y, z are permuted cyclically in successive factors. This relation cannot be shortened or extended by simply removing or adding links as was done with the chain relation, and the negative sign should be noted.

c) Integration in Two Variables:

The function z in

$$dz = A\,dx + B\,dy \qquad \text{(Ic1)}$$

is not always known. The functions A and B may be given and the problem is to find $z(x,y)$.

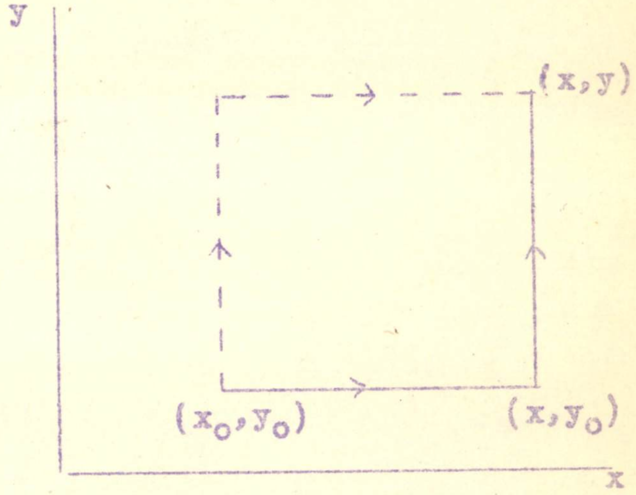


Fig. Ic

Let z_o be the value of z at x_o,y_o. This has to be assumed known or else it appears as a constant of integration in the answer, and of course the point (x_o,y_o) may be at the origin. The value of z at (z,y) is then found by integrating along two lines as shown in fig. Ic. In the first integration

$$z_1\,(x,y_o) - z_o = \int_{x_o}^{x} A\,(x,y_o)\,dx$$

the variable y is held constant, so this is an ordinary integration and z_o is the constant of integration. Then a second integration is performed

$$z\,(x,y) - z_1 = \int_{y_o}^{y} B\,(x,y)\,dy$$

holding x constant, so that finally

$$z\ (x, y) - z_o = \int_{x_o}^{x} A\ (x, y_o)\ dx + \int_{y_o}^{y} B\ (x, y)\ dy \qquad \text{(I c 2)}$$

x_o and y_o also appear in the answer as constants of integration. Thus it is seen that the two parts of the differential are integrated separately as simple indefinite integrals, but one must not forget to give to the variable y in A its value y_o, which is the lower limit of the second integral. Failure to do this frequently leads to an answer which is twice too big. In integrating with respect to two variables one should <u>always</u> check the answer by differentiation.. One can, of course, equally well integrate over the path indicated by dashes in the figure and represented by the formula

$$z - z_o = \int_{x_o}^{x} A\ (x\ y)\ dx + \int_{y_o}^{y} B\ (x_o, y)\ dy \qquad \text{(I c 3)}$$

d) <u>Exact and Inexact Differentials:</u>

If z is a function of x and y equations (I c 2) and (I c 3) will both lead to the same answer. This can be differentiated to give (I c 1), which is then termed "exact". It may happen, however, that (I c 2) and (I c 3) give different answers even though the integrations have been done correctly. The differential expression is then called "inexact", and in order to make this distinction clear it will be written with a bar across the d:

$$\bar{d}w = A'\ dx + B'\ dy \qquad \text{(I d 1)}$$

This situation is familiar to students of electricity and magnetism. If A and B or A' and B' are thought of as components of a force, expressions (I c 1) and (I d 1) are the element of work done by that force in going the differential distance (dx, dy). z is minus the potential of that force, but all forces do not have a potential and magnetic fields are a typical example. The work then depends on the path and $\bar{d}w$ is an inexact differential. The condition that a differential be exact is well known to be

$$\left(\frac{\partial A}{\partial y}\right)_x = \left(\frac{\partial B}{\partial x}\right)_y \qquad \text{(I d 2)}$$

In fact, by Stokes' theorem, the quantity

$$\left(\frac{\partial A'}{\partial y}\right)_x - \left(\frac{\partial B'}{\partial x}\right)_y$$

measures the amount of work done per unit enclosed area in going around a closed path. In thermodynamics, as in electricity and magnetism, one generally knows from fundamental principles whether a differential is exact or inexact, and (I c 2) is an extra equation available in the former case.

When it is necessary to integrate an inexact differential a bar will be put across the integral sign to indicate that the path must be specified. Thus

$$w = \int\!\!\!\!- (A' \, dx + B' \, dy) \qquad \text{(I d 3)}$$

e) Lagrange Multipliers:

In statistical mechanics it will be necessary to deal with functions of not simply two, but millions of independent variables x_i, $i = 1, 2 \ldots\ldots N$. The particular problem which arises is that of finding the maximum (or minimum) of a function $Z (x_1 \ldots\ldots x_n)$ of these variables subject to two (or more) constraints

$$\left. \begin{array}{l} X (x_1 \ldots\ldots x_n) = 0 \\ Y (x_1 \ldots\ldots x_n) = 0 \end{array} \right\} \qquad \text{(I e 1)}$$

These constraints determine a "surface" in the N-dimensional space of the x_i's and one seeks the extremal of Z on this surface. This is called a constrained extremal. Thus there are only N-2 independent variables and one might logically solve (I e 1) for two of the x_i's in terms of the others and substitute these in the function Z. But this is impractical and one resorts to the method of Lagrange multipliers. One defines the function $\phi (x_1 \ldots\ldots x_n)$ by

$$\phi = Z - \alpha X - \beta Y \qquad \text{(I e 2)}$$

where α and β are undetermined constants and then determines the free extremal of ϕ. This is found by solving the N equations:

$$\frac{\partial \phi}{\partial x_i} = 0$$

or

$$\frac{\partial Z}{\partial x_i} = \alpha \frac{\partial X}{\partial x_i} + \beta \frac{\partial Y}{\partial x_i} \qquad \text{(I e 3)}$$

This gives the position of the extremal of ϕ, the N $x_i(\alpha, \beta)$, as functions of α and β. Substituting these in (I e 1) one can solve these two equations for α and β, thus insuring that the extremal of ϕ falls on the surface of constraint. But on this surface ϕ and Z are identical by (I e 2) and (I e 1). The position of the constrained extremal of Z has therefore been found, and its value is obtained by substituting the x_i (α, β)'s, α, and β, in the function Z.

II EQUATIONS OF STATE

a) Law of Force Between Atoms

Atoms are known to consist of a nucleus surrounded by a number of electrons. The nucleus contains almost the entire mass m of the atom and has a positive charge equal to, though opposite in sign from, that of Z electrons, where Z is the atomic number of the element whose atom is considered. The nucleus is surrounded by a cloud of Z electrons, so that the whole atom has no net charge. The study of the energy and motions of these electrons belongs to atomic structure and we need consider here only briefly the net effect of one atom on another.

Because of the electrical nature of atoms they become polarized when placed in an electric field; that is they act like a dielectric, their positive charges being displaced slightly in the direction of the field relative to their negative charges. Now a dielectric sphere is always attracted towards regions of large electric field irrespective of the direction of the electric intensity E. Thus if one molecule is slightly polarized it will attract other molecules and cause them to become polarized also. These in turn will tend to increase the polarization of the first one. Thus because molecules are polarizable they polarize each other in such a way as to attract. This type of force varies inversely as the seventh power of the distance, is called a Van der Waals force, and explains the force between atoms at large distances.

As atoms get closer together, of the order of a millimicron between nuclei, their electron clouds interact in more complicated ways than electric polarization. This may result in an additional attraction which is called a chemical valence force, or in a repulsion. Two nitrogen atoms attract in this range whereas two argon atoms repel. At yet closer distances there is always a repulsion due to the interactions of the inner shells of electrons, or eventually of the nuclei themselves. This repulsive force generally increases very rapidly with decreasing distance. The result of all these interactions is a variation of the force and potential energy on internuclear distance represented in figure IIa. This figure does not give the full story because valence forces depend on angles as well as on distance, but it is sufficient for most purposes.

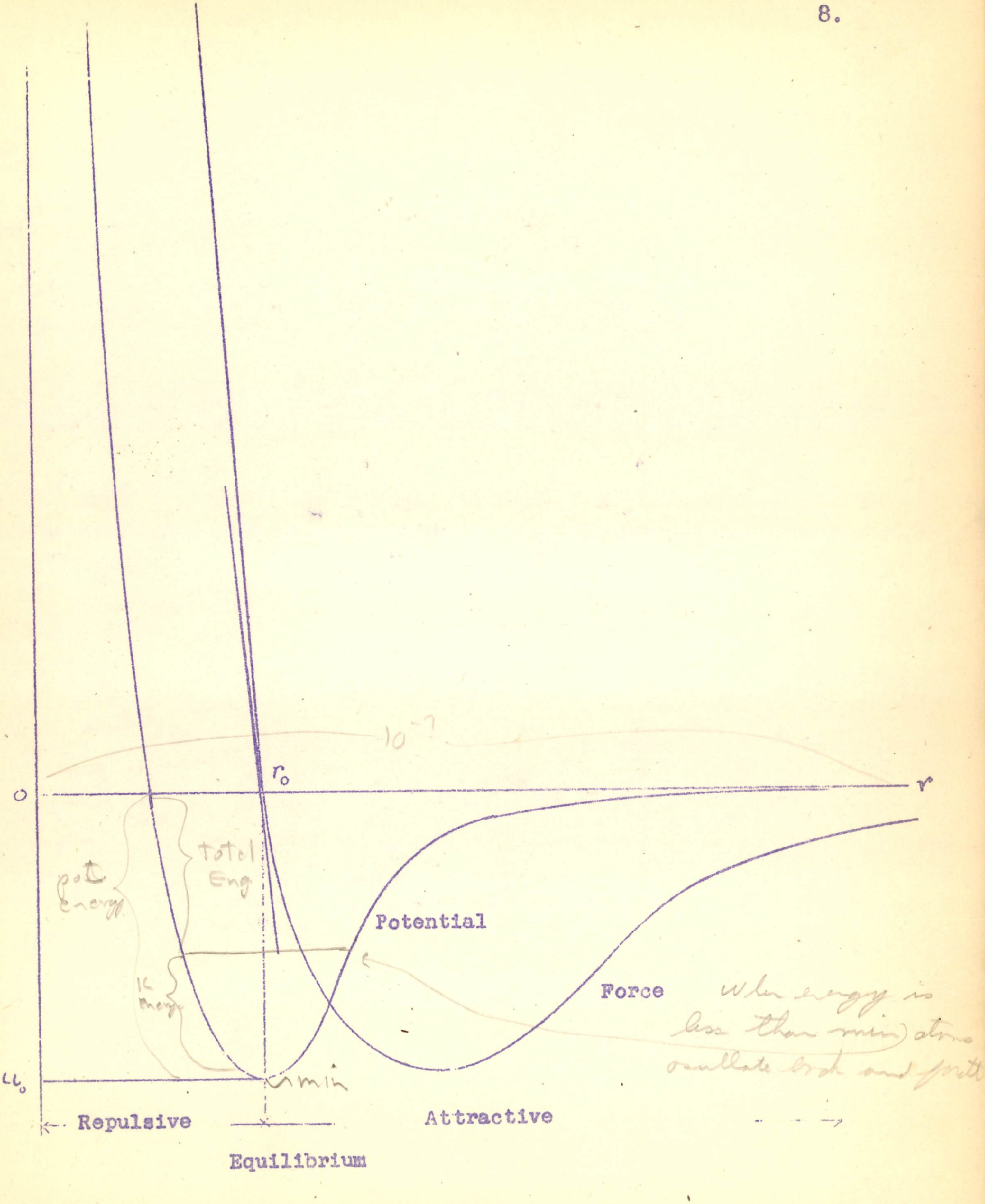

10⁻⁷
r₀
0
r
u₀
pot energy
total Eng
K energy
Potential
Force
min
When energy is less than min) atoms oscillate back and forth
Repulsive
Attractive
Equilibrium

FIG. IIa

In static equilibrium two atoms will occupy the position r_o of minimum energy u_o. The quantities r_o and u_o can be computed, in the case of atoms which form molecules, from band spectra, and for atoms which do not form molecules they may be estimated from the viscosity of the gas. The latter method can also be applied to the interaction of molecules. Table IIa gives some results of both methods, and some obvious conclusions can be drawn from these data. In the first place the force between molecules is not much different from that between atoms which do not form molecules. Compare for instance methane with krypton. On the other hand atoms which do form molecules have an energy minimum about ten times as deep and half as far out. This shows th e influence of the additional chemical binding force over the polarization force. Indeed these atoms form molecules at room temperature because the binding energy is so great.

Atom	r_e mx10^{-12}	u_o ergx10^{-12}	Molecule	r_e mx10^{-12}	u_o ergx10^{-12}
H	74	7.15	He	217	.19
Li	267	1.82	H_2	273	.20
N	110	11.8	Ne	259	.15
O	121	8.13	CH_4	416	.47
Na	308	1.22	NH_3	442	.90
P	189	8.05	N_2	376	.25
S	189	5.75	O_2	362	.33
Cl	199	3.97	A	366	.38
K	392	.82	CO_2	463	.57
I	267	2.46	Kr	417	.45
Hg	330	.12	Xe	491	.61

TABLE IIa

Atomic and molecular radii and dissociation energies. Left hand columns from band spectra, right hand columns from viscosity.

b) The State of Lowest Energy

The "molecular weight" μ of a substance is a number proportional to the mass m of a molecule and such that it has the value 16 for atomic oxygen. A mass M of substance contains

$$N = M/m \text{ molecules} \qquad \text{(IIb 1)}$$

An amount of substance whose mass is equal to the molecular weight is called a "mole". Thus the mass M contains

$$n = M/\mu \text{ moles} \qquad \text{(IIb 2)}$$

Thus the number of molecules in a mole depends on the unit of mass and there are two units in common use: the gramm-mole and the kilogramm-mole. The number of molecules in a gramm-mole is called Loschmidt's number and is

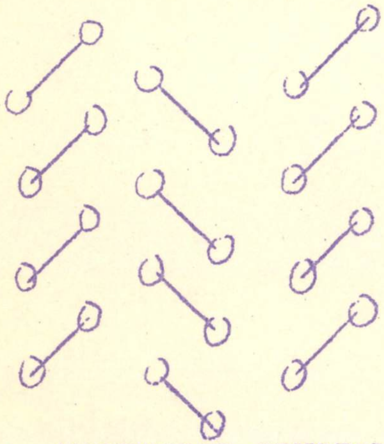
$$N/n = 6.023 \times 10^{23} \text{ molecules/gramm-mole} \qquad \text{(IIb 3)}$$

This is a tremendous number; so large in fact that no matter how far we subdivide matter so long as we can still see or weigh it, it will still contain a very large number of molecules. Many of the laws which are studied in Thermodynamics depend on the fact that one is dealing with an aggregate of a very large number of identical particles.

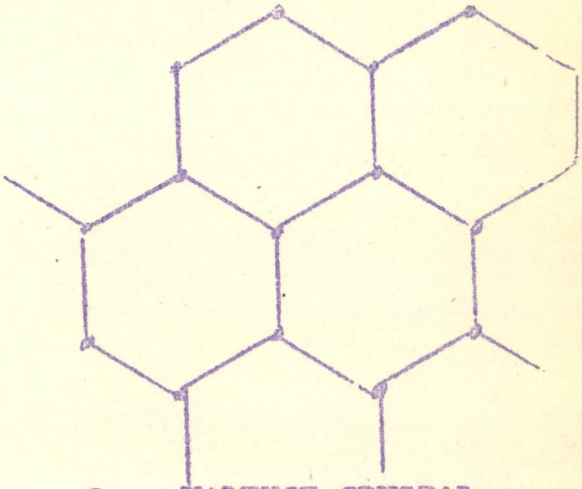
Consider then an aggregate of a very large number of identical atoms in static equilibrium. Each atom will be in a position of equilibrium relative to all the others, and as there will be so many more interior molecules than ones near the surface we shall neglect surface effects.

The distance of nearest neighbors will then be close to r_o, the departure from r_o being due to the influence of the next-to-nearest neighbors, and the total energy will have its lowest possible value U_o. Let V_o be the corresponding volume. The condition of equal separation of nearest neighbors imposes a regularity on the structure, and it is called a perfect crystal.

The particular configuration will depend on the nature of the valence forces and these differ greatly between different atoms. However, one can distinguish three basic types of structure in which the elements crystallize and one additional one for compounds. These are all shown in fig. IIb.: (1) When an element forms diatomic molecules it generally means that the valence force between two atoms is strong but that it saturates when the two atoms are united so that there is no remaining bond to attract a third atom. The molecules may, however, be held together by their Van der Waals attraction, forming a molecular crystal. Nitrogen and iodine are typical examples of this type, as are also many compounds as ice or methane. (2) Atoms with many valence bonds such as carbon may continue to bind additional atoms, forming chains, sheets, or solid valence crystals. In these cases the entire crystal may be considered as a single molecule, and because valence forces are strong these crystals are generally hard. Diamond is the typical example of a valence crystal in which each carbon atom is attached to four neighboring carbon atoms by valence bonds, this bonding extending throughout the crystal. Quartz and carborundum are also valence crystals formed by compounds.



1. - **MOLECULAR CRYSTAL** I_2



2. - **VALENCE CRYSTAL GRAPHITE**

3. - **METAL COPPER**

Na^+	Cl^-	Na^+	Cl^-
Cl^-	Na^+	Cl^-	Na^+
Na^+	Cl^-	Na^+	Cl^-
Cl^-	Na^+	Cl^-	Na^+

4. - **IONIC CRYSTAL**

FIG. IIb

In crystal:
$U = $ min $=$ at equi point $= f(x)$ $\therefore$ $p = -\frac{du}{dV}$, $K = -\frac{1}{v}\frac{dv}{dp}$
$S = $ min $=$ (most order) $= 0$
If $U > U_0$, $S > 0$

Carbon also crystallizes as graphite which is a different form than diamond, and is a mixed type. Here the carbon atoms unite by valence bonds in sheets, the pattern of one sheet being shown in fig. IIb. The sheets are the held together by Van der Waals forces, and this is responsible for the softness of graphite. Asbestos is a similar example among compounds in which the valence bonds form chains.

③ In the metals the bonding force is neither valence nor Van der Waals but is simply Coulomb attraction. The atoms each lose one or more electrons and these occupy the intersteces between the atoms. As the atoms are now positively charged they are attracted by the neighboring electrons, and, reciprocally, the ions hold the electrons in. However the electrons have considerable freedom and for this reason the metals are good conductors of electricity, Most of the elements crystallize in this way. ④ Salts are compounds of a metal and an electronegative atom or radicle. When they crystallize the molecules dissociate into positive and negative ions, and these are arranged in a lattice so that each positive ion is surrounded by negative ones and vice versa. The crystal is held together by the Coulomb attraction of the ions and is in this way similar to a metal, but the negative ions, being larger and heavier, are not free to move as are the electrons of a metal.

Table IId gives the volume per gram-atom (volume per mole divided by the number ν of atoms in a molecule) for a number of crystalline solids. From this table the following qualitative relations may be observed: First the atomic volume does not vary very much except for hydrogen, which is very small, and the alkalies, which are very large. Very heavy atoms like lead are also large. Second that the valence compounds are relatively compact, the metals and ionic compounds are less so, and the molecular compounds are quite lose. (In computing the atomic volume for ice the hydrogens have been neglected, so it is the molar volume which is given.) This is in agreement with the strength of the binding forces, valence, Coulomb, and Van der Waals, for these classes of compounds.

We have spoken of the state of lowest energy as being one of static equilibrium. This is not true. If the electrons came to rest in their positions of lowest energy they would fall into the positive nuclei and all matter as we know it would disappear. It is known that the electrons in atoms move in stable orbits in their states of lowest energy, and similarly the electrons in a metal are not stationary in the interstices but are constantly moving at a high speed. Atoms may similarly have some motion in their state of lowest energy but, because of their very much larger mass, this motion is quite small and may for most purposes be overlooked. This zero-point kinetic energy is to be included with the potential energy in the value of U_o.

c) Thermodynamic Variables

The state of lowest energy described above is called absolute zero and is not observed in nature, but may be approached in the laboratory as a limit of experiments designed to remove as much energy as possible from a system. In order to define the state of a system one must therefore specify one or more parameters in addition to the numbers and kinds of atoms present. An obvious parameter would be the energy U. This is, in principle, directly measurable. Let M_o be the mass of the system at absolute zero. Then by Einstein's relation

$$U - U_o = (M - M_o)c^2 \qquad \text{(IIc1)}$$

where c is the velocity of light. However the energy differences that we are interested in are of the order of one Joule per gram and therefore $\frac{M - M_o}{M_o}$ is of the order of 10^{-15}. Such an accuracy is quite unattainable. The energy $U - U_o$ will therefore have to be calculated from other data.

Another parameter would be the degree of disorder. In the higher energy states the atoms are oscillating with independent amplitudes and phases and therefore the crystal is not as regular. This lack of regularity appears on x-ray diffraction patterns and a suitable parameter might be computed from them. This also lacks accuracy, and the disorder parameter called the entropy S and to be defined more exactly later, is, like the energy U, derived from thermal data. This will be explained later.

Then there is the volume change $V - V_o$. This, though often small is directly measurable.

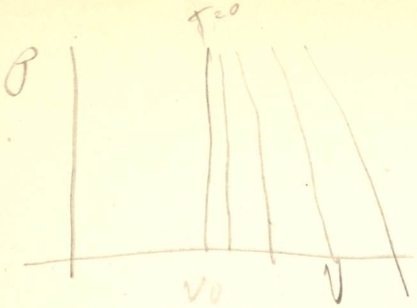
Other parameters such as shear deformations, surface tension, polarization, etc. can also be measured, but they will not be considered here purely for the sake of simplicity. Each such parameter leads to relations quite similar to those of the volume changes and if the latter are once understood it is very easy to extend them to these other variables.

U, S, and V are called "extensive" variables because they are proportional to the amount of material considered. The "specific" variables which are properties of the kind and not the amount of material may be defined per mole

$$u = U/n, \quad s = S/n, \quad v = V/n \qquad \text{(IIc 2)}$$

per gram

$$u' = U/M, \quad s' = S/M, \quad v' = V/M \qquad \text{(IIc 3)}$$



[illegible] always looks low

$P = -\left(\frac{dU}{dV}\right)_S$

@ u = min S = 0

@ u > u₀ , S > 0

$K_T = -\frac{1}{V}\left(\frac{dV}{dP}\right)_T$, $K_S = \frac{1}{V}\left(\frac{dV}{dP}\right)_S$

$du = -PdV + TdS = đQ - đW$

$\beta = \frac{1}{V}\left(\frac{dV}{dT}\right)_P$

$\frac{dV}{V} = \beta dT + K_P dP$

not đP.

Total diffs

B, K, C_V, C_p are the measurable quantities in thermo

$C_V = \left(\frac{dU}{dT}\right)_V = T\left(\frac{dS}{dT}\right)_V = \left(\frac{đQ}{dT}\right)_V$

$C_p = \left(\frac{dH}{dT}\right)_p$

It could be nice to [illegible]

$dU = A'dT - BdV$

we know $A' = C_p$

$du = C_p - BdU$

$A = U - TS$ Lagschon transformation

$dA = dU - TdS - SdT = -SdT - PdV$

$\left(\frac{dS}{dV}\right)_T - \left(\frac{\partial V}{\partial t}\right)_V$

or per gram-atom

$$u'' = U/_{\nu n}, \quad s'' = S/_{\nu n}, \quad v'' = V/_{\nu n} \qquad \text{(IIc 4)}$$

where ν is the number of atoms in a molecule. The last set are particularly useful in solids where it is not always certain how many atoms to include in the molecule, but the quantity $\mathcal{M}/_{\nu}$ is known as it depends on the composition only. If the extensive variables were directly measurable thermodynamics would be a great deal simpler, for all the other thermodynamic variables could then be obtained by differentiation, as will be shown. But such is not the case and what one measures are two other variables, called "intensive", because their differences determine departure from equilibrium. If two bodies are pressed together their volumes will both decrease. The changes in general will not be the same and may not even be proportional, but if a pressure gauge is placed between them it will read the same towards which ever body it is oriented. This is a consequence of Newton's Third law. Pressure P is the intensive variable which must be equal in two bodies in mechanical equilibrium. It is not measured by examining the body itself but by putting a gauge in contact with the body and examining the gauge. It is not the only intensive variable. Electric potential, for example, is one which will not be discussed here. When all mechanical, chemical, electrical, and other known disturbances are eliminated there still remains a variable of which our senses give us an indication and which is called Temperature. When two bodies at different temperatures are placed in contact their properties are observed to change progressively until the temperatures are equalized. Any device which is sensitive to temperature differences, such as mercury in a glass bulb at the end of a capillary, may be used as a thermoscope, the criterion that we are truly observing the equilibrium parameter being that the instrument give the same reading when placed successively in contact with, and preferably inside, two bodies in equilibrium. That such a thing is possible is called the Zeroth law of Thermodynamics. It is analogous to Newton's Third law.

Different thermoscopes, while all agreeing when indicating equality of temperature, will not give the same measure for differences of temperature unless callibrated against a standard instrument. Such an instrument is the ideal gas thermometer which will be described at the end of the chapter in connection with the laws of gases. It defines the absolute temperature scale. One of the virtues of the ideal gas thermometer is that is reads zero in the state of lowest energy. Another thermometer having this property is the platinum resistance thermometer, the electrical resis- of a strip of platinum approaching zero as the state of lowest energy is approached.

Having chosen a standard instrument, and therefore a temperature scale, there remains to chose a temperature unit. The unit universally used in scientific work is the centigrade unit, which is such that there are 100 units between the freezing and boiling points of pure water under one atmosphere pressure.

The units of pressure are unfortunately not so universal as, besides the consistent CGS and MKS units, the "millimeter of mercury" is the universal laboratory unit, and one "atmosphere" is the normal pressure. These units are related as follows:

$$10^6 \text{ dynes/cm}^2 = 10^5 \text{ Newton/m}^2 = 750.06 \text{ mm of mercury} = 1 \text{ Bar}$$

$$760 \text{ mm of mercury} = 1 \text{ atmosphere} \qquad \text{(IIc 5)}$$

The variables V, P, and T are the ones most easily measured. The relation between these variables for any substance is called its Equation of State. We must, however, immediately give up the expectation of being able to write down a single mathematical expression to represent all the phases of a pure substance. Such an expression if it were found would be too complicated to be readily used and would have to be broken down into parts representing the different phases. We shall in the remainder of this chapter summarize the empirical equations of state for the different phases of pure substances.

d) The Ideal Solid

The volume of solids does not change very much under experimentally realizable pressures, rarely more than a few percent. This means that the internuclear separation of the atoms does not depart very much from its equilibrium value. Taking a small portion of the force curve in figure IIa in the neighborhood of r_o it can be seen that it does not depart much from a straight line. It follows from these facts that the volume of a solid will vary sensibly linearly with the pressure

$$\frac{dv}{dp} = b$$

$$V \approx V_o (a - bP) \qquad \text{(IId 1)}$$

Good to 1000 at

This is Hooke's law. It is written with the sign $\approx$ instead of a straight equality sign to indicate that it is an empirical and not a rigorous equation. The compressibility κ is defined by

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \approx \frac{b\,V_o}{V} \approx \frac{b}{a} \qquad \text{(IId 2)}$$

$$\frac{dv}{dp} = KV$$

$$V = \int kvp + c$$

The quantities a and b are functions of the temperature, so that the coefficient of thermal expansion β is given by

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \approx \frac{V_o}{V}(a' - b'P) \approx a'/a \qquad \text{(IId 3)}$$

where the primes represent differentiation with respect to T.

The compressibility and volume coefficient of thermal expansion of a number of crystalline solids is given in table IId. It is noted that the valence compounds and metals, the alkalies excepted, are relatively incompressible, the ionic compounds are more so, and the molecular compounds even more.

The variation with temperature of $\varkappa$ and β for copper is shown in figure IId, and is rather typical of all solids. The slow increase of $\varkappa$ with temperature is a consequence of the thermal expansion. As the atoms get further apart the slope of the force curve (fig IIa) gets less, which implies a greater compressibility. The gradual rise of β may be similarly explained, but not the sudden drop in β as absolute zero is approached. It might be thought that this is due to the choice of temperature scale in this region, but as the drop occurs at a different temperature, characteristic of each solid no change in scale can straighten out all these curves. It is found to be related to a similar change in the specific heat for which a theory has been developed by Einstein-Debye-Brillouin.

P — Intensive

$$\left.\begin{array}{l} U = U_0 + \\ V = V_0(a - bP) \\ S = \end{array}\right\} \text{Extensive (additive)}$$

$$\left. v = \frac{V}{n},\ v' = \frac{V}{m},\ v'' = \frac{V}{rh} \right\} \text{Specific}$$

atm. = 760 mm of Hg

$$P \left\{ \begin{array}{lll} \text{CGS} & \text{dyne/cm}^2 & = \text{bar} \\ \text{MKS} & \text{Newton/m}^2 & \\ \text{Bar} = 10^6\ \text{dynes/cm}^2 & = 750.06\ \text{mm of Hg} & \end{array} \right.$$

mm of Hg.

V — liter

SUBSTANCE	FORMULA	DENSITY	ATOMIC VOLUME	COMPRESSIBILITY	THERMAL EXPANSION
		d gm/cm^3	v" cm^3/~~mole~~ gm atom	$\kappa \times 10^{12}$ m^2/Newt.	$\beta \times 10^6$ deg^{-1}
VALENCE					
Diamond	C	3.52	3.41		2.67
Graphite	C	2.25	5.34		9
Carborundum	$Si\ C$	3.15	6.35		6.35
Corundum	Al_2O_3	3.95	5.17	4	17
Quartz	$Si\ O_2$	2.65	7.55	27	33.6
METAL					
Sodium	Na	.97	23.7	156	200
Aluminum	Al	2.70	10.0	13	73
Potassium	K	.86	45.4	360	239
Iron	Fe	7.88	7.06	5.8	36
Copper	Cu	8.94	7.10	7.2	49
Silver	Ag	10.50	10.3	9.9	59
Tungsten	W	19.3	9.53	2.9	12
Lead	Pb	11.34	18.35	2.4	74
IONIC					
Salt	$Na\ Cl$	2.17	13.5	42	121
Sphalerite	$Zn\ S$	4.02	12.1	13	20
Fluorite	$Ca\ F_2$	3.18	8.19	12	55
Calcite	$Ca\ CO_3$	2.71	7.39	14	14
Barite	$Ba\ SO_4$	4.47	8.71	18	163
MOLECULAR					
Iodine	I_2	4.92	25.8		300
Ice I	H_2O	.917	19.6 *	120	150
Carbon dioxide	CO_2	1.56	9.40		850
Benzene	C_6H_6	1.04	12.5 *	329	

TABLE II d

DENSITY, COMPRESSIBILITY, AND THERMAL EXPANSION OF SOLIDS

* Not counting hydrogen.

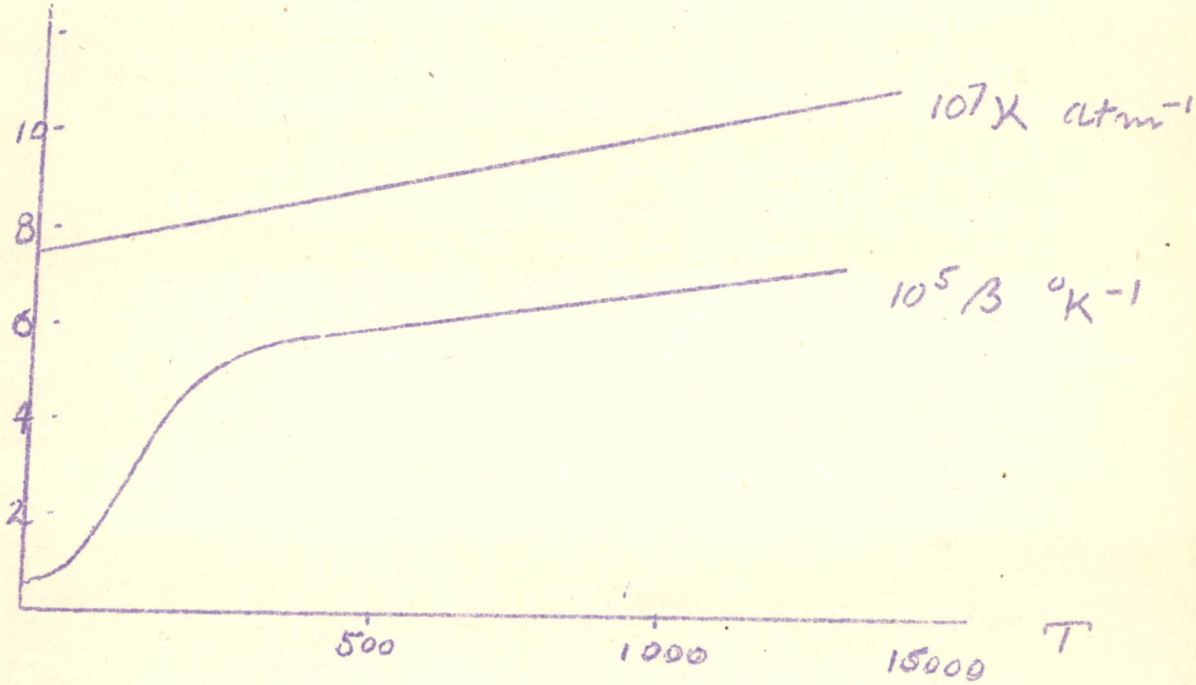


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FIG. II d

e) Polymorphic Transitions and Melting

The volume of a solid is not always a continuous function of the pressure and temperature as represented by equation (II d 1). For many solids there are discontinuous changes in which the atoms rearrange themselves. Ice is a particularly good example, six different polymorphic forms having been discovered. These may be represented by lines on a P-T diagram which give the values of P and T at which discontinuous transitions occur (Fig. IIe). These lines are fairly straight and can be well represented by equations of the form

$$T-T_o \approx aP-bP^2 \qquad \text{(IIe1)}$$

where a and b are new experimental constants differing from those used previously and b~~P~~ is generally quite small compared to a.

The P-T diagram is incomplete and a better representation is given by a surface in which V is plotted against P and T. The different phases are then given by surfaces whose equations are like (IId1), separated by vertical steps along the lines (IIe1). This surface for ice is shown in Zemansky, Heat and Thermodynamics, Fig. 11.10, but not many such surfaces have been prepared.

It should be pointed out that the surfaces of each phase, and the corresponding equation (IId1), may be extended beyond its vertical boundaries, and this is not mere mathematics but can in many cases be realised physically. If the pressure is released on ice II it will not instantaneously change to ice I and thus, for a while, ice II may exist at zero pressure. It is, however, not in equilibrium and will in time change spontaneously to ice I. The surface shown in figure 11.10, and the areas of figure IIe, show only the equilibrium states. This explains the absence of ice IV, another crystalline form of ice which can be produced but is never in equilibrium.

As may be seen in figure IIe the boundaries separating the different phases are oriented pretty much at random. On the other hand a definite statement can be made concerning the volume change on crossing a line along which two phases are in equilibrium. In an isothermal process in which the pressure is increasing, the volume decreases as the equilibrium line is crossed. If this were not so and the volume increased when the pressure increased the system would, of course, be unstable. Generalizing on this behavior Le Chatelier enunciated a general principle which may be applied to any intensive variable (condition): "When the conditions under which a system is in equilibrium are caused to change while equilibrium is still maintained, the system always tends to oppose that change." In this case as one attempts to increase the pressure on ice, it will change to a phase of smaller volume and thus "oppose" the increase in pressure.

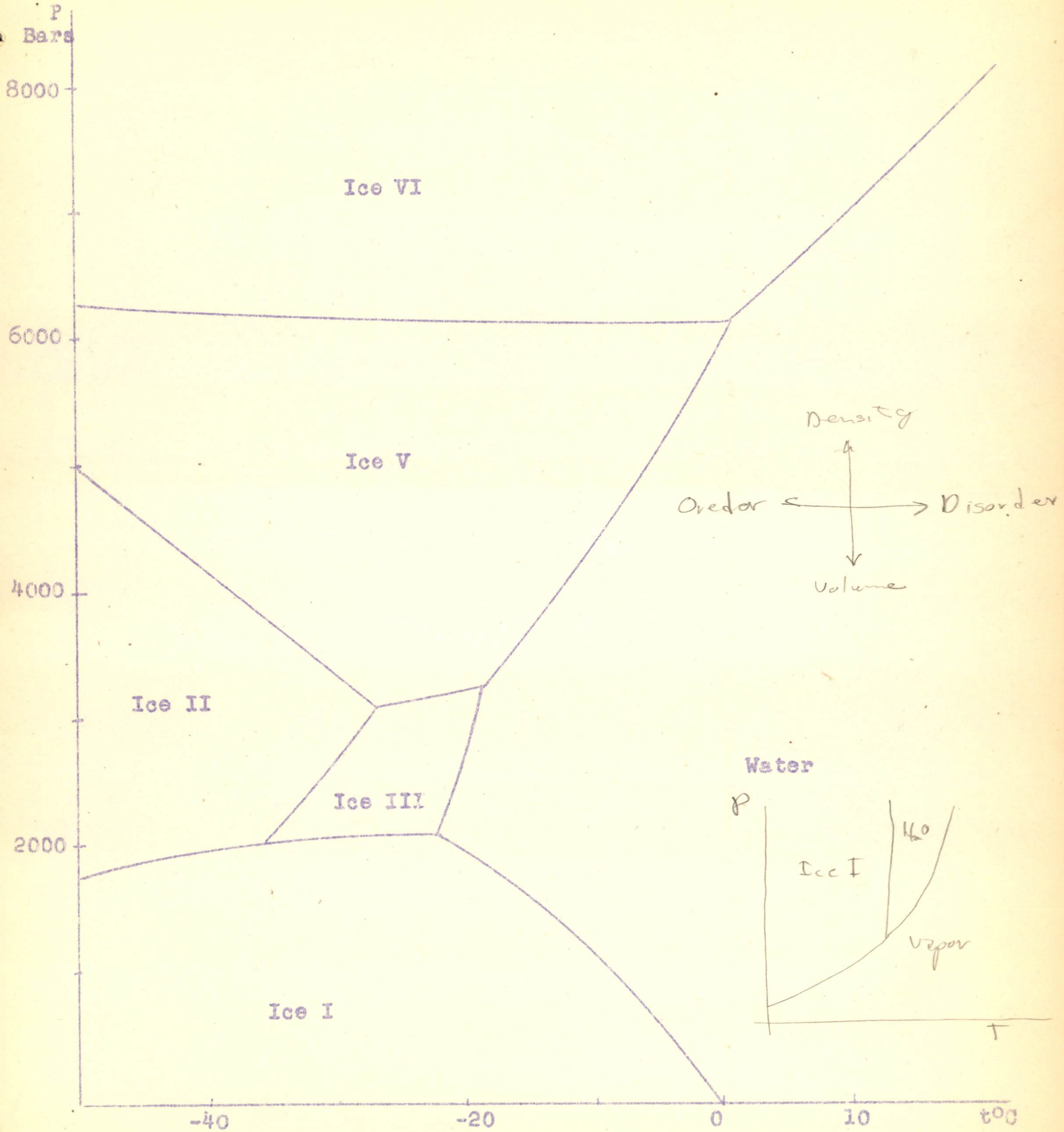
These volume changes enter in important thermodynamic formulae and will be represented by

$$\Delta V = V_2 - V_1 \qquad \text{(IIe2)}$$

$$\kappa = -\left(\frac{\partial \ln V}{\partial P}\right)_T$$

$$\beta = \left(\frac{\partial \ln V}{\partial T}\right)_P$$

liquid — long range order



PHASE CHANGES IN ICE

FIG. IIe

where phase 2 is the higher temperature phase. From Le Chatelier's principle it follows that $\triangle V$ is positive if the transition line on a P-T diagram slopes upward to the right, and negative if it slopes upwards to the left. Thus ice I contracts on changing to water whereas ice V expands. When the transition line is horizontal the convention for the sign of $\triangle V$ breaks down, but this occurs seldom.

There is a completely analogous law governing isobaric changes: as the temperature increases the system changes to a phase of greater entropy, or disorder, though how this opposes the rise in temperature can be explained only in the next chapter.

As the temperature is increased a state is reached in which long range order has disappeared, and this will be defined as a liquid. But first "long range order" must be defined. In a perfect crystal at absolute zero, if the positions of any three atoms not on a line are given, this fixes all the positions which any other atom may occupy, in principle out to infinity. This is perfect order. As the temperature is increased the positions become uncertain first on account of vibrations about the equilibrium positions, but eventually the positions of equilibrium themselves vanish except in the immediate neighborhood of a molecule. Here the requirements of space allow about 12 molecules to be simultaneously in contact with another one, and they cannot change their relative positions without bumping into each other. This forces a short-range order which appears very clearly in x-ray patterns of liquids.

Ordinarily a liquid is defined as a condensed phase (meaning that the molecules are essentially in contact) which cannot support a shearing stress in equilibrium. The slightest shearing stress causes it to flow, which implies long range disorder. On the other hand liquids do not differ much in compressibility or thermal expansion from the solids with which they are in equilibrium. As we have agreed to study only the thermodynamics of hydrostatic pressure and not of shearing stresses, the usual definition is not applicable and a liquid appears as simply another modification of a solid. Perhaps this is fortunate as our definition in terms of long-range disorder includes glasses and other amorphous solids with the liquids. These solids are pretty rigid and yet if a shearing stress is applied continuously they will, in time, flow in the direction of the stress. They are therefore very viscous liquids, and in many cases supercooled liquids. This means that there exists a crystalline form to which the glass will, in time, transform spontaneously the transition temperatures lying above that considered and having been passed too quickly for the crystallization to take place. This is not an uncommon occurance. Water, for instance, if free from dust, may be cooled many degrees below zero centigrade without immediately turning to ice. The formulae of thermodynamics apply equally well to these unstable states, but it must be remembered that the return to equilibrium is an irreversible process. The melting point data at atmospheric pressure of some solids is given in the first four columns of table IIe. The melting temperatures follow the pattern already indicated by the nature of the binding forces: molecular compounds melt below, or near, room temperature; the ionic compounds and metals are quite comparable; and the valence compounds are quite refractory. Almost without exception there is

MELTING POINT DATA

	v_s cc/mole	v_ℓ cc/mole	T_m °K	ℓ_m kg.cal/mole	Δs_m cal/deg.mole	ℓ_v kg.cal/mole	ℓ_v/ℓ_m
Metals							
Na	24.2	24.6	371	0.63	1.70	26.2	41
Al	10.6	11.0	932	2.55	2.73	67.6	26
Fe	7.50	8.12	1802	3.56	1.97	96.5	27
Ag	10.8	11.3	1234	2.70	2.19	69.4	26
Sn	16.50	16.97	505	1.72	3.40	68.0	39
Hg	14.15	14.65	234	.58	2.48	15.5	27
Ionic							
NaCl	29.6	37.7	1073	7.22	6.72		
AgBr	30.4	33.6	703	2.18	3.10		
NaOH	18.8	- -	591	1.60	2.71		
$AgNO_3$	39.0	- -	583	6.45	3.76		
Molecular							
A	24.2	28.1	83	.280	3.38	1.88	6.7
H_2	26.5	28.7	14	.028	2.0	.22	7.9
N_2	27.2	32.8	63	.218	3.46	1.69	7.7
H_2O	19.65	18.02	273	1.43	5.25	11.3	7.9
CO_2	28.8	37.0	217	1.99	9.16	6.44	3.2
Valence							
C			3800			140.	
SiO_2			1980				
Al_2O_3			2320				

TABLE IIe

expansion on melting so that the solid sinks in its melt. It is noticeable, however, that the metals expand very little on melting. This is probably because the solid metal is itself already half melted: its negative elements, the electrons, do not occupy fixed lattice positions. The liquid metal therefore differs less from the solid than is the case with other substances, except of course the glasses.

f) Vaporization

It has been seen that a liquid differs qualitatively from a solid in its inability permanently to support shear and in the long-range disorder of its molecules, the glasses occupying an ambiguous position with respect to the first criterion. There is another state of matter, the gaseous state, which differs qualitatively from both liquids and solids in its inability to support tension and in the great disorder of its molecules.

If the pressure on a solid is reduced there comes a point where the piston, or whatever device was used to exert the pressure, separates from the solid and leaves a space which the solid does not fill. This space is empty, however, only in appearance. Actually it contains many molecules of the solid moving freely across the available volume. When these molecules strike the solid they may condense on it and, reciprocally, surface molecules of the solid may spontaneously leave it and join those of the gas. In equilibrium these two processes take place at equal rates. The pressure exerted by the gas in equilibrium with the solid is called the vapor pressure of the solid. Liquids also exert a vapor pressure. Usually these pressures are quite small and that is why they do not show in figure IIe, but if the pressure scale of that figure is increased a millionfold one obtains figure IId1. The fusion curve now appears vertical and there are boundaries between ice and vapor and water and vapor regions. These are the vapor pressure curves. These three lines intersect at T which is known as the triple point. At this pressure and temperature water, ice, and water-vapor may be in equilibrium. The triple point data of some substances is given in Table IIf1.

Figure IIf1 gives the vapor pressure over a range of 60 degrees, but a P-T plot is not satisfactory to represent vapor pressures over greater ranges because the pressure changes by several orders of magnitude. It is evidently necessary to plot the logarithm of P, and it turns out that it is best to plot log P against 1000/T. This is done in figure IIf2 for water and for mercury. The most striking feature of this figure is the tremendous range of vapor pressures which are observed, and measured: a factor of 10^{11} in the case of mercury; and there is no reason to believe that these curves may not be extended indefinitely to the right. This is not so for their extension to the left for in this direction they terminate. The terminal point c for the water curve is shown in the figure. Next it is observed that the vapor pressure curves are almost straight lines on this plot, and the slight curvature may be taken into account by a term in log T, so that one has:-

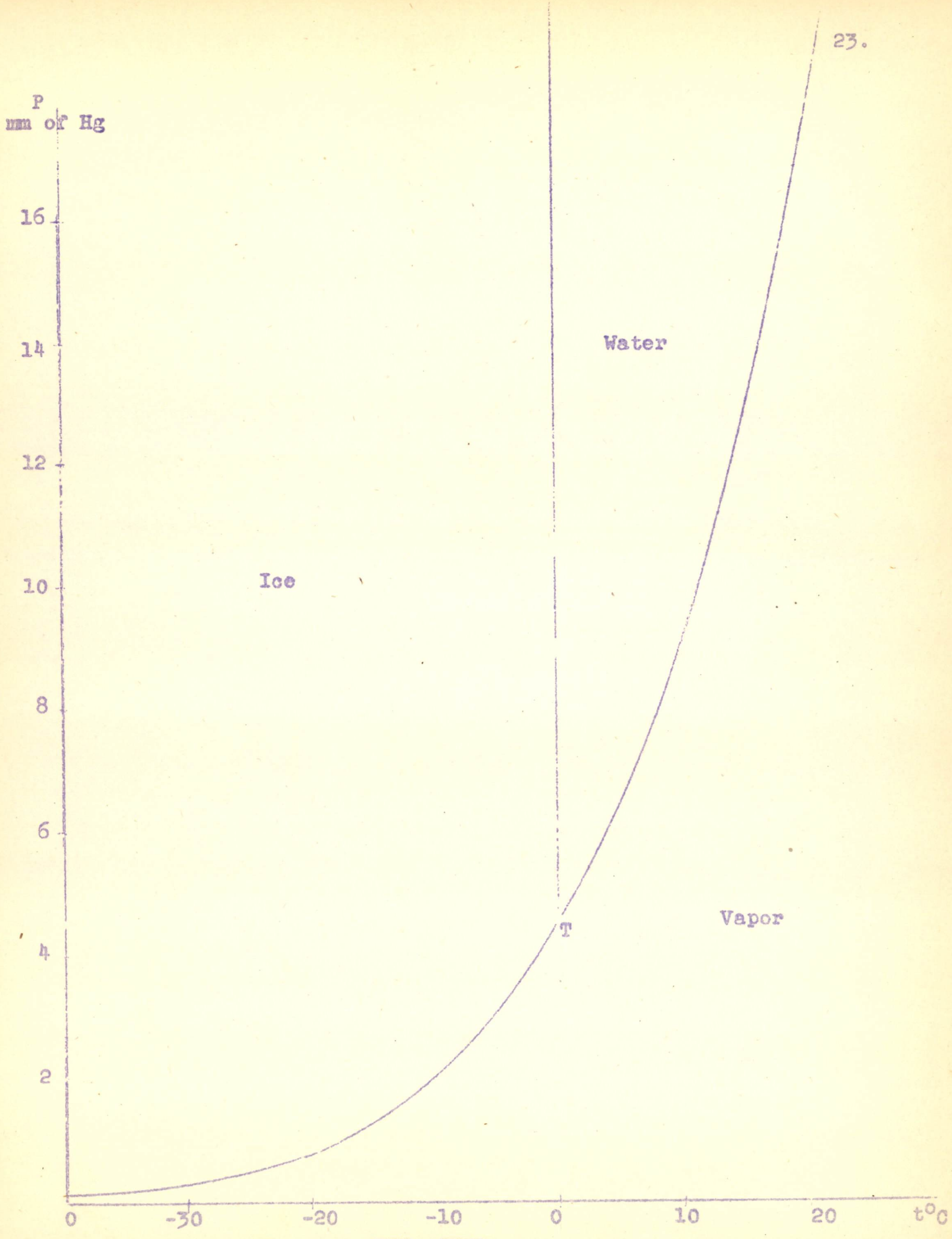


FIG. IIf1

SUBSTANCE	TEMPERATURE	PRESSURE	DENSITY IN gm/cm^3	
	°C	mm.	Liquid	Solid
H_2O	.0098	4.579	.9982	.917
SO_2	- 72.7	16.3	1.247	
CO_2	- 56.6	3885	1.179	1.53
O_2	-218.4	2.0	1.304	1.43
A	-189.2	512.2	1.44	1.65
N_2	-209.8	96.4	.873	1.025
H_2	-259.1	51.4	.075	.076
Hg	- 38.8	$1.24\ 10^{-6}$	13.690	14.193

TRIPLE POINT DATA

Table IIf1

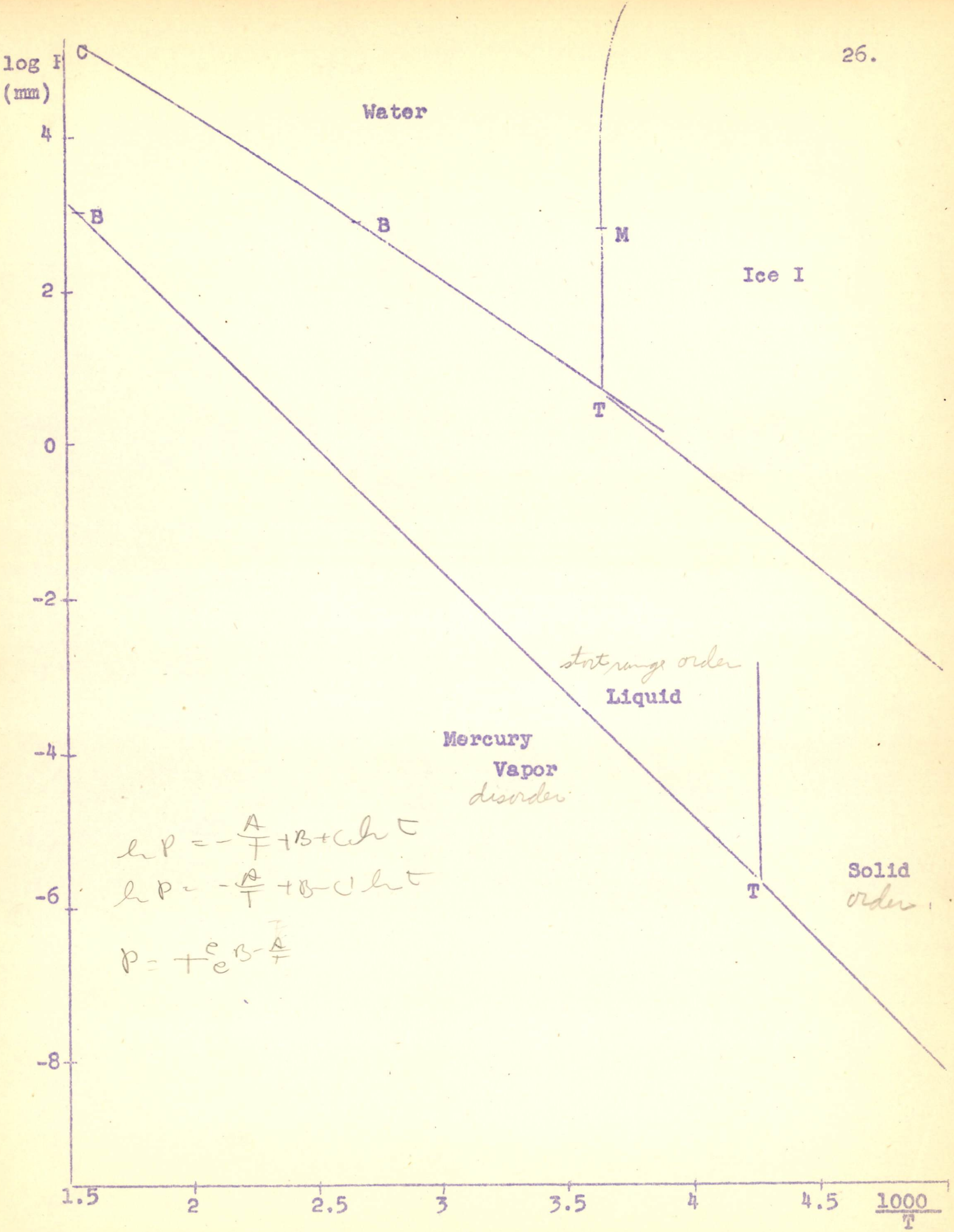
$$\left.\begin{array}{ll} & \log P \approx -\frac{A'}{T} + B' + C' \log T \\ \text{or} & \ln P \approx -\frac{A}{T} + B + C \ln T \\ \text{or again} & P \approx T^{C} e^{B-A/T} \end{array}\right\} \quad \text{(IIf1)}$$

but one must beware that in the last equation, where one has raised e to a power, slight errors in the logarithm are greatly magnified.

The water vapor pressure curve is shown in figure IIf2 extended into the ice region. This is in accord with observation that water free from dust may be supercooled considerably below the freezing temperature. In this condition the water is not in equilibrium and should a speck of ice be dropped in it ice crystals will grow very rapidly. Similarly if a beaker of supercooled water is in an evacuated region containing also a piece of ice, the water will distill onto the ice. For example at -16°C the vapor pressure of water is 1.323 mm and that of ice is 1.132 mm so that there is a pressure difference of 0.191 mm to produce the distillation.

The values of the constants in equation IIf1 for some substances are tabulated in table IIf2 and the following regularities may be noted: The constant A is roughly proportional to the melting temperature Tm, the ratio A'/Tm being about 5 for substances with Van der Waals binding and about 12 for metals. Water classes with the metals in this respect because the water molecule has such a strong dipole moment that its binding is almost ionic. The constant C is relatively small and nearly always negative.

If the temperature of a liquid is raised to the value corresponding, on the vapor pressure curve, to the pressure in the liquid plus the pressure necessary to maintain a bubble against surface tension, the phenomenon of boiling will be observed. Because of this additional pressure due to surface tension, the boiling point of a liquid is defined as the temperature of the vapor above a boiling liquid. The vapor-pressure curve is therefore also the curve of boiling points at different pressures. The boiling point at atmospheric pressure is called the normal boiling point. The normal boiling point (B) and melting point (M) are shown in figure IIf2 as well as the triple point (T).



$\ln P = -\frac{A}{T} + B + C \ln T$

$\ln P = -\frac{A}{T} + B - C \ln T$

$P = T^{C} e^{B - \frac{A}{T}}$

FIG. IIf2

TABLE IIf2

VAPOR PRESSURE CONSTANTS

ELEMENT	Tm	A'	B'	C'	Additional Terms	A'/Tm
Solids						
Ne	24.6	112.8	4.218	-		4.58
N_2	73.3	359.4	4.790	-		4.90
A	83.9	412.5	4.747	-		4.98
Kr	116	578	4.847	-		4.98
Hg	234	3347	5.766	-		14.3
H_2O	273	2790	10.595	-1.07		10.2
Cs	299	4120	7.571	-1.0		13.8
Cd	594	6073	8.845	- .9		10.2
Zn	692	6750	6.041	-		9.77
Liquids						
He	-	3.018	-.678	2.484	$-.00297T^4$	-
H_2	14.0	46.65	1.190	.84		3.33
Ne	24.6	97.4	3.591	-		3.96
O_2	54.7	485.6	11.450	-3.1		8.86
N_2	73.3	356.6	8.291	-1.96		4.86
A	83.9	357.7	4.095	-		4.26
Kr	116	569	7.763	-1.45		4.90
Hg	234	3308	7.4984	- .8		14.1
H_2O	273	2799	17.218	-3.77		10.2
Cs	299	4042	8.301	-1.4		13.5
K	335	4552	5.918	- .5		13.6
Na	370	5567	6.360	- .5		14.8
Cd	594	5982	11.188	-		10.1
Zn	692	6697	9.372	-1.2		9.67

Pressures are in bars, temperatures in degrees kelvin.

g) The Ideal Gas:

The laws of gases are particularly simple when their density is very much less than that of the corresponding liquid or solid. The laws obeyed in the limit of low density are called the ideal gas laws, and these laws are good approximations at ordinary densities. If the density is one thousandth of that of the liquid the deviations are a few tenths of a per cent. The ideal gas laws are therefore good approximations for ordinary gases as well as being exact laws for an ideal gas.

1. Law of Boyle: If the volume V of a gas is measured as a function of the applied pressure P, time being allowed between each observation for the gas to come to thermal equilibrium with its surroundings, it is observed that the product PV is constant

$$\boxed{PV \approx B} \qquad \text{(IIg1)}$$

Boyle's law for gases corresponds to Hooke's law for solids, Both are approximations good in the limit of low pressures, the departures from Hooke's law occuring at pressures roughly 1000 times larger than the departures from Boyle's law. Boyle's law may be represented graphically by plotting P against V at constant T (Fig. IIg1). The curve obtained is a hyperbola. It is also convenient to use logarithmic scales for P and V, in which case the curves are straight lines sloping downward at 45°. The experiment is commonly performed by allowing the gas to enter the closed end of a U-tube and trapping it with a column of mercury. The length ℓ occupied by the gas is then measured as a function of the difference in level h of the mercury in the two arms. The volume is then

$$V = A\ell$$

and the pressure

$$P = \rho g(h+h_o)$$

where h_o is the barametric height at the time and place of the experiment.

The product PV has the dimensions of energy and should therefore be expressed in ergs (CGS) or joules (MKS). However, pressures are always measured in atmospheres or millimeters of mercury. A conversion is therefore always necessary. It is convenient to know that

$1 \text{ cm}^3 \times 1 \text{ mm} = 1351$ ergs

1 liter x 1 bar = 100 joules

1 liter x 1 atmosphere = 101.325 joules

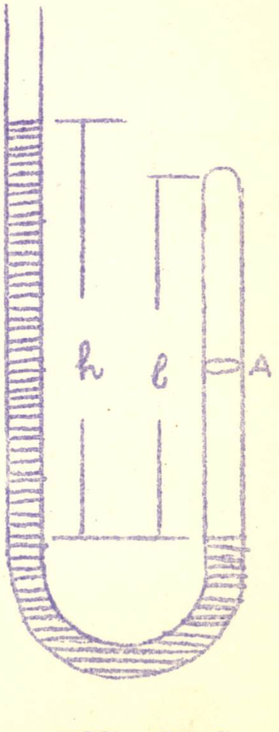


FIG. IIg1

2. Law of Charles and Gay Lussac: The constant B depends, of course, on the temperature. If the temperature, t, is measured with a conventional mercury-in-glass thermometer it is found that PV depends linearly on t

$$PV \approx C\ (1 + \alpha t) \qquad \text{(IIg2)}$$

and that the constant α has the same value for all gases. More precisely, α is found to depend slightly on pressure, temperature and the nature of the gas, but as the pressure is decreased α tends towards the same limit, irrespective of the nature of the gas and approximately irrespective of the temperature.

3. The Ideal Gas Thermometer: The independence of α, in the limit, on the substance, suggests that the law expressed by (IIg2) is fundamental, and that the dependence of other properties on temperature will become simpler if the mercury-in-glass temperature scale is corrected so that α is exactly independent of the temperature. Its value, a universal constant, is then obtained by applying (IIg2) exactly to any gas, in the limit of low pressure, at the normal melting ($t = 0$) and boiling ($t = 100$) points of water. Within experimental error the value is

$$\alpha = 1/273.16 \quad {}^{\circ}C^{-1}$$

The following equation then defines the ideal gas temperature scale

$$\left.\begin{array}{c} PV \longrightarrow C'\ (t + 1/\alpha) \\ P \longrightarrow 0 \end{array}\right\} .$$

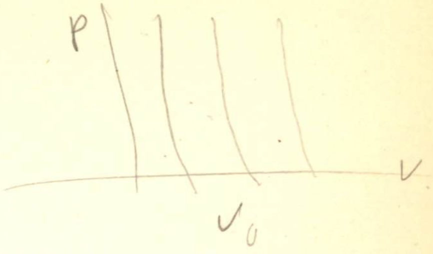
The law is simpler if the zero point of the temperature scale is shifted so that

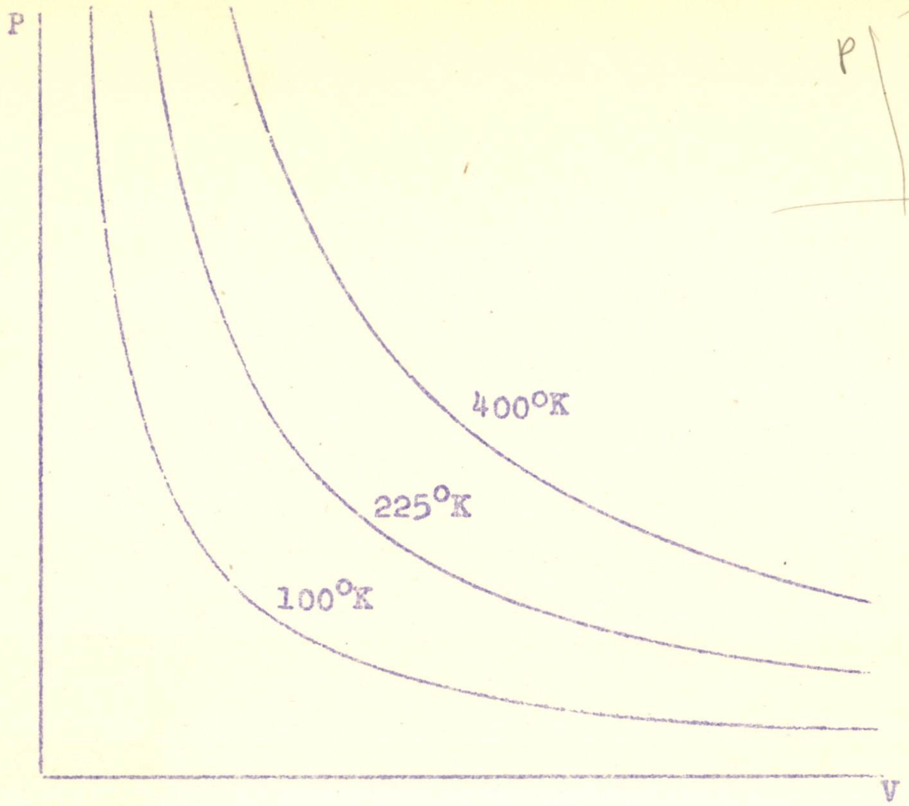
$$\begin{array}{c} T = t + 1/\alpha \\ PV \longrightarrow C'\ T \\ P \longrightarrow 0 \end{array} \qquad \text{(IIg3)}$$

and this defines the absolute centigrade ideal gas temperature scale.

Nothing is implied yet about the absolute nature of $T = 0$ or even the possibility of negative values for T. Equation (IIg3) merely implies that ideal gases do not exist at such temperatures.

solved 30.





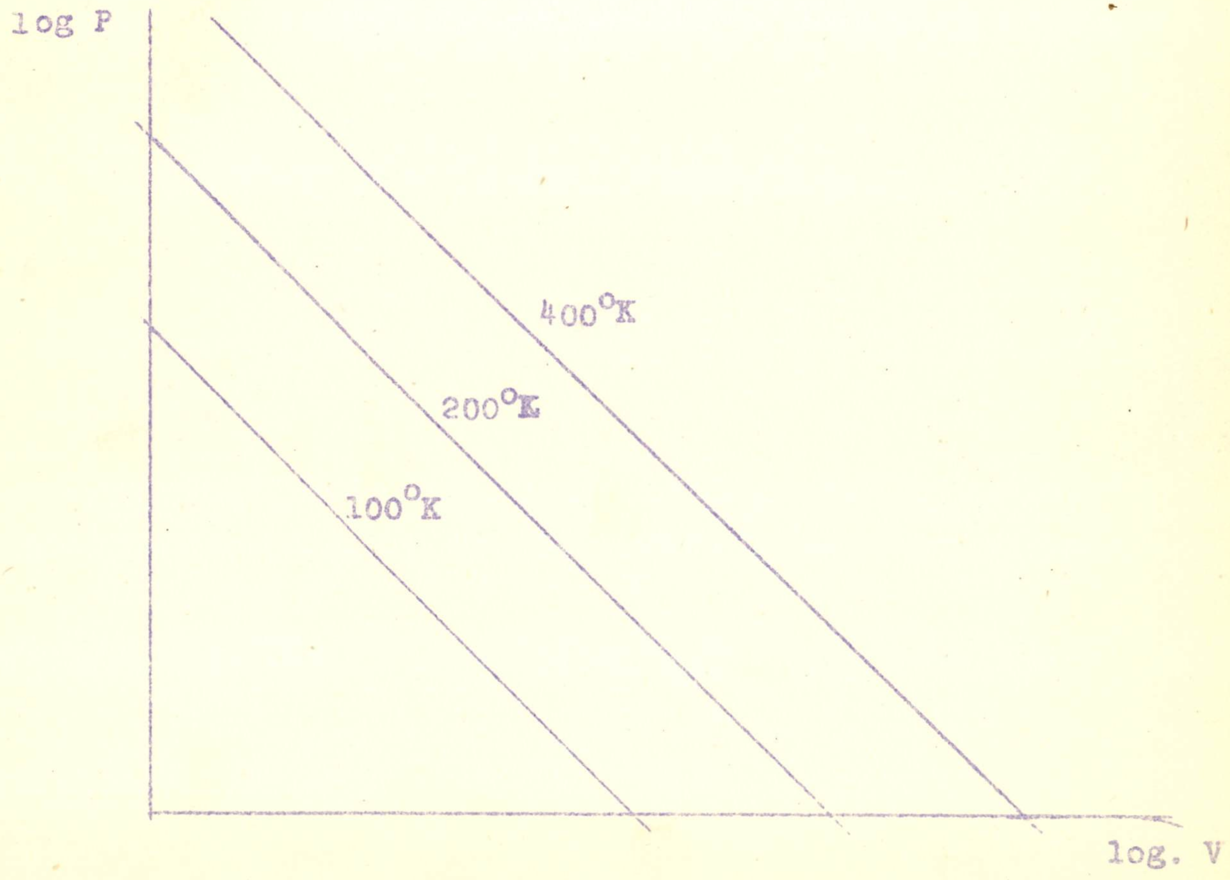


FIG. IIg3

Isothermals of an Ideal Gas

As a practical matter it does make a difference what gas is used because equation (IIg3) can not be applied if the gas is condensing. If mercury gas were used this would oblige, at the ice point, using pressures below 1.85×10^{-4} mm, which is impractical. Obviously gases with very low boiling points are best, and hydrogen and helium are standard. However even here there is a limit at the normal boiling of helium, at 4.3° absolute, at which the ideal gas thermometer becomes impractical. Below this temperature the vapor pressure equation of helium (Table IIf2) is used, but it will be first necessary to show that the temperature thus defined is identical with that which would be measured with an ideal gas thermometer if the latter were practical.

The ideal gas thermometer is not a convenient instrument as it is always necessary to verify that the pressure is low enough so that the limit has been reached. In practice one uses a finite volume (8.45 liters for 1 gm of hydrogen is standard) and applies corrections; but even so it is clumsy to use so that in practice one determines a certain number of fixed points with a gas thermometer and uses more convenient instruments to interpolate. The normal melting point of solids are convenient fixed points if the solid is easily obtained pure as melting points are little affected by small changes of pressure. Boiling points are also convenient although here care must be exercised that the pressure is exactly 760mm of mercury because of the great variation of boiling point with pressure. Table IIg3 gives a number of fixed points which have been determined carefully.

4. Law of Avogadro: The constant C' in equation (IIg3) is proportional to the amount of gas used so that one can write

$$PV = NkT = nRT \tag{IIg4}$$

where N stands for the number of molecules and n for the number of moles. Now it turns out that k and R are universal constants, independent of the nature of the gas

Boltzmann's constant: $k = 1.380 \times 10^{-16}$ erg/molecule, degree

Gas constant: $R = 8.314$ Joules/gram-mole, degree

where it must be noted that R is in mixed MKS - CGS units. Another way of expressing this constant, and one which is easier to remember, is to note that at 300° absolute and one bar pressure the volume of a gram mole of ideal gas is 24.942 liters.

5. Law of Dalton: The proportionality between P and n and the universal value of k and R shows that each mole exerts a pressure RT/V independently of the presence of other molecules in the same volume and in virtue of some property common to all kinds of molecules. It should therefore make no difference if different kinds (i) of gases are mixed, each kind will independently exert its own partial pressure

TABLE IIg3

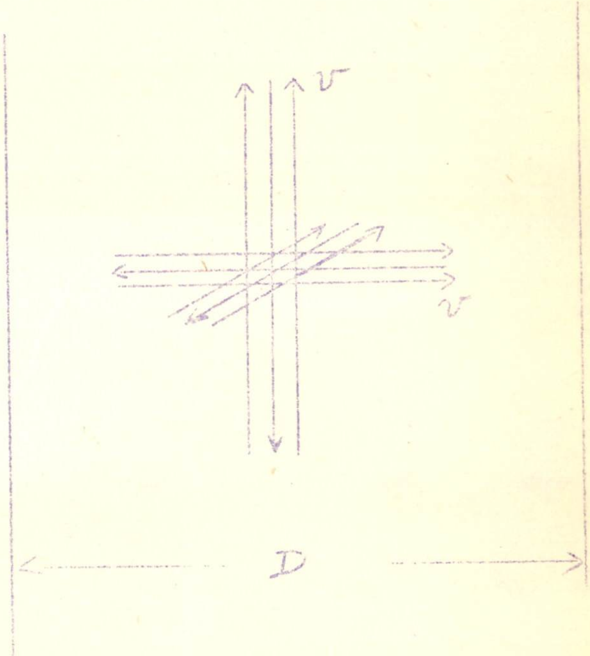
Transition	Substance	Absolute Temperature
B.P.	Hydrogen	20.38
B.P.	Neon	27.07
B.P.	Nitrogen	77.35
B.P.	Oxygen	90.19
M.P.	Mercury	234.30
M.P.	Ice	273.16
Transition	Sodium Sulphate	305.54
B.P.	Water	373.16
M.P.	Tin	505.01
M.P.	Lead	600.5
B.P.	Sulphur	717.76
M.P.	Antimony	903.7
M.P.	Silver	1233.7
M.P.	Gold	1336
M.P.	Palladium	1827
M.P.	Platinum	2036
M.P.	Tungsten	3659

$$\left.\begin{array}{l} P_i \approx n_i\, RT/V \\ P \approx n\, RT/V \end{array}\right\} \qquad \text{(IIg5)}$$

where $\left\{\begin{array}{l} n = \sum n_i \\ P = \sum P_i \end{array}\right.$

This is Dalton's law of partial pressures.

6. Kinetic Theory: It was clear to the ancients that the pressure of a gas might be due to the beating of the molecules against the walls, but is remained for Bervoulli to show that Boyle's law followed from this assumption. The following is a crude kinetic picture but which nevertheless gives the correct results:



Assume that there are N particles in a rectangular volume V, that they all have the same kinetic energy

$$u = mv^2/2 \;;$$

that they move in directions perpendicular to the walls, N/3 in each direction so defined, and rebound elastically from the walls. Consider two opposite walls of area A and separation D. It takes each particle a time

$$\tau = 2D/v$$

to make the round trip between the walls, so that in this time all N/3 particles have rebounded off both walls, delivering to each wall an impulse

$$F\tau = 2\ mv \cdot N/3$$

The average pressure on each wall is

$$P = \frac{F}{A} = 2\ mv\ \frac{N}{3}\ \frac{v}{2AD} = \frac{mv^2}{V}\ \frac{N}{3} = \frac{2}{3}\ \frac{Nu}{V}$$

$$PV = \frac{2}{3}\ Nu \qquad \text{(IIg6)}$$

From this formula it is seen that Boyle's law follows if u is constant at constant temperature, Charles' law follows if u is proportional to T, Avogadro and Dalton's laws follow if the translational energy per particle is the same for different gases in equilibrium. The last follows from mechanics, for it can be shown that in the elastic collision between two particles, the energy difference between the two will, in the average, be reduced in the ratio $\left(\frac{m_1 - m_2}{m_1 + m_2}\right)^2$ by each collision. The average value of u tends therefore to become the same.

Relating (IIg6) to (IIg4) gives the value of the average energy per particle

$$\bar{u} = \frac{3}{2} kT \qquad \text{(IIg7)}$$

h) Real Gases

1. Dissociation: Certain gases exhibit marked deviations from the ideal gas laws at densities at which one would expect these laws to be satisfied. Nitrogen tetroxide N_2O_4 is a good example and the deviation is best shown by plotting PV/RT, a quantity which should be constant, against the temperature. (Fig. IIh1). If one mole of liquid is allowed to evaporate at the normal boiling point, 21.3°C, it is observed that the vapor occupies 16 percent more space than is expected. The situation becomes worse as the temperature is increased at constant pressure until 150°C where it has practically leveled off at twice the normal volume. The curve can be extrapolated to lower temperatures and this is done in the figure. Plotted in this way it is seen that this substance behaves as an ideal gas both below -40°C (if it did not liquefy) and above 150°C, but that the number of moles is twice as large at the higher temperature than at the lower. In the middle range it is dissociating according to the formula

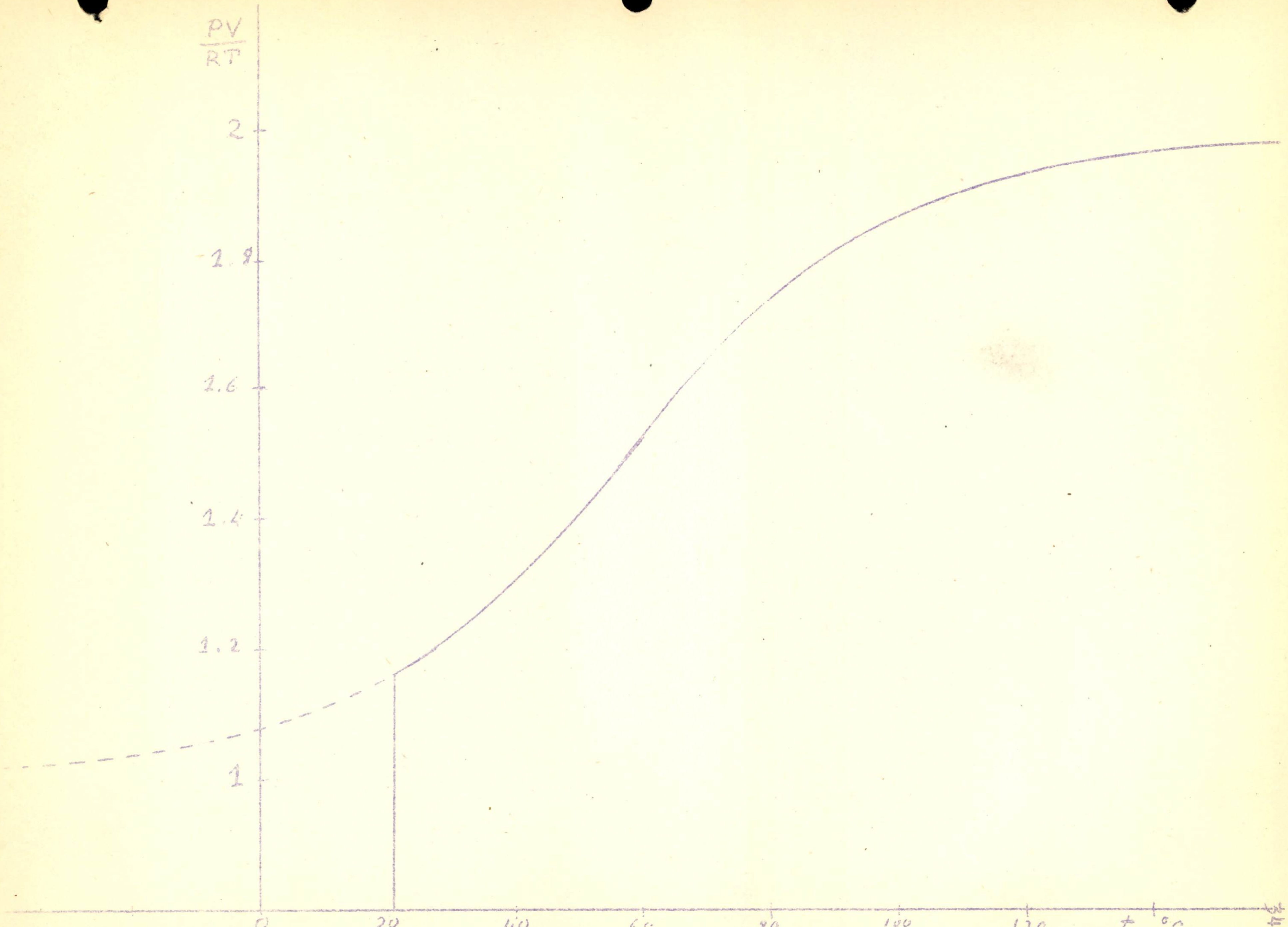
$$N_2O_4 \rightleftharpoons 2\,NO_2$$

Let α be the fraction of N_2O_4 molecules which have dissociated. Then there are

$$\begin{aligned} &1 - \alpha \text{ molecules of } N_2O_4 \\ &\underline{\quad 2\alpha \text{ molecules of } NO_2} \\ n = \ &1 + \alpha \text{ molecules.} \end{aligned}$$

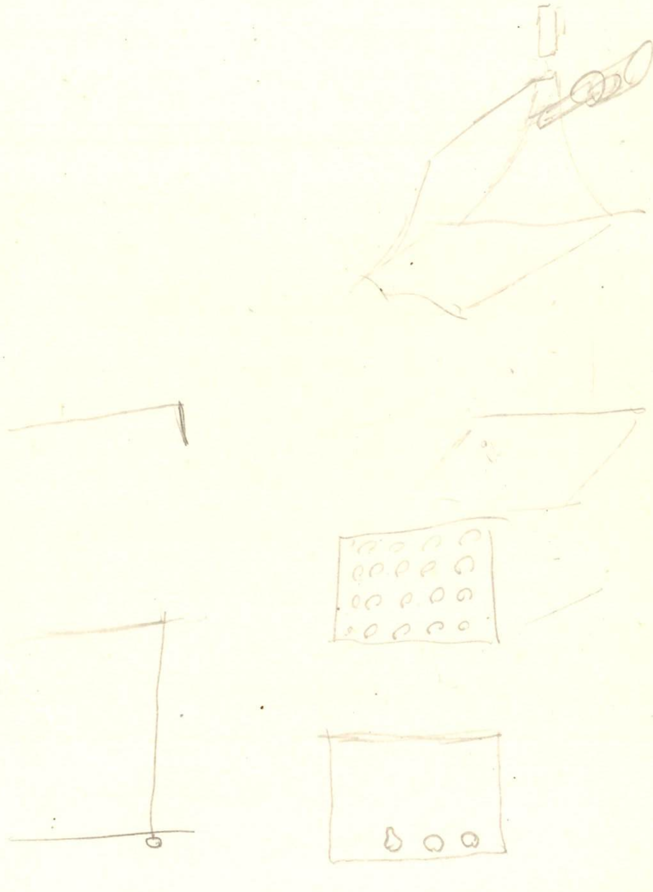
Figure IIh1 is a plot of $1 + \alpha$ and shows how the dissociation proceeds with increasing temperature.

The observed anomaly is therefore not a real departure from the ideal gas laws. What we have is a mixture of two ideal gases undergoing a reversible chemical reaction, and the ideal gas laws are applied to both of them to compute the degree of dissociation α.



Dissociation of Nitrogen Tetroxide

Fig II h 1



2. Evaporation and Condensation:

The isothermals shown in figure IIg3 do not extend indefinitely to smaller volumes. When the vapor pressure corresponding to the temperature of the isothermal is reached the gas begins to condense, and the pressure cannot exceed this value until the gas is entirely condensed. The isothermal therefore has a bend in it joining the ideal gas section to a horizontal section. This is shown in figure IIh2 with logarithmic scales.

The locus of the bends in the isothermals is called the condensation curve. It is readily obtained by eliminating T between equations IIf1 and IIg4. This curve divides the P-V plane, points to the right of it representing gas, and points to the left of it a mixed phase: liquid and vapor if above the pressure of the triple point, solid and vapor if below. The word "vapor" is used to represent a gas in equilibrium with its condensed phase, and does not signify any departure from the ideal gas laws. At the normal boiling point steam occupies a volume 1.3 per cent less than predicted by the ideal gas laws and the departures are less than that at larger volumes. To the left of the liquid and vapor and solid and vapor regions there is another sharp bend in the isothermals and one enters the liquid or solid regions, respectively, of the P-V plane.

Each point of the mixed phase regions represents a definite proportion of vapor and condensed phase. Let V_c and V_g represent the volumes at the evaporation and condensation lines, and V an intermediate point, all at the same temperature. Let there be n_c moles of condensate and n_g moles of gas at V. Then

$$n = n_c + n_g \quad ,$$

$$V = n_c v_c + n_g v_g = \frac{n_c}{n} V_c + \frac{n_g}{n} V_g$$

$$\alpha = \frac{n_g}{n} = \frac{V - V_c}{V_g - V_c} \qquad \text{(IIh2)}$$

α is the fraction evaporated, and one sees that it is proportional to the distance from the evaporation curve.

3. Real Gases: The departure of real gases from the ideal laws is well shown by plotting I = PV/nRT, a quantity which is one for an ideal gas, against the pressure P. Figure IIh3 shows the isothermals for carbon dioxide plotted in this way. Similar plots are obtained for all other gases if the scales are suitable altered. This is the "law of corresponding states" which will be stated more precisely in paragraph IIh5. The following features of the plot may be noted.

- α) All the curves go through 1 at P = 0. This is the ideal gas limit.
- β) The initial slope of the isotherms depends on the temperature, and its dependence can be approximated by

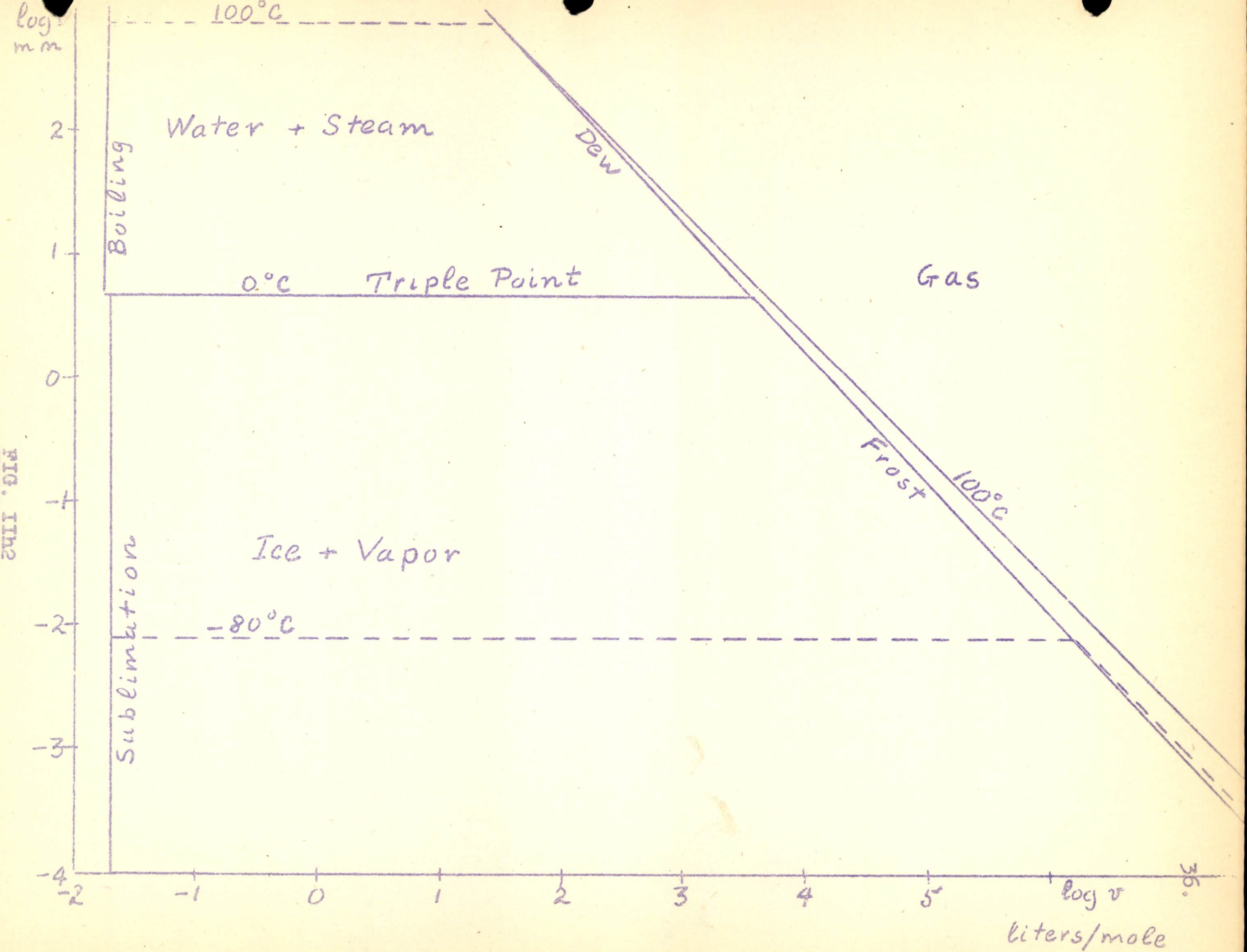


FIG. IIh2

P - V diagram for water

$PV = nRT$

$$\boxed{RT = \frac{PV}{n}}$$

$$\frac{PV}{nRT}$$

$I - \int(\quad)\,dP$

$$\frac{dI}{dp} \approx \left(\frac{b_o}{RT} - \frac{a_o}{R^2T^2}\right) \qquad \text{(IIh3)}$$

This defines the two constants a_o and b_o and also gives a measure of the departure from the ideal gas laws.

$$\frac{\Delta I}{I} \underset{\rho}{\approx} \frac{n}{V}\left(b_o - \frac{a_o}{RT}\right) \qquad \text{(IIh4)}$$

It is seen that it is directly proportional to the molar density. The temperature a_o/Rb_o at which the initial slope changes from negative to positive is called the characteristic temperature. It is the temperature at which the gas is most ideal and is about 370°C for carbon dioxide, 52°C for nitrogen and -165.72°C for hydrogen.

γ) At very high pressures the isotherms all slope upward. This is because the gas has become very incompressible and obeys Hooke's law more nearly than the ideal gas laws. The isotherms therefore approximate parabolas with the concave side down.

δ) In this region the different isotherms cross over, a phenomenon called inversion. At low pressures the gas contracts greatly, and may even condense, as the temperature is lowered. Above the inversion pressure the volume changes less than the factor 1/T and therefore the isotherms for low T lie above these for high T. This inversion is important in the liquifaction of gases.

4. Van der Waals' equation

These properties of real gases were explained qualitatively by considering two properties of molecules which are

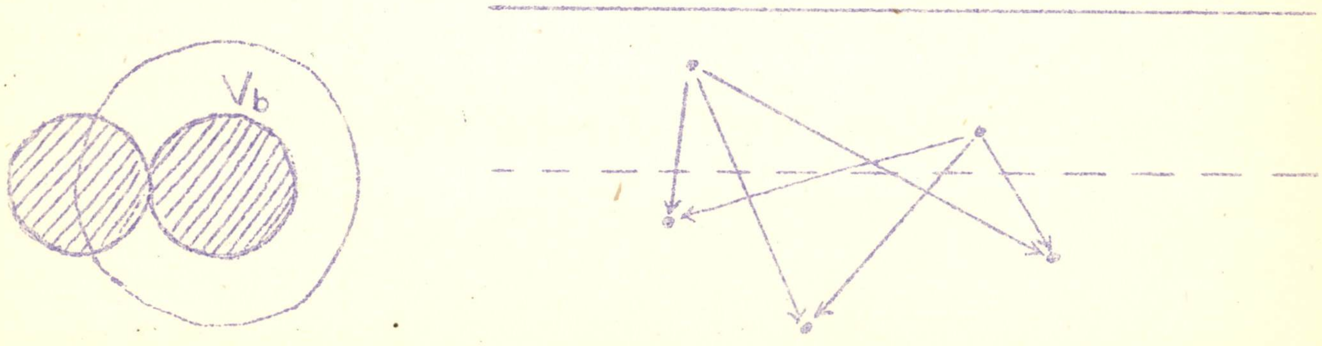
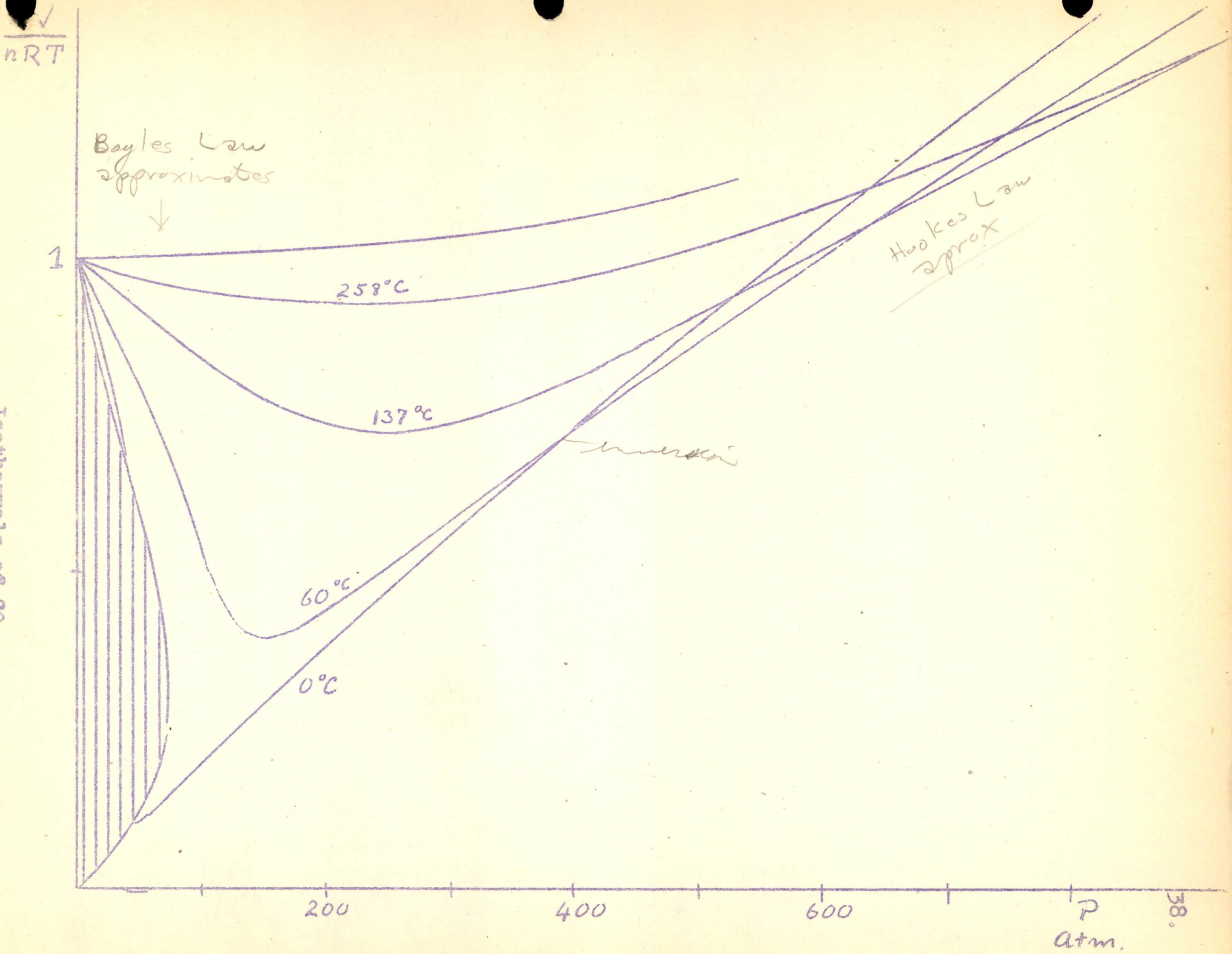


Fig. IIh4



Isothermals of CO_2

FIGURE III3

neglected in the ideal gas theory. First the entire volume V is not available to any given molecule. There is a volume V_b denied to it due to its own finite size and that of the other molecules. Thus

$$V = V_a + V_b$$

Similarly the pressure is only partly due to the kinetic impacts of the molecules on the walls. It is also partly of static origin due to the attractions of the molecules.

$$P = P_K + P_s$$

The kinetic theory developed in paragraph IIg6 applies between V_a and P_K so that

$$(P - P_s)(V - V_b) \approx nRT$$

Now V_b is proportional to the number of molecules so that

$$V_b \approx nb$$

To obtain a formula for P_s consider the attractions between the molecules in a thin layer near the surface of the gas and those beneath that layer but within range of the Van der Waals forces. These attractions acting on the molecules as they approach the surface will retard them and thus reduce P_K by the amount P_s, which must be negative. Neglecting the dependence of the force on distance, one sees that the number of force vectors acting across the boundary of the surface layer is proportional both to the density of molecules in that layer and to that beneath; that is to the density squared. Hence

$$P_s \approx - a\, n^2/V^2$$

and

$$(P + \frac{n^2a}{V^2})(V - nb) \approx nRT \qquad \text{(IIh5)}$$

This is Van der Waals' equation.

The isothermals of Van der Waals' equation are shown on a P-V plot with logarithmic scales in figure IIh4. At large volumes the isotherms are nearly straight and at 45° in agreement with the ideal gas laws. At small volumes they turn up steeply corresponding to the relative incompressibility of a liquid. All the curves below that marked 27 have a dip in them corresponding to the behaviour of a real gas. 27 corresponds to the characteristic temperature.

At low values of P and V, however, the behavior is singular as a portion of the curve has a positive slope, indicating a negative compressibility. If this part of the curve were realizable the substance would expand when the pressure is increased and contract when it is decreased, an obviously explosive situation. Fortunately it need not be realized, for a given pressure and temperature in this region determine three volumes and the substance may choose any one of the three, or part may be in one state (or phase) and part in another. It is just a question of what combination is most stable, and this will, in fact, never include the unstable phase. It turns out that the condensed phase is more stable at the higher pressures, the expanded phase at the lower pressures, and that they are equally stable at the pressure P_v. The actual isotherm is then the broken curve with a horizontal section at P_v. This is exactly the observed behavior during condensation. P_v is the vapor pressure and the horizontal section represents a combination of liquid and vapor phases. There remains the question of where to draw the horizontal line. It will be shown later that it should be drawn so that the two areas enclosed between it and the horizontal are equal when the P and V scales are linear (Fig IIh5) not logarithmic. Van der Waals' equation is therefore capable of explaining qualitatively (the quantitative checks are not good) the condensation phenomena and the liquid phase as well as the departure of real gases from the ideal laws.

5. The Condensation Curve:

Some isotherms for carbon dioxide are shown in figure IIh6. The line joining the left hand ends of the horizontal portions of the isotherms may be called the boiling curve as it gives the pressure-volume relation of a liquid on the point of boiling. Similarly the right hand curve may be called the condensation curve. The whole curve may be called the saturation curve as the right hand side corresponds to a saturated vapor, the left to a saturated liquid. There is no simple equation for the saturation curve, but if one plots the densities of saturated liquid and vapor against the temperature (figure IIh7) it is found that the diameter of the curve (the average of the two densities) the line obtained is quite accurately straight.

$$1/v_\ell + 1/v_g \approx 2/v_c - C\,(t_c - t) \qquad \text{IIh6}$$

this is called the law of Cailletet and Mathias.

The point where the boiling and condensation curves meet is called the critical point. Peculiar phenomena occur at this point which will not be described here. Suffice it to say that the phenomena are similar for all substances whose critical point has been observed. This unfortunately limits us to liquids whose binding is molecular as the critical point of liquids whose binding is by valence or coulomb forces are above the experimental range. The critical points of some molecular substances are given in table IIh5.

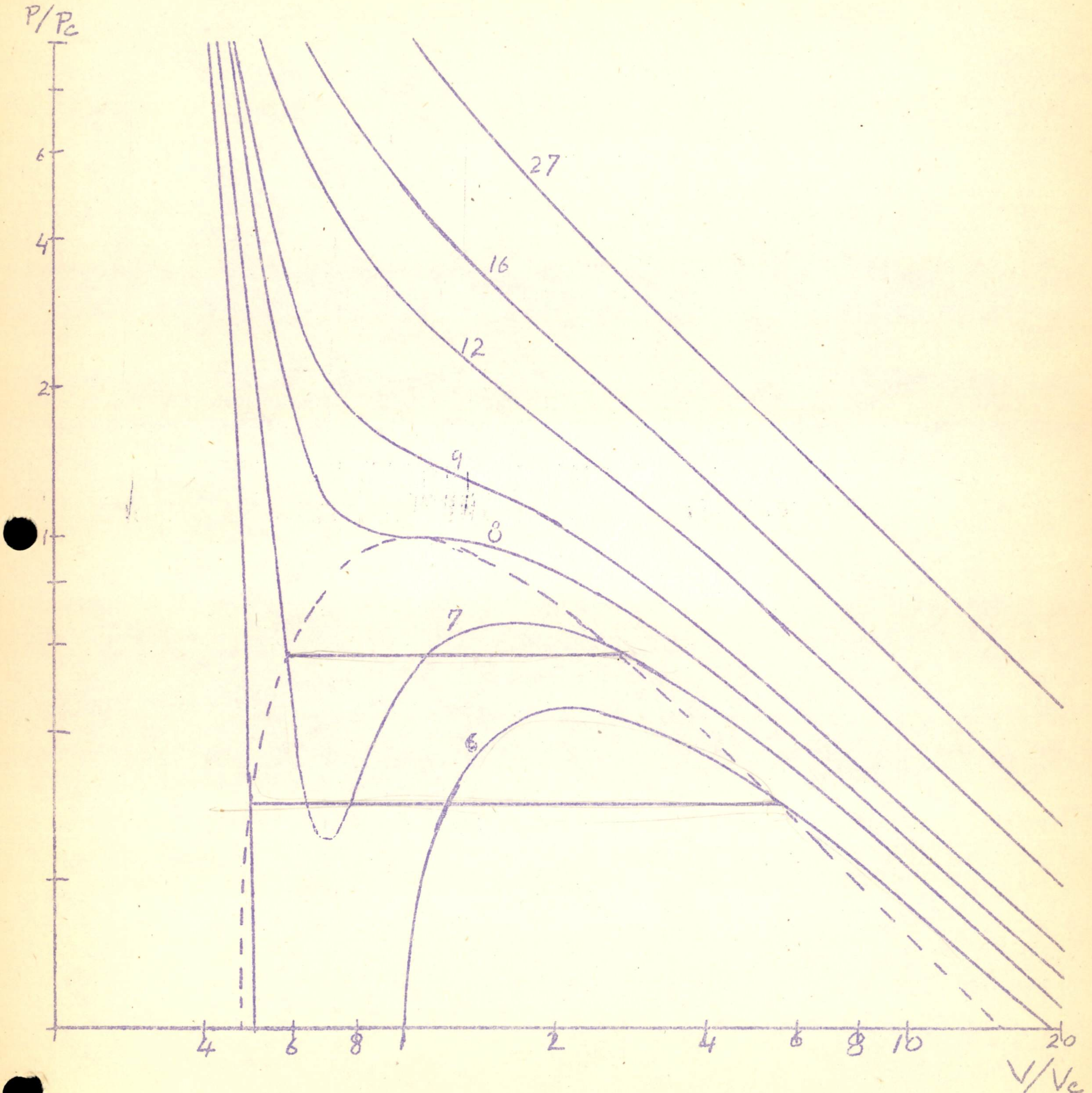
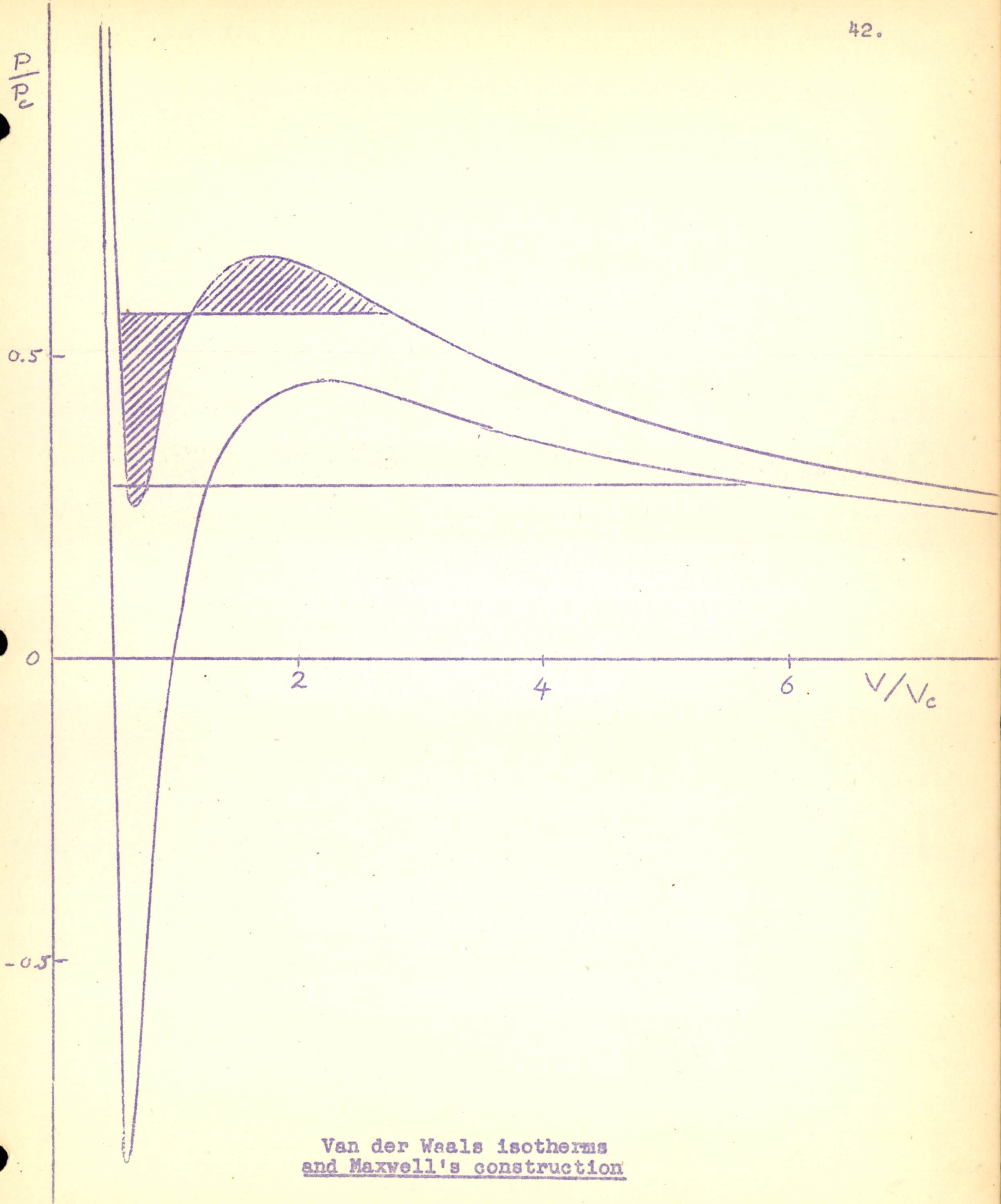


Figure IIh4

Isotherms of Van der Waals' Equation



Van der Waals isotherms
and Maxwell's construction

FIG. IIb5

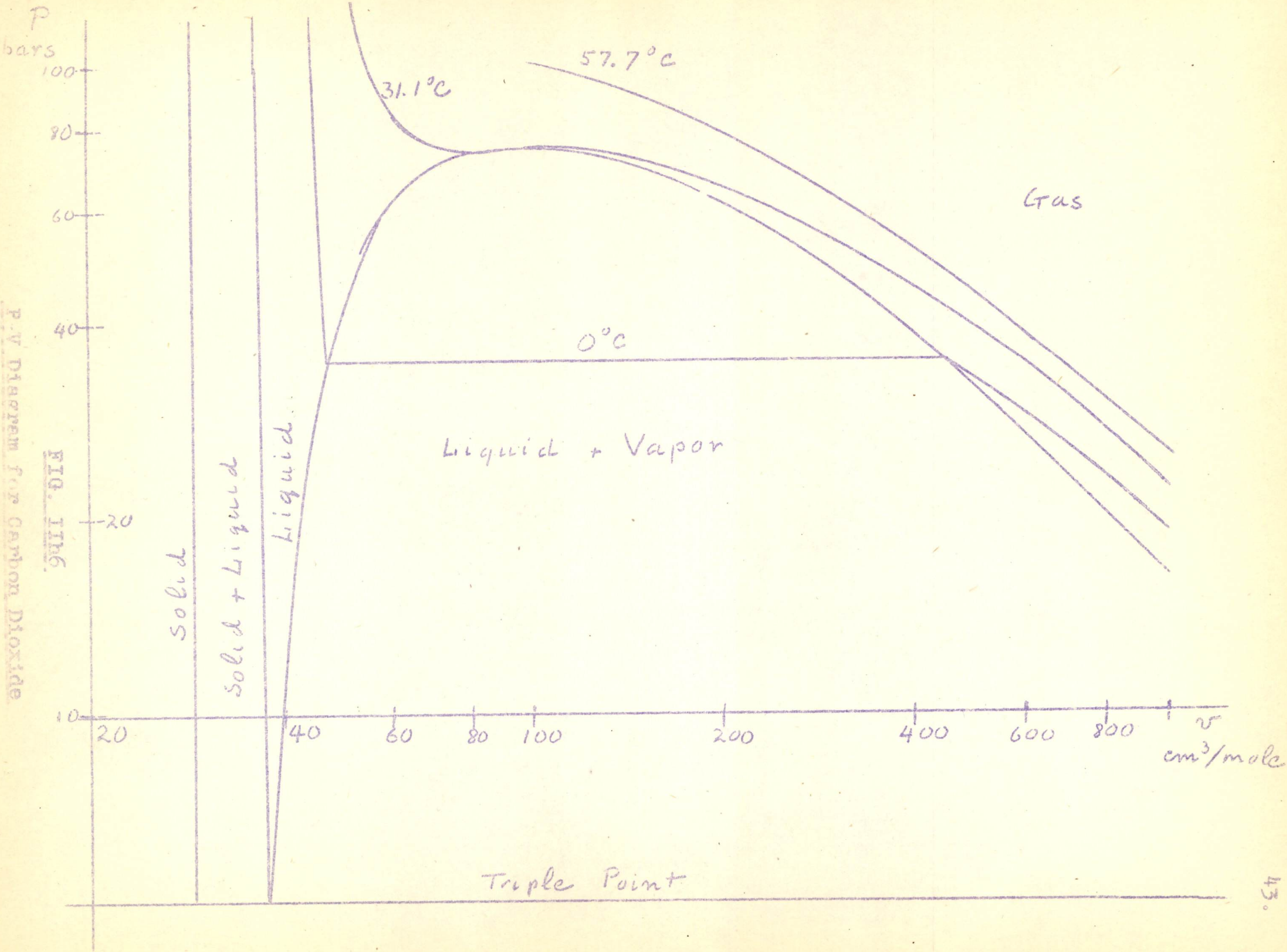


FIG. III6

P-V Diagram for Carbon Dioxide

Not only are the phenomena at the critical point similar, the entire curves which have been given for CO_2 in figures IIh3, 6, and 7 hold with fair accuracy for all gases provided the scales of pressure, temperature, and volume are changed so that the critical point corresponds to the same values. This is called the law of corresponding states.

As an example of the accuracy of this law we have given in Table IIh5 the volume of the liquid far from the critical point and compared it to the critical volume. It is seen that the ratio v_c/v_l is constant within 20 % . To be correct the volumes of the liquids should have been taken at corresponding temperatures, that is at a definite fraction of the critical temperature, and if this were done the constancy would be somewhat better. The accuracy of the law of corresponding states is much better than the accuracy of Van der Waals' equation.

6. The Critical Point:

The transition between the stable isotherms and those with an unstable portion occurs when the point of inflexion is horizontal. This point, which is also the point of highest pressure at which liquid and vapor can be in equilibrium, is called the critical point. The values of P, v, and T at the critical point for a number of gases are given in table IIh5. It is noted that the critical volume is generally close to 3 times the molar volume of the liquid. The theoretical values of these variables for Van der Waals' equation are readily obtained by solving IIh5 for the pressure

$$P \approx \frac{nRT}{V-nb} - \frac{n^2a}{V^2} \qquad \text{IIh7}$$

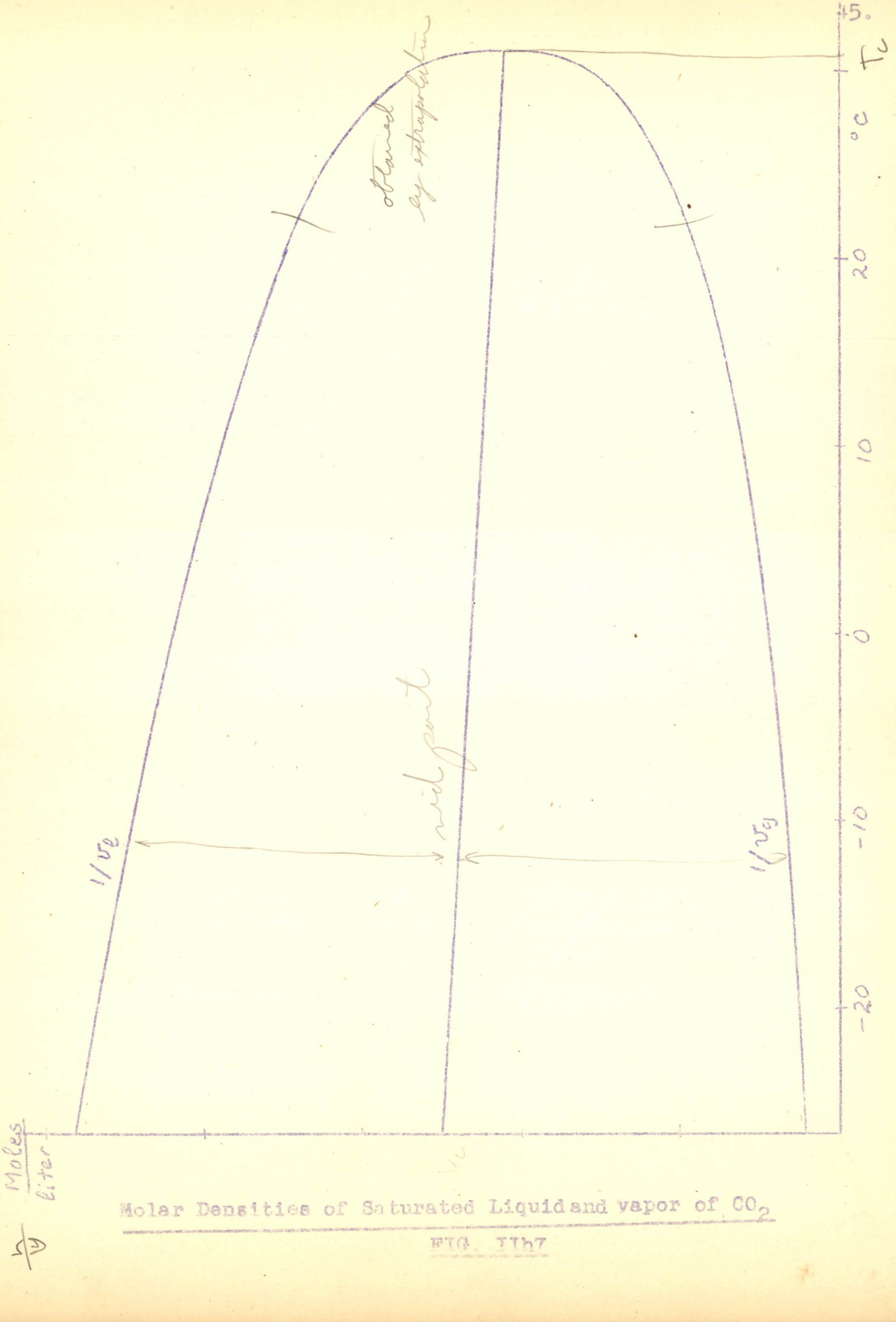
and differentiating twice

$$\left(\frac{\partial P}{\partial V}\right)_T \approx -\frac{nRT}{(V-nb)^2} + \frac{2n^2a}{V^3} \qquad \text{IIh8}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T \approx \frac{2nRT}{(V-nb)^3} - \frac{6n^2a}{V^4} \qquad \text{IIh9}$$

Equating IIh7 and IIh8 to zero, nRT is readily eliminated to give

$$V_c - nb \approx \frac{2}{3} V_c$$



Molar Densities of Saturated Liquid and vapor of CO_2

FIG. IIh7

TABLE IIh5

Gas	v_ℓ $\frac{cm^3}{mole}$	$\frac{v_c}{v_\ell}$	v_c $\frac{cm^3}{mole}$	P_c bars	T_c °K	$\frac{RT_c}{P_c v_c}$	a_c $\frac{\text{liter-Joule}}{mole^2}$	b_c $\frac{cm^3}{mole}$
He	27.2	2.26	61.5	2.29	5.19	3.69	3.4	23.4
H_2	26.4	2.46	65.0	13.0	33.2	3.27	24.8	26.6
Ne	16.7	2.50	41.7	27.2	44.4	3.25	21.2	17.0
H_2O	18.0	2.50	45.0	220.6	647.2	5.81	580.	31.9
NH_3	20.8	3.5	73.0	113.	405.6	4.10	425,	37.3
CH_4	38.6	2.57	99.3	46.3	190.7	3.45	229.	42.9
N_2	34.7	2.60	90.2	33.9	126.0	3.41	137.	38.6
CO	34.5	2.68	92.4	35.4	134.2	3.41	144.	38.3
HCN	38.6	3.5	135.	51.	456.7	5.50	1190.	93.
C_2H_2	42.5	2.66	113.	63.	309	3.60	433.	51.0
NO	23.8	2.42	57.6	66.	179.2	3.92	143.	28.2
O_2	28.	2.66	74.5	50.4	154.4	3.42	138.	31.8
C_2H_4	49.5	2.57	127.5	51.5	282.9	3.58	453.	57.0
A	28.4	2.65	15.3	48.5	151.2	3.44	137	32.4
$HC\ell$	30.5	2.82	86.0	82.6	324.7	3.80	372	40.8
PH_3	45.6	2.48	113.	65.	324.	3.67	460	51.8
CH_3OH	40.5	2.90	117.6	79.7	513	4.54	960	66.6
N_2O	35.9	2.71	97.5	72.6	309.7	4.55	385	44.3
CO_2	37.3	2.54	94.8	73.96	304.3	3.61	366	42.9
O_3	28	3.18	89	68	268.2	3.68	423	41.0
$CH_3C\ell$	54.9	2.78	152.5	66.6	416.3	3.41	759	65.0
CH_4S	55.4	2.69	149	72.2	470.0	3.63	891	67.6
SO_2	43.8	2.83	123.7	78.7	430.4	3.68	686	56.9
$C\ell_2$	41.5	2.98	123.7	77.1	417.2	3.64	668	56.2
Kr	38.9	2.78	108.0	54.8	210.0	2.92	234	39.8
SO_3	41.6	3.05	127	84.6	491.5	3.80	832	60.4
$C\,C\ell_2O$	71	2.68	190	57	455	3.49	1060	83
Xe	43	2.64	113.7	58.9	289.8	3.59	415	51.1
$C\,C\ell_4$	96.3	2.87	276	45.5	556.3	3.68	1910	122
Hg	14.8	2.70	40	3600	1900	1.10	292	5.5
Average		2.74				3.68		

whence

$$\left.\begin{aligned} V_c &\approx 3nb \\ T_c &\approx 8a/27\,Rb \\ P_c &\approx a/27b^2 \end{aligned}\right\} \qquad \text{IIh10}$$

and there is a simple relation between these:

$$\frac{1}{I_c} \approx \frac{nRT_c}{P_c V_c} \approx \frac{8}{3} \qquad \text{IIh11}$$

The value of this ratio is also shown in table IIh5 and it is seen that the actual value is definitely larger than that predicted by Van der Waals. This is evidence of the approximate nature of Van der Waals' equation, but the situation is actually not as bad as these particular numbers would indicate, as the position of the point of inflection on the almost horizontal section of the critical isotherm may be changed a good deal by a very slight alteration of the curve.

Equations IIh9 may be used to compute the Van der Waals constants a, and b, from the critical constants P_c, v_c, T_c. There are too many equations, but we have seen that the first equation is unreliable and we must use the last two

$$\left.\begin{aligned} a_c &\approx \frac{27}{64}\left(\frac{RT_c}{P_c}\right)^2 \\ b_c &\approx \frac{RT_c}{8P_c} \end{aligned}\right\} \qquad \text{IIh12}$$

The subscript c has been used to distinguish the Van der Waals constants determined in this way from those a_o, b_o, determined from low pressure measurements, but fortunately they do not differ very much. Values of these constants are given in table IIh5. The value of b is generally larger than the molar volume of the liquid, probably because the molecules of a liquid are compressed by their mutual attractions. It will be noticed that v_ℓ and b differ most when a is large, and this is true for molecules with large dipole moments. The quantity $RT_c/P_c v_c$ is fairly constant, but not as constant as v_c/v_ℓ.

The fraction of the volume of a gas which is actually occupied by the molecules may be estimated from the values of b. Thus the molecules of a mole of air occupy about 37 cm^3, whereas the gas occupies, under standard conditions, 22400 cm^3, or about 600 times as much space.

On the other hand if we wish to compare linear dimensions we must take the cube root of this figure, or the separation between molecules is about 8.5 times their diameter.

7. Continuity of State:

The P-V diagram contains a region, under the boiling and condensation curve, which represents a combination of liquid and vapor. It is commonly agreed that points to the right of the condensation curve represents gas and points to the left of the boiling curve, but before the solidification line, represent liquid. But what about points above the critical point? There is no boundary here and a substance can be brought continuously from the "gas" to the "liquid" region without change of phase. Where there is no free surface the words "liquid" and "gas" are undefined so it is a question of convenience which one to use, provided one understands that there is no sharp physical distinction. It is convenient to use "gas" where the ideal gas laws are approximated and "liquid" where Hooke's law is more nearly true. A glance at figure IIh4 shows that this is more a question of volume than either pressure or temperature: if the volume is much less than the critical volume the substance is like a liquid, if it is much larger the substance is like a gas.

III THE FIRST LAW

(a) Work

1) Definition

If a substance exerting a pressure P undergoes expansion DV it performs an amount of work

$$\text{đ}W = PdV \qquad \text{(IIIa1)}$$

and if the expansion continues from A to B along the path AB the total amount of work performed is

$$W_{AB} = \fint_A^B PdV = \text{Area under AB (IIIa2)}$$

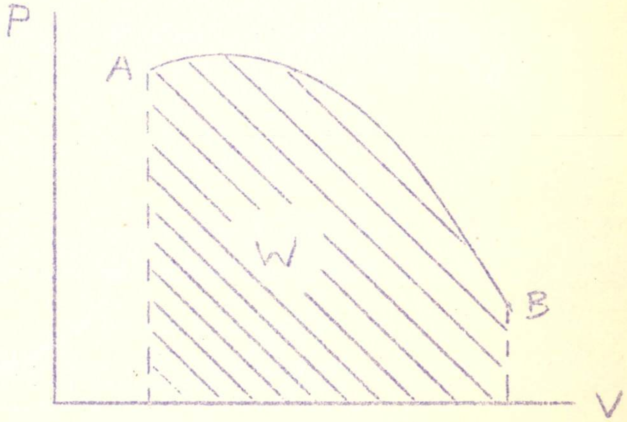


FIG. IIIa1

W obviously depends on the path chosen in going from A to B and this is indicated in equation (IIIa2) by the bar across the integral sign. Therefore W is not a function of the state of the gas and cannot be expressed in terms of V, P and T. It is called a functional. Thus $\text{đ}W$ is not obtained by differentiating a function and this is expressed by saying that it is not an exact differential and is indicated by the bar across the đ. This distinguishes it from exact differentials such as

$$dT = \frac{T}{V}\,dV + \frac{T}{P}\,dP$$

which integrates to

$$T = VP \times \text{const}$$

There are, of course, other forms of work than that defined by (IIIa1), such as electrical work or magnetizing work, but these will not be considered here.

2) Units

The CGS and MKS ~~units of work are the Erg and the Joule~~ respectively. In dealing with gases it is convenient to use the liter-Bar defined by equation (IIIa1) in which V is expressed in liters and P in Bars.

$$\boxed{1 \text{ liter-Bar} = 100 \text{ Joules}} \qquad \text{(IIIa3)}$$

3) Reversible and Irreversible Processes

The work obtained in going from A to B also depends on the speed with which the process is carried out. Imagine that the substance is a gas working against a piston. If the piston is withdrawn rapidly the pressure exerted on the piston may be less than the pressure in the gas. It can even be imagined that the piston is withdrawn faster than the speed of the molecules in the gas, in which case the pressure on the piston is zero and no work is done by the gas. Reciprocally when the piston is pushed in and dV and $\text{đ}W$ are negative the pressure on the piston may be larger than that in the gas. In both cases

$$\text{đ}W \leq PdV \qquad \text{(IIIa4)}$$

where P has any value between its extremes at the piston or far from the piston. It is assumed only that pressure waves have not been set up and the piston is not withdrawn in such a way as to follow a pressure crest. Such an unlikely circumstance will be considered in discussing irreversible processes. In general the difference between PdV and W is internal work which parts of the system do on other parts but which never appears on the outside.

If the process AB is done slowly so that the equality sign holds it may be repeated in exactly the reverse direction BA and the work done <u>on</u> the substance will be equal to that done <u>by</u> bye gas before. The process is then said to be reversible. On the other hand if the inequality holds less work is obtained from and more is done on the gas so that there is a net loss of work and the process is irreversible.

In discussing a process such as the expansion AB we are departing from the agreement to deal only with equilibrium states, for the very fact that the state is changing shows that there is not equilibrium. However if the process is carried out very slowly it can be, at every step, very close to equilibrium (quasi-static). The line AB on the P-V diagram then represents the equilibrium states to which it passes very close. On the other hand a process which is carried out very fast does not go near equilibrium states and cannot be represented on a P-V diagram. We shall generally restrict ourselves to quasi-static, reversible, processes.

4) Cyclic Processes

Particular importance attaches to cyclic processes in which a substance at the end of the process has returned to its initial state A. If performed reversibly the process is represented by a closed figure on a P-V diagram and the area enclosed is the work of the process.

$$W_o \leq \oint PdV \qquad \text{(IIIa5)}$$

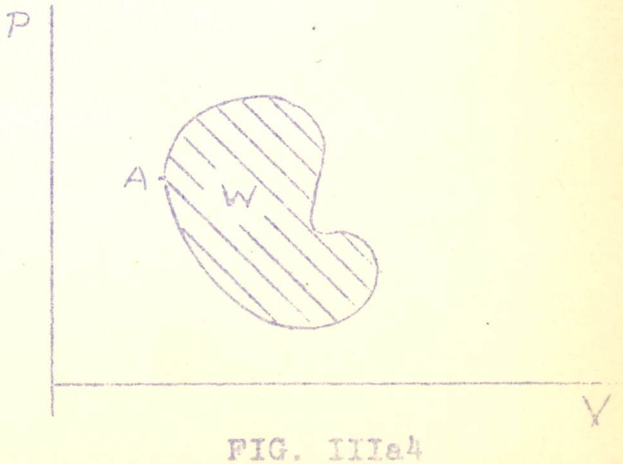


FIG. IIIa4

If the figure is described in the direction of motion of the hands of a clock the work is done by the substance and is considered positive. As the cycle may be repeated as often as we please and each time we obtain the work W there must be some compensation in the form of a quantity Q which has not yet been discussed. However this property of W of increasing indefinitely as one goes around a cycle illustrates a characteristic property of inexact differentials. An exact differential, such as dT, returns to exactly its initial value when a substance returns to its initial state.

(b) Heat

1) Method of Mixtures:

When two masses M_1 and M_2 of the same substance but at different temperatures T_1 and T_2 are placed in contact their temperatures change and eventually reach the same value T_3, which, if T_1 and T_2 do not differ by too much, is given by

$$\frac{T_1 - T_3}{T_3 - T_2} = \frac{M_2}{M_1} \qquad \text{(IIIb1)}$$

If the two substances are different this equation must be extended to read

$$\frac{T_1 - T_3}{T_3 - T_2} = \frac{C_2}{C_1} = \frac{c_2' M_2}{c_1' M_1} \qquad \text{(IIIb2)}$$

The quantities C are called heat capacities and the quantities c are called specific heats. Specific heats depend (a) on the substance used, (b) on the mean pressure and temperature of the experiment, and (c) on the conditions of the experiment such as whether the pressure or the volume is held constant. In order to measure specific heats it remains only to refer them to a standard substance: water, at standard pressure and temperature: one atmosphere and 15° centigrade, under standard conditions: constant pressure, whose specific heat is taken as unity.

2) The Calorie

Equation (IIIb2) as well as many other observed relations, follow from the hypothesis that a quantity Q, of something called heat, flows from the hotter body to the colder one, and that

$$\text{đ}Q = C_x \, dT \qquad \text{(IIIb3)}$$

where

$$C_x = c_x' M = c_x n \qquad \text{(IIIb4)}$$

C_x is the heat capacity, c'_x the heat capacity per mole, c_x the specific heat, and the subscript x is used to denote the parameter which is to be held constant in the process.

The unit of heat, the calorie, is the quantity of heat which will raise one gram of water from 14.5°C to 15.5°C under one atmosphere pressure

Equation IIIb3 is correct as it stands for the process described, but it is possible to raise the temperature of a body in other ways than by conducting heat to it, such as by vigorous stirring of a liquid or rubbing a solid. To include such processes one must write

$$\text{đ}Q \leq C_x\, dT \tag{IIIb5}$$

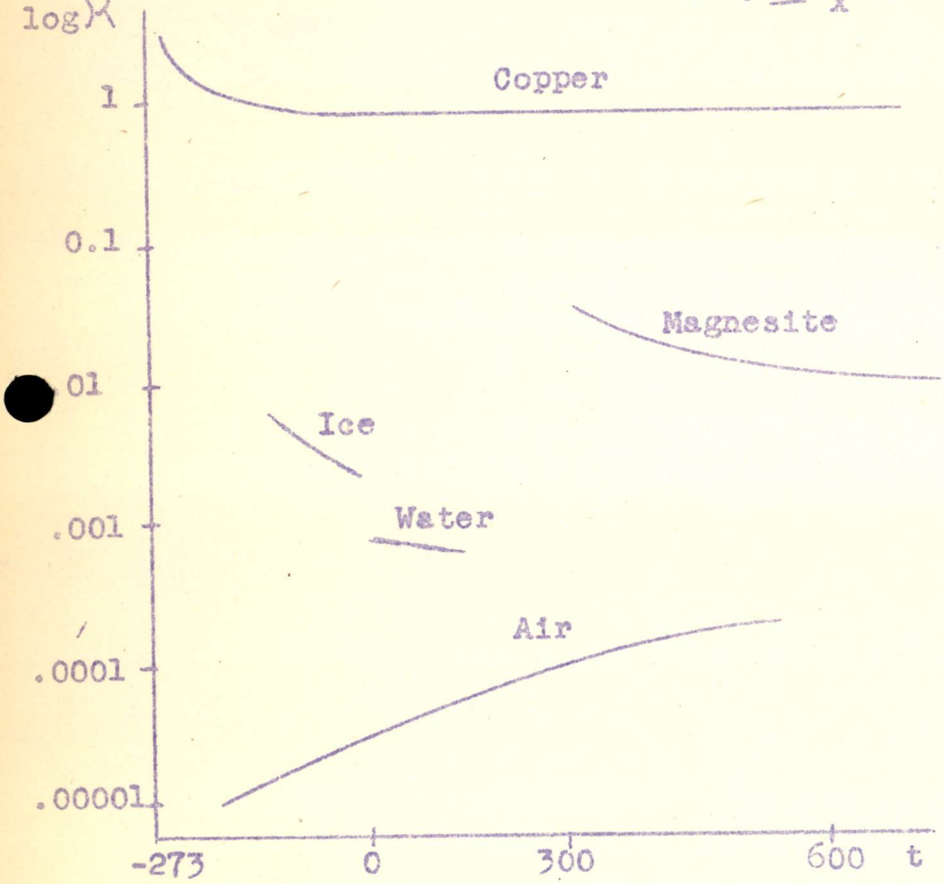


FIG. IIIb3

3) Conduction

The rate of heat flow, $\text{đ}Q/dt$, through a material is found to be proportional to the area A through which it flows and to the temperature gradient $dT/d\ell$

$$\text{đ}Q/dt = -K\, A dT/d\ell \tag{IIIb6}$$

The factor of proportionality K is called the thermal conductivity. Metals have the highest conductivities, that of silver being about 1 cal/sec. cm. °C. Liquids are poorer conductors than solids and gases are poorer yet being about 6×10^{-5} cal/sec. cm. °C. at normal pressure and temperature. There is also a characteristic difference between solids and fluids that in the former the conductivity decreases with the temperature while in the latter it increases. For ideal gases it varies as $T^{3/2}$.

4) Temperature Equation

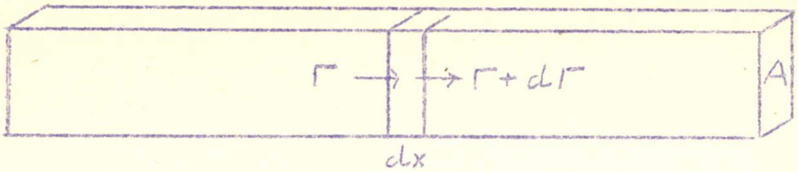


FIG. IIIb4

The equation for the distribution of temperature along a rod of cross-section A can be derived from (IIIb6) and (IIIb3) as follows: The heat flow along the rod is, by (IIIb6),

$$\Gamma = -KA\frac{\partial T}{\partial x} \tag{IIIb7}$$

and therefore the net rate at which heat is flowing into a section dx of the rod is

$$\frac{\partial}{\partial t}(\mathscr{x}Q) = -d\Gamma = KA\,d\,\frac{\partial T}{\partial x}. \tag{IIIb8}$$

The heat capacity of the section of rod is

$$dC_p = c_p'\,dM = \rho\,c_p'\,Adx \tag{IIIb9}$$

where ρ is the density of the rod. Now from (IIIb3)

$$-d\Gamma = dC_p\frac{\partial T}{\partial t} = \rho c_p'\,Adx\,\frac{\partial T}{\partial t} \tag{IIIb10}$$

whence

$$\boxed{\frac{\partial^2 T}{\partial x^2} = \frac{\rho c_p'}{K}\,\frac{\partial T}{\partial t}} \tag{IIIb11}$$

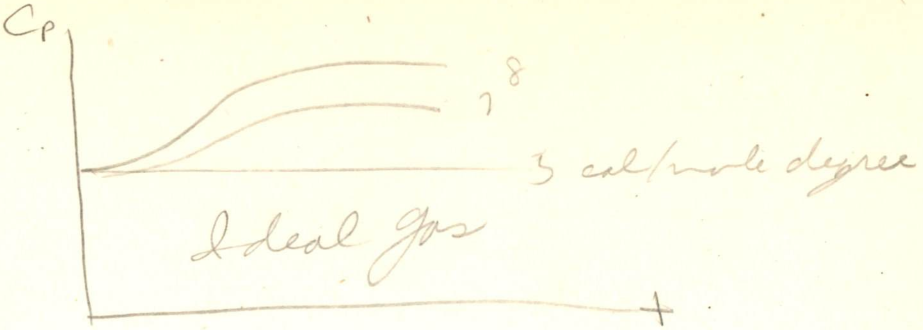
Eq. (IIIb11) connects the distribution of temperature along the rod with its rate of change with time. Note that the first derivative with respect to time enters instead of the second derivative as in the wave equation

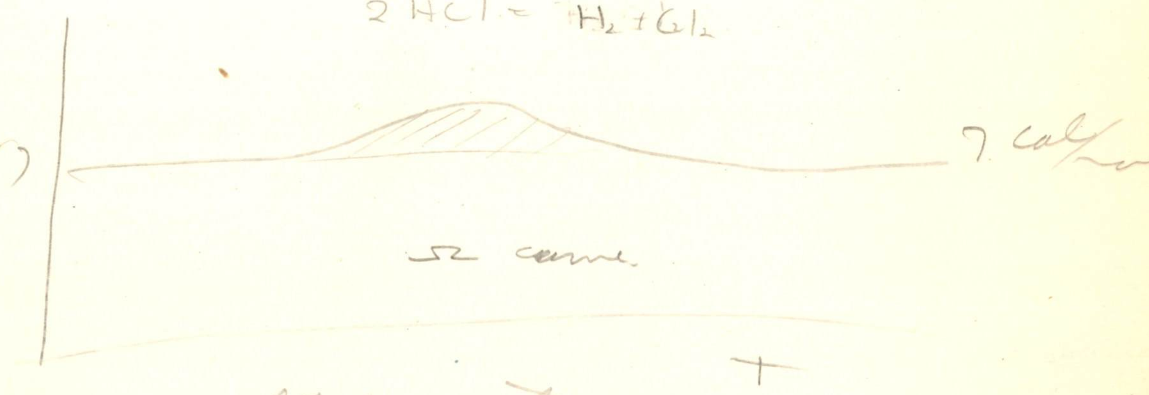
$$\frac{\partial^2 P}{\partial X^2} = -K_s\rho\,\frac{\partial^2 P}{\partial t^2} \tag{IIIb12}$$

The propagation of temperature therefore differs greatly from that of pressure. The solution of (IIIb12) is any wave propagated with a definite velocity

$$\underline{v_p = 1/\sqrt{K\rho}}$$

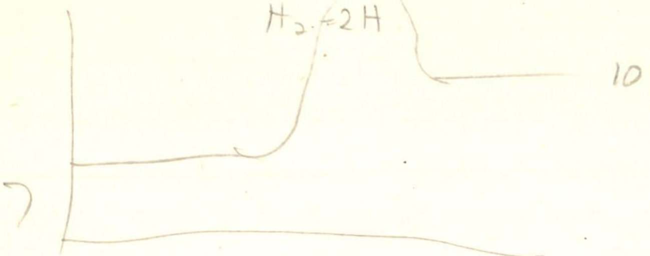
but there is no such definite velocity connected with (IIIb11).

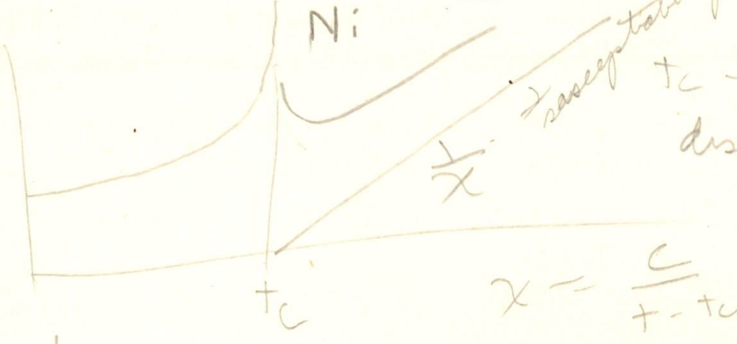




Ω anomaly

Heat cap detects reaction





T_c – where ferro mag. disappears = Curie temp

λ anomaly

$$\chi = \frac{C}{T - T_c}$$

5) Specific Heats

It has been seen that the specific heat (Eq. IIIb3) differs according to the process, and whatever parameter remains constant is indicated by a subscript. We are commonly concerned with c_p and c_v, but one can also consider an isothermal process for which $c_T = \infty$ because $dT = 0$. Similarly a reversible process for which there is no heat transfer is called adiabatic and the corresponding specific heat $c_a = 0$ Each one of these processes defines a direction on the P-V plane and these are indicated on Fig. IIIb5. For directions between the isothermal and adiabatic the specific heat is negative and for all others it is positive.

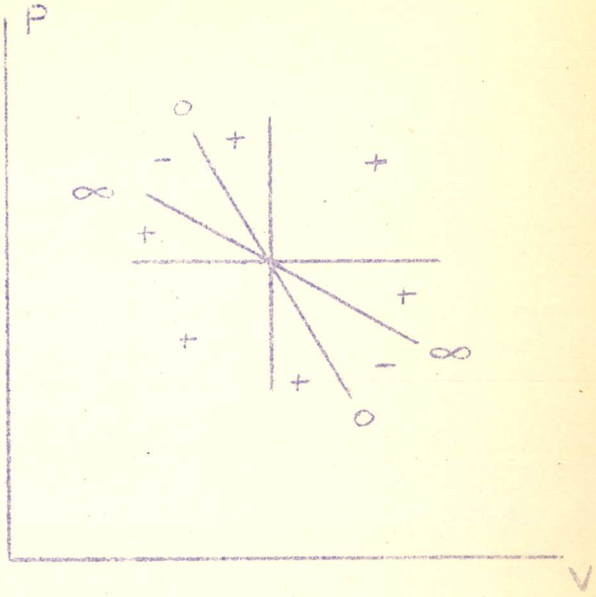


FIG. IIIb5

Experimental values of c_p and c_v for copper are shown in figure IIIb6, and the general shape is typical of all solids. The temperature at which the curves bend over sharply is called the characteristic temperature, and it is found that the specific heat curves of all solids agree fairly well if temperatures are measured in terms of the characteristic temperature and if the specific heats are computed per gram-atom instead of per mole. If there are v atoms in a molecule the number of gram-atoms is

$$n_a = vn \tag{IIIb13}$$

Above the characteristic temperature the specific heat at constant volume for most solids remains near 6 cal/gm atom°C. This is Dulong and Petit's Law. c_p is found to be practically independent of the pressure. Comparing figures (IId) and (IIIb6) it is noticeable that c_p and β vary in much the same way. Indeed there is a result of the theory of the solid state known as Gruneisen's Law which says that

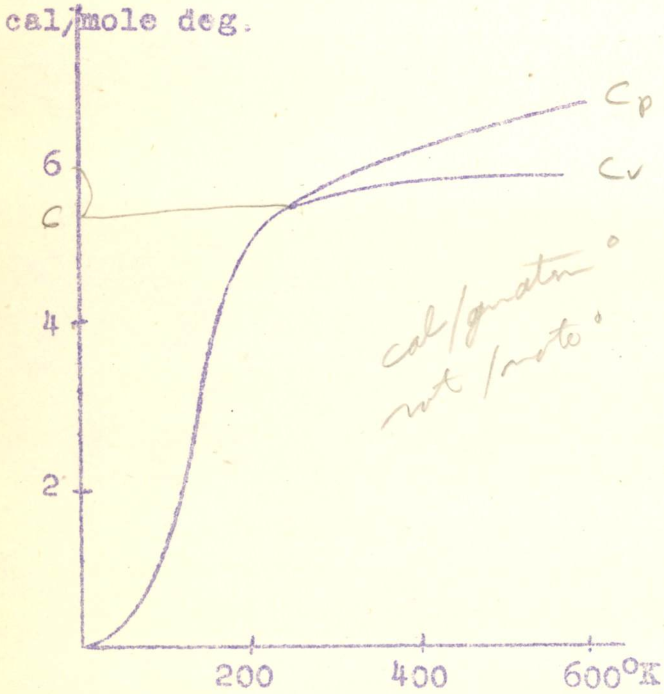
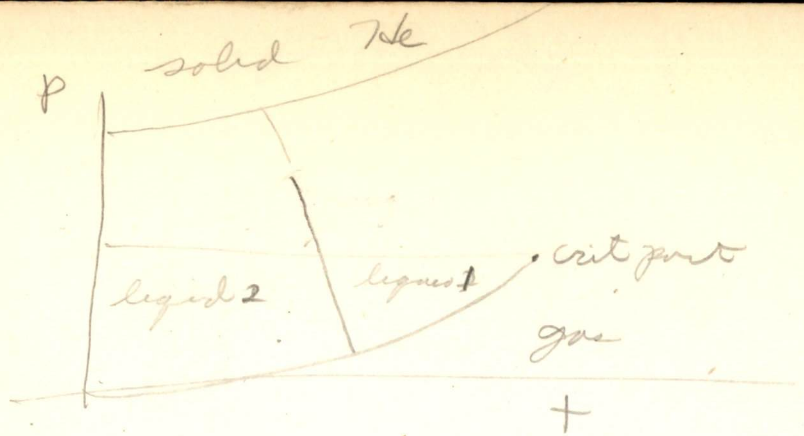
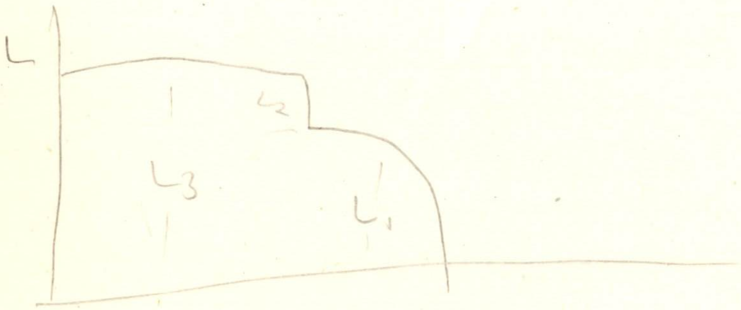


FIG. IIIb6

$$\frac{V\beta^2}{n\kappa c_p^2} \approx A \tag{IIIb14}$$


solid He
P
liquid 2
liquid 1
crit point
gas
T


L
L_2
L_3
L_1

where A is approximately constant. The presence of V and $\varkappa$ in this formula does not alter much the proportionality of c_p and β as V and $\varkappa$ vary little and in the same direction. This formula is useful to obtain values of β at low temperatures from measurements of c_p.

The specific heats of gases have a similar temperature dependince although their characteristic temperatures are much lower and at absolute zero they approach 3 cal/mole degree instead of zero. At normal temperatures c_v has approximately the value 3, 5, or 6 calories per mole degree according to whether the gas is monatomic, diatomic, or polyatomic. The specific heat of a solid is therefore always smaller than that of its vapor at low temperatures and larger than it at high temperatures.

6) Heat and Work

It will presently be shown that heat, like work, is energy in transit. Heat differs from work in that no macroscopic motion is necessarily involved. It is transferred either by conduction through a material or between surfaces in contact or by radiation through free space and in no other way. In the process of convection there are two heat transfers: from the hot body to the fluid and from the fluid to the cold body. In flowing from the hot to the cold body the fluid carries not heat but enthalpy as will be seen.

c. First Law

1) Equivalence of Work and Heat

In a series of classic experiments Rumford (1798), Joule (1840), and others showed that irreversible work and heat were equivalent. In Joule's first experiment paddle wheels wore caused to stir water by falling weights, and the loss of potential energy of the weights compared to the temperature rise in the water. A similar experiment was performed using the I^2R loss of electrical energy in a conductor. In all cases it is found that 4.1858 Joules of irreversible work produce the same effect as the transfer of 1 calorie of heat.

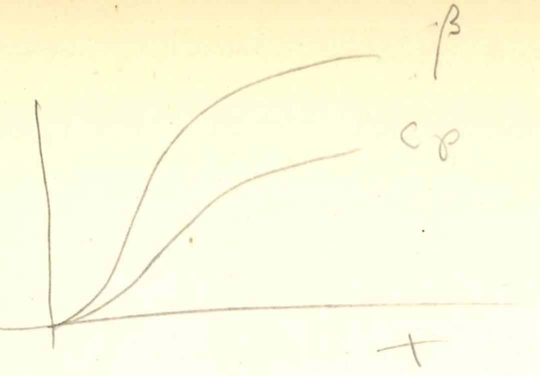
2) Cyclic Process

It is, however, not necessary that the work be performed irreversibly. If a substance is taken around a reversible cycle as shown in Fig. (IIIa4) it has been seen that a quantity of work

$$W = \oint đW$$

appears or disappears in each cycle. Experiment shows that an equivalent amount of heat

$$Q = \oint đQ \qquad \text{(IIIc1)}$$

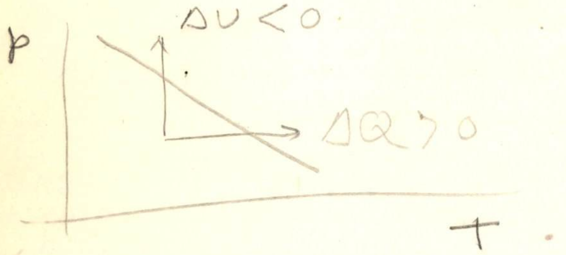


$$\frac{V\beta^3}{n K c_p^2} = A \text{ (a constant)}$$

solids

thermal expansion
Gruneisen Form.

La Chatelier Prin



Equilibrium
Quasistatic
Irreversible process

$W = \int F\,dx = \int P\,dV$ – quasistatic process

$dW = P\,dV$

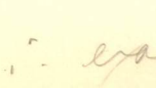
$$\left.\begin{aligned} đW &\leq P\,dV \text{ (when } dV \text{ is +)} \\ đW &\geq P\,dV \text{ (when } dV \text{ is −)} \end{aligned}\right\} \text{for fast expansion}$$

đW is not exact (đW)
because when ∫ around a closed
loop not = to 0.

mechanical – heat

$\Delta T \sim W$ $\quad Q = C\Delta T$

Heat is transferred by
conduction or radiation only



$\frac{W}{\Delta T} = 4.186C$

4.186 Joules/calorie

$\oint (dW - dQ) = 0$ ∴ exact

1st Law

disappears or appears also, so that

$$\oint (\text{đ}Q - \text{đ}W) = 0 \qquad \text{(IIIc2)}$$

This equation cannot, of course, be proved in general, but no contradiction has ever been found provided $\text{đ}W$ includes all known forms of work: mechanical, electrical, magnetic, chemical, etc.

3) Internal Energy

The universal validity of (IIIc2) is the condition that $\text{đ}Q - \text{đ}W$ be an exact differential

$$dU = \text{đ}Q - \text{đ}W \qquad \text{(IIIc3)}$$

The function U is called the Internal Energy, and the existence of this function constitutes the First Law of Thermodynamics.

If we restrict ourselves to volume changes eq. (IIIc3) becomes

$$dU \geq \text{đ}Q - PdV \qquad \text{(IIIc4)}$$

where the inequality sign holds for processes that are mechanically irreversible.

4) Heat Capacities

Equation (IIIc4) can be written

$$\text{đ}Q \leq dU + PdV \qquad \text{(IIIc5)}$$

also

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Hence

$$\text{đ}Q \leq \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV \qquad \text{(IIIc6)}$$

and

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad \text{(IIIc7)}$$

Defining the Enthalpy as

$$H = U + PV \qquad \text{(IIIc8)}$$

$$\text{đ}Q \leq dH - VdP \qquad \text{(IIIc9)}$$

Proceeding as above we find that

$$\text{đ}Q \leq \left(\frac{\partial H}{\partial T}\right)_P dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] dP \qquad \text{(IIIc10)}$$

$$dQ = dU + dw = dU + P\,dv$$

$$dV = \left(\frac{\partial u}{\partial t}\right)_v dt + \left(\frac{\partial u}{\partial v}\right)_t dv$$

$$dQ = \left(\frac{\partial u}{\partial t}\right)_v dt + \left(p + \left(\frac{\partial v}{\partial v}\right)_t\right) dv$$

if v = constant $dv = 0$, $dQ \approx C_v dQ = \left(\frac{\partial v}{\partial t}\right)_v dt$

$$e_v \underset{\overset{\uparrow}{\text{note}}}{=} \left(\frac{\partial v}{\partial t}\right)_v$$

and

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \qquad \text{(IIIc11)}$$

Thus C_V and C_p measure, respectively, the change in internal energy and enthalpy with temperature. U and H are not generally measured experimentally and C_p is much easier to measure than C_V. Therefore the enthalpy H is generally calculated first from measurements of C_p and the energy deduced from (IIIc8). In fact the enthalpy is given directly in the cooling-curve method of measuring specific heats. In this method the substance to be studied is disposed so that it is maintained at a constant pressure P but loses (or gains) heat at a known rate r and which we shall assume to be constant.

$$\text{đ}Q/dt = r \qquad \text{(IIIc12)}$$

This can be done, for example by heating through a resistance wire. The temperature is then plotted against the time and the slope of the curve

$$\frac{dT}{dt} = \frac{r}{C_p} \qquad \text{(IIIc13)}$$

is inversely proportional to the specific heat. However from (IIIc9) it is seen that

$$dH = \text{đ}Q = r\,dt$$

and therefore

$$H = H_o + rt \qquad \text{(IIIc14)}$$

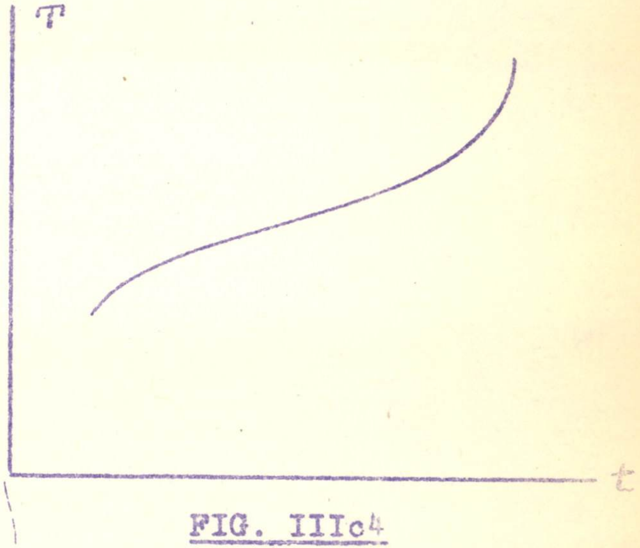


FIG. IIIc4

If we plot rt against the temperature we have immediately a plot of the enthalpy.

One could similarly obtain a plot of the internal energy U if one could perform the experiment at constant volume, but this is generally not possible.

5) **$đQ$-Equations:**

The heat absorbed in any process can be deduced from C_p and C_V as follows:

$$dU = \left(\frac{\partial U}{\partial V}\right)_p dV + \left(\frac{\partial U}{\partial P}\right)_V dP \qquad \text{(IIIc15)}$$

Substituting this in (IIIc5)

$$đQ \leq \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right] dV + \left(\frac{\partial U}{\partial P}\right)_V dP$$

$$đQ \leq \left(\frac{\partial H}{\partial V}\right)_P dV + \left(\frac{\partial U}{\partial P}\right)_V dP$$

$$đQ \leq \left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial V}\right)_p dV + \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V dP$$

$$đQ \leq C_p \left(\frac{\partial T}{\partial V}\right)_p dV + C_V \left(\frac{\partial T}{\partial P}\right)_V dP \qquad \text{(IIIc16)}$$

$$đQ \leq \frac{C_p}{\beta} \frac{dV}{V} + \frac{C_V}{\beta} K \, dP \qquad \text{(IIIc17)}$$

$\frac{1}{V}\frac{dV}{dP} = \frac{C_V}{C_p} K$

$= \frac{1}{K}$

Substituting

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT$$

from [illegible]

and using the cyclic relation we find

$$đQ \leq C_V \, dT + (C_p - C_V) \left(\frac{\partial T}{\partial V}\right)_p dV \qquad \text{(IIIc18)}$$

$= \frac{1}{V\beta}$

and similarly

$$đQ \leq C_p \, dT - (C_p - C_V) \left(\frac{\partial T}{\partial P}\right)_V dP \qquad \text{(IIIc19)}$$

These equations will give the heat absorved by a substance in any reversible process. In particular the second terms of (IIIc18) and (IIIc19) give the "isothermal heat" or heat required by a reversible isothermal process.

6) **Adiabatics**

The equation of an adiabatic curve on a P-V diagram is readily obtained by setting $đQ = 0$ in equation (IIIc17). Using the subscript s to denote an adiabatic process -

$$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_s = \frac{C_V}{C_p}\kappa = \kappa_s$$

Defining adiabatic compressibility by

$$\kappa_s = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_s \qquad \text{(IIIc20)}$$

and also indicating by a subscript the compressibility measured isothermally

$$\boxed{\gamma = \frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_s}} \qquad \text{(IIIc21)}$$

Frequently the two compressibilities can be measured: κ_T by direct measurements of P and V and κ_s from the velocity of sound. C_V is then obtained from the above relation.

The velocity of sound in an ideal gas is given by

$$v_{\text{sound}} = \sqrt{1/\kappa_s\rho} = \sqrt{\gamma/\kappa_T\rho} = \sqrt{\frac{\gamma PV}{M}}$$

where the ideal gas laws have been used to get κ_T. However it has been seen that

$$PV = \frac{1}{3}\,m\,v^2_{\text{molecules}}$$

hence

$$\frac{v_{\text{sound}}}{v_{\text{molecules}}} = \sqrt{\frac{\gamma}{3}}$$

Thus sound, in an ideal gas, travels almost as fast as the molecules.

7) Energy Equation

also cal from pg 32 & pg 36

Combining (IIIc18) with (IIIc4) we have

$$dU = \overset{\text{energy to speed up mole.}}{C_V dT} + \overset{\text{energy to pull apart}}{\left[(C_p - C_V)\left(\frac{\partial T}{\partial V}\right)_P - P\right]} dV \qquad \text{(IIIc22)}$$

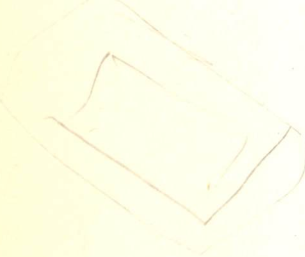
If C_V, C_p, and the equation of state are known this relation can be used to compute the internal energy U. Note that the inequality has not been kept in this equation because it is impossible to tell which way it would go. Equation (IIIc22) applies only to a reversible process, that is to equilibrium states. This is a common restriction for thermodynamic equations and prevails whenever the inequality sign is not specifically indicated.

$$du = C_V(T_2 - t_1)$$

Cp = 5 — 3 degrees of
rotn
2 degrees of rotation

Cv = 5 + R = 7

= 8 for polyatomic
(3 degrees of rotation)



7-10 – Humint
10-12 Ec 11
12-1 – Ec lu
1-2 Ec 11
2-3 Go 1

Combining similarly equations (IIIc19) and (IIIc9) we have for the enthalpy

$$dH = C_p\, dT + \left[V - (C_p - C_V)\left(\frac{\partial T}{\partial p}\right)_V\right] dP \qquad \text{(IIIc23)}$$

8) Free Expansion

There are two simple though irreversible expansions of a gas which will illustrate the use of thermodynamic relations in irreversible processes. The first is free expansion.

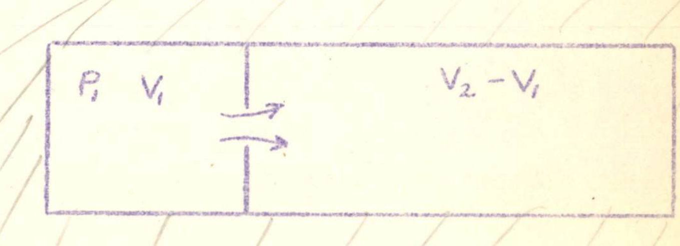


FIG. IIIc6

Imagine a vessel of volume V_2 with a portion of it V_1 separated by a partition. Let V_1 contain a gas at pressure P_1, and the remainder be evacuated. Then imagine the partition to be punctured or otherwise removed. The gas will then expand irreversibly occupying the entire volume V_2. However pressure and temperature will not be constant, or even measurable, during the process. No external work has been done, so $đW = 0$, and if the vessel is insulated $đQ = 0$. Hence from (IIIc3) $dU = 0$ and the process proceeds at constant energy.

Consider now a reversible process at constant energy. Using the cyclic relation we obtain

$$\mu = \left(\frac{\partial T}{\partial V}\right)_U = -\frac{(\partial U/\partial V)_T}{(\partial U/\partial T)_V} = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T \qquad \text{(IIIc24)}$$

This quantity is called the Joule coefficient. Integrating

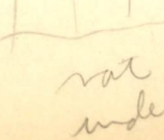
$$T_2 - T_1 = \int_{V_1}^{V_2} \mu dV \qquad \text{(IIIc25)}$$

The end states of the free expansion being equilibrium states the temperature difference computed in this way for a reversible process will be the same as for the irreversible one.

Actually equations (IIIc24) and (IIIc25) are used in the reverse way, measurements of the temperature change $T_2 - T_1$ giving a sensitive way of obtaining the change of internal energy with volume at constant temperature.

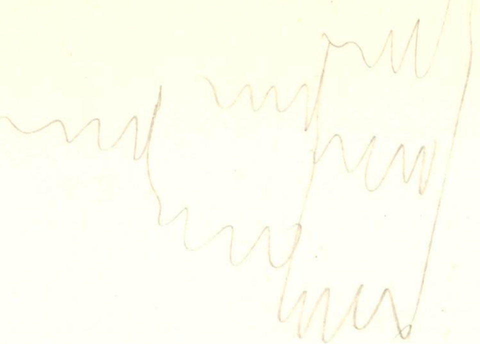
In terms of this coefficient one can write the energy equation

cannot be represented on a pv diagram



$$dU = C_V (dT - \mu dV) \qquad \text{(IIIc26)}$$

not = to area under curve } irreversible



9) Throttling Process

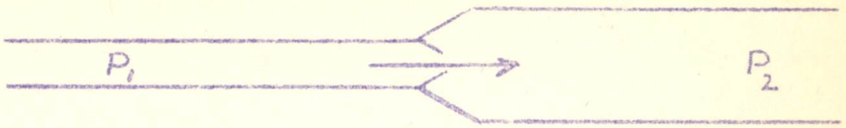


FIG. IIIc7

The second simple irreversible process is that in which a gas flowing through a pipe at pressure P_1 expands through a nozzle into a second pipe at pressure P_2. This differs from a free expansion because as n moles go through the nozzle an amount of work $P_1 V_1$ is done on it by the gas behind it and in turn it does $P_2 V_2$ on the gas ahead. Then the net work is $W = P_2V_2 - P_1V_1$ and if there are no heat losses to the pipe $Q = 0$. Then

$$U_2 - U_1 = Q - W = P_1 V_1 - P_2 V_2$$

$$H_2 = U_2 + P_2 V_2 = U_1 + P_1 V_1 = H_1 \qquad \text{(IIIc27)}$$

The enthalpy before and after passing through the nozzle is therefore the same. It would be incorrect, however, to say that the enthalpy is constant as the pressure is not well defined at the nozzle. However the temperature change may be calculated by considering a reversible process having the same end points. Using the cyclic relation we find for the Joule-Kelvin coefficient

$$\mu' = \left(\frac{\partial T}{\partial p}\right)_H = -\frac{(\partial H/\partial p)_T}{(\partial H/\partial T)_p} = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T$$

$$dH = C_p(dT - \mu' \, dP) \qquad \text{(IIIc28)}$$

It turns out that when the temperature is less than about 5 times the critical temperature this coefficient is positive (cooling on expansion) and may be quite large. The Linde process for liquefying gases is based entirely on this principle.

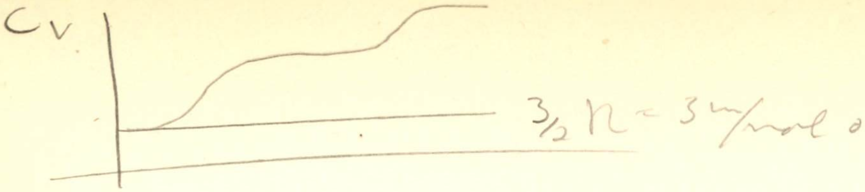
10) Reversible Flow

For stream-line, insulated, flow

$$\left.\begin{aligned} dU &= -PdV \\ dH &= dU + PdV + VdP = VdP \end{aligned}\right\} \qquad \text{(IIIc29)}$$

Now from the force equation $\frac{F}{A} = \left(\frac{\partial p}{\partial x}\right) dx$

$$\frac{F}{A} \qquad \frac{dP}{dx} = -\rho\frac{d^2x}{dt^2} = -\rho v \frac{dv}{dx}$$



$U_{k\text{-}t.rnv} = \left(\frac{3}{2} - \frac{2}{2} - 1\right) nRT$

whence

$$dP = -\frac{1}{2}\rho\, dv^2$$

so that

$$dH = -\frac{1}{2} M\, dv^2$$

and

$$H/M + \frac{1}{2} v^2 = \text{const} \qquad \text{(IIIc30)}$$

This is the extension of Bernoulli's equation to the flow of a compressible gas.

d. Applications

1) Kinetic Picture

From the simple Kinetic picture of an ideal gas given earlier it was shown that

$$VP = \frac{1}{3} Nmv^2 \qquad \text{(IIId1)}$$

It follows that the Kinetic energy of translation of the particles is

$$U_{KT} = \frac{1}{2} Nmv^2 = \frac{3}{2} VP = \frac{3}{2} nRT \qquad \text{(IIId2)}$$

If this were the only internal energy it would fillow that

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}\ nR \qquad \text{(IIId3)}$$

$$c'_V = \frac{3}{2} R = 2.98 \text{ cal/mole deg.}$$

and this is very nearly correct for monatomic gases. To explain the additional heat capacity of diatomic and polyatomic gases it is assumed that the molecules have rotational Kinetic energy as well and that

$$U_{KR} = \frac{v}{2} nRT \qquad c'_v = \frac{3 + v}{2} R \qquad \text{(IIId4)}$$

where $v = 0$, 2 or 3 according to whether the molecules are monatomic, diatomic, or polyatomic. This, however, is not an exact relation as can be seen from the decrease of specific heats at low temperatures.

2) Ideal Gas

Experimentally it is not found that the specific heats become constant in the limit $n/V \to 0$ but it is found that the Joule coefficient vanishes in this limit. Therefore for an ideal gas

From (IIIc24) $$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

From (IIIc26) $$dU = C_V\ dT \tag{IIId5}$$

Applying the condition for an exact differential to this equation it is seen that

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial C_V}{\partial p}\right)_T = 0 \tag{IIId6}$$

so that C_V can be a function of T only. Integrating (IIId5)

$$U = U_o + \int_o^T C_V\ dT$$

From (IIIc5) $$\text{đ}Q \leqq C_V\ dT + PdV$$

Whence

$$C_p = C_V + P\left(\frac{\partial V}{\partial T}\right)_p = C_V + mR \tag{III7}$$

and $$dH = C_p\ dT$$

The difference in the heat capacities comes, in an ideal gas, entirely from the term PdV which represents the external work done when the gas is heated at constant pressure. It also gives the heat necessary to expand a gas isothermally.

From (IIIc16) $$\text{đ}Q \leqq T\ (C_p\ dV/V + C_V\ d\ P/P)$$

so that along an adiabatic

$$\gamma\ dV/V + dP/P = 0$$

or

$$PV^{\gamma} = \text{const.} \tag{IIId8}$$

3) Latent Heat

In the parts of a P-V diagram where two phases are in equilibrium the isobars are also isotherms and

$$C_p = C_T = \infty \tag{IIId9}$$

It is therefore impractical to use the $\text{đ}Q$-equations. However equation (IIIc9) applied to an isotherm in these regions gives

$$\text{đ}Q \leqq dH \tag{IIId10}$$

The latent heat L is defined as the amount of heat absorbed in passing completely and reversibly at constant temperature and pressure, from one state to another. Integrating (IIId10)

$$L_{12} = H_2 - H_1 \qquad \text{(IIId11)}$$

where the subscripts 1 and 2 may stand for solid and vapor, solid and liquid, or liquid and vapor. From this simple relation it is seen that at the triple point

$$L_{\text{sublimation}} = L_{\text{melting}} + L_{\text{boiling}} \qquad \text{(IIId12)}$$

and at the critical point

$$L_{\text{critical}} = 0$$

In general the latent heat varies with the temperature as shown in Fig. IIId

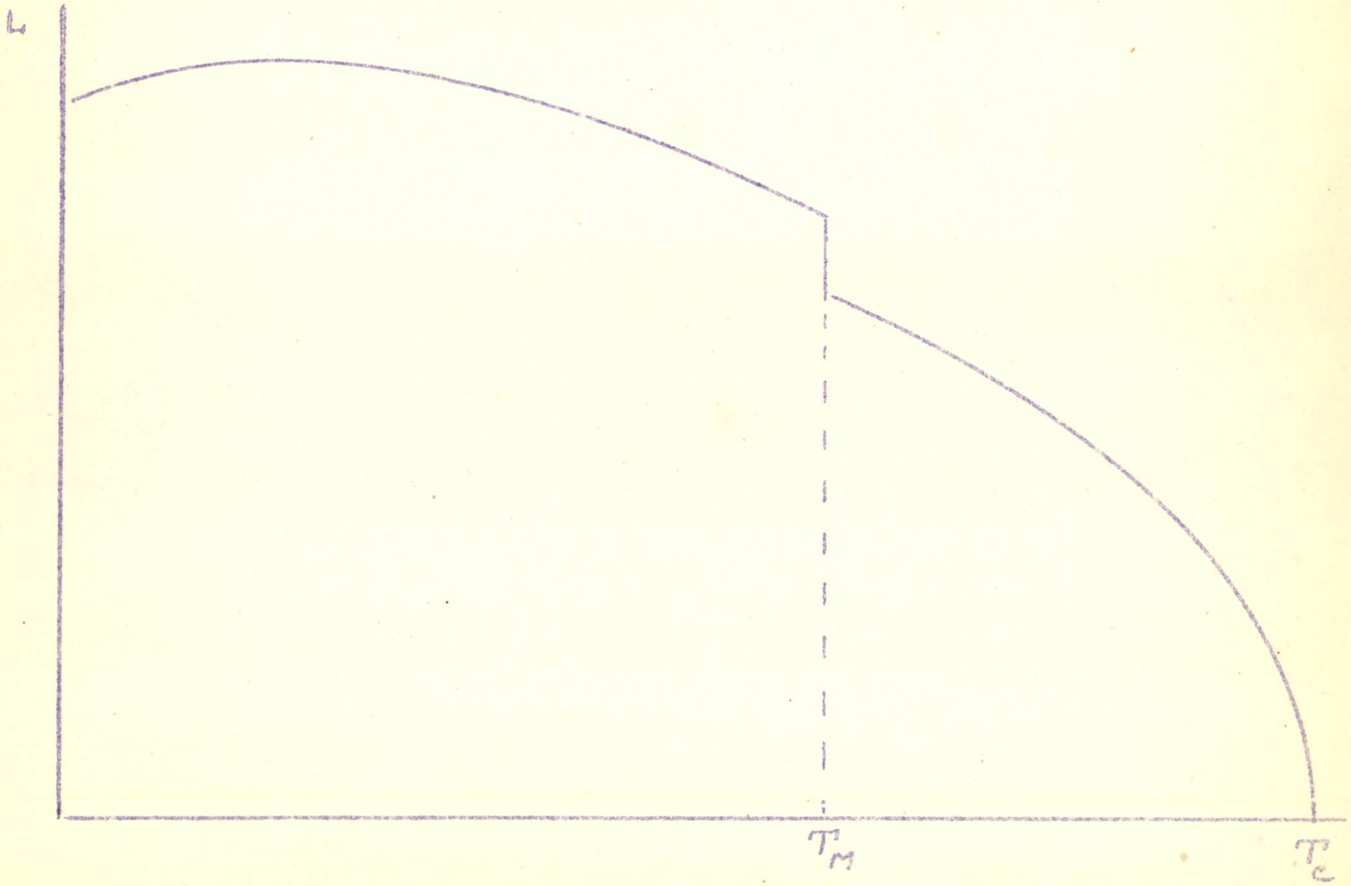


FIG. IIId

From the definition of the enthalpy

$$L_{12} = U_2 - U_1 + P\,(V_2 - V_1) \qquad \text{(IIId13)}$$

The latent heat may therefore be considered as the sum of two parts: an "internal" part which goes into changing the internal energy of the substance and an "external" part which goes into work against the external pressure. This latter part is quite small unless the second phase is vapor.

As an example of the orders of magnitude encountered we may take water at one atmosphere pressure. Then

At $0^\circ C$	$L_{melting} = 80$ cal/mole
from $0^\circ C$ to $100^\circ C$	$\Delta H = 100$ cal/mole
at $100^\circ C$	$L_{boiling} = 539$ cal/mole

of which 40 cal/mole go into external work.

The latent heat of boiling divided by the temperature is found to be remarkably constant for all substances provided the pressure is such that the molar volume of the vapor is about the same. Choosing arbitrarily 197 liters per mole one finds that L/nRT is remarkably close to 13.5 Water and other liquids with molecules having a high dipole moment lead to higher values. This is the Trouton-Hildebrand law.

Differentials

inexact – $\left\{ \begin{array}{l} dW \le PdV \\ dQ \end{array} \right.$

exact $\left\{ \begin{array}{l} dP \\ dT \\ dU = dQ - dW \\ dV \ge dW/P \end{array} \right.$

– nentans. 3rd law

– 0th law

– 2 inexact = 1 exact = 1st law

– 1 " " = due to integrating factor.

$\frac{1}{P} = \int$ factor

ideal gas

$$\frac{dQ}{T} = \frac{C_v dT + PdV}{T} = \frac{C_v}{T} dT + nR\frac{dV}{V} = dS \text{ entropy}$$

$$S = \int^T \frac{C_v}{T} dT + nR \ln V + S_0$$

$$\ln(PV) = \ln(nRT)$$

$$\frac{dP}{P} + \frac{dV}{V} = \frac{dT}{T}$$

$$\frac{dQ}{T} = \frac{C_v + nR}{T} dT - nR\frac{dP}{P}$$

$$S = \int^T \frac{C_p}{T} dT - nR \ln P + S_0$$

2nd law = $\frac{1}{T}$ is $\int$ factor for all substances

$dU = TdS - PdV$
$H = U + PV$
$\therefore dH = TdS + VdP$

– quasi equilibrium states

$\oint dU = 0 \therefore \oint \frac{dQ}{dT} \le \oint dS \; 0$ – if irreversible
" not "

IV THE SECOND LAW

(a) Entropy

1) Ideal Gas

It is readily seen that the difference $\text{đ}Q - \text{đ}W$ is not the only exact differential that can be formed out of the inexact ones $\text{đ}Q$ and $\text{đ}W$. For instance

$$\text{đ}W/p = dV \qquad \text{(IVa1)}$$

is exact if we consider only reversible processes. In the case of an ideal gas it is easy to see that

$$\frac{\text{đ}Q}{T} = \frac{C_v dT + PdV}{T} = dS \qquad \text{(IVa2)}$$

is also exact with the same limitation and thus defines the function S, which is called the entropy, to within an additive constant, by simple integration. Indeed as $P = nRT/V$ and C_v is a function of T only

$$S = \int^T \frac{C_v}{T}\, dT + nR\, \ell n\, V + S_o \qquad \text{(IVa3)}$$

$$= \int^T \frac{C_p}{T}\, dT - nR\, \ell n\, P + S_o' \qquad \text{(IVa4)}$$

$$= \ell n (V^{C_p} P^{C_v}) + S_o'' \qquad \text{(IVa5)}$$

These three forms for the entropy follow from integrating the three $\text{đ}Q$-equations (IIIc18, 19, and 17) of the last section. To derive the third form (IVa5) it has been assumed that C_v and C_p are constant and therefore this expression is not as general as the other two, but it does bring out clearly the equation of an adiabatic: PV^γ = constant, when the entropy is constant. The three constants S_o, S_o', and S_o'' are in general different and depend on the lower limit of the integral. Without further assumptions it is impossible to determine these constants although their differences are readily found.

Equations (IVa1) and (IVa2) may be introduced into the energy equation (IIIc3) to give

$$dU = TdS - PdV \qquad \text{(IVa6)}$$

This equation is not quite as general as (IIIc3) as it can only be used when P and T are well defined, that is for quasi-equilibrium states. Similarly one has

$$dH = TdS + VdP \qquad \text{(IVa7)}$$

Equations (1) and (2) can be generalized to apply to irreversible processes by introducing inequalities:

$$\text{đ}W \leq PdV \qquad \text{(IVa8)}$$

$$\text{đ}Q \leq TdS \qquad \text{(IVa9)}$$

We have seen that the first of these inequalities is due to pressure gradients in the system so that work is done internally and does not all appear as external work. Similarly the second inequality, called the Clausius inequality, is due to internal thermal gradients so that heat flows internally. In an irreversible process having the same end states as a reversible one, the work done by a gas is less and the heat absorbed by it is less, but the difference must be the same as the internal energy change is the same whether (IVa6) or (IIIc3) is used.

Equations (IVa8) and (IVa9) show the analogy between entropy and volume. Entropy is extensive like volume and it also generally increases with temperature and decreases with pressure. It differs from volume in that it is not directly measurable, and in this it is similar to energy. Like energy it contains an additive constant. Unlike energy it is conserved only in reversible processes:

$$\oint (\text{đ}Q - \text{đ}W) = \oint dU = 0 \qquad \text{(IVa10)}$$

but

$$\oint \text{đ}Q/T \leq \oint dS = 0 \qquad \text{(IVa11)}$$

2) Second Law

Equation (IVa2) is really not surprising as it is shown in mathematics that it is always possible to find an integrating factor (in this case 1/T) which, when multiplied into an inexact differential such as $\text{đ}Q$ will produce an exact differential such as dS. A similar equation must therefore hold not only for an ideal gas but for all substances. However it turns out that the integrating factor is the same, 1/T, for all substances. This fact together with the statement that negative temperatures do not exist constitute the Second Law of Thermodynamics. This means that the equations (IVa6, 7, 8, 9, 10, and 11) are perfectly general and apply to any system. The proof of this is not direct but rests in the verification of conclusions from these equations and will be discussed later.

3) T-S Diagrams

From analogy it is clear that plots of temperature against entropy will have many properties equally useful to those of P-V diagrams. Thus from equation (IVa9) it is seen that the heat absorbed in a reversible process AB is given by the area under the curve AB. An irreversible process cannot be represented by a curve as the temperature is then not dffined. Also from (IIIb5) and (IIIb4) we have for the heat capacity

$$\left(\frac{\text{đ}Q}{dT}\right)_x \leq C_x = T\left(\frac{\partial S}{\partial T}\right)_x \qquad \text{(IVa12)}$$

T/C_x is therefore the slope of the curve of constant x on a T-S diagram, just as $-1/V\chi_x$ is the slope of the curve of constant x on a P-V diagram.

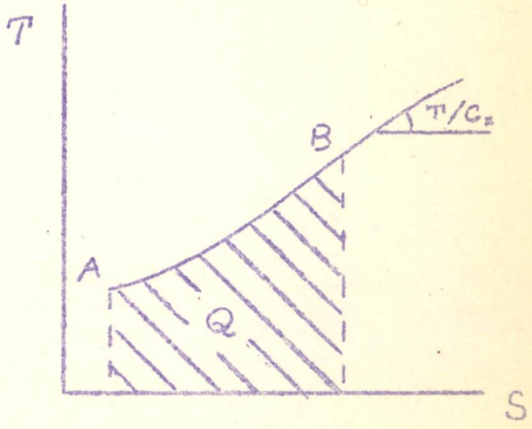


FIG IVa1

Adiabatic and isothermal processes are, of course, represented by vertical and horizontal lines. If infinitesimal processes of constant T, P, V, and S are shown on a P-V and a T-S diagram it is seen that these diagrams are obtained, one from the other, by a shear

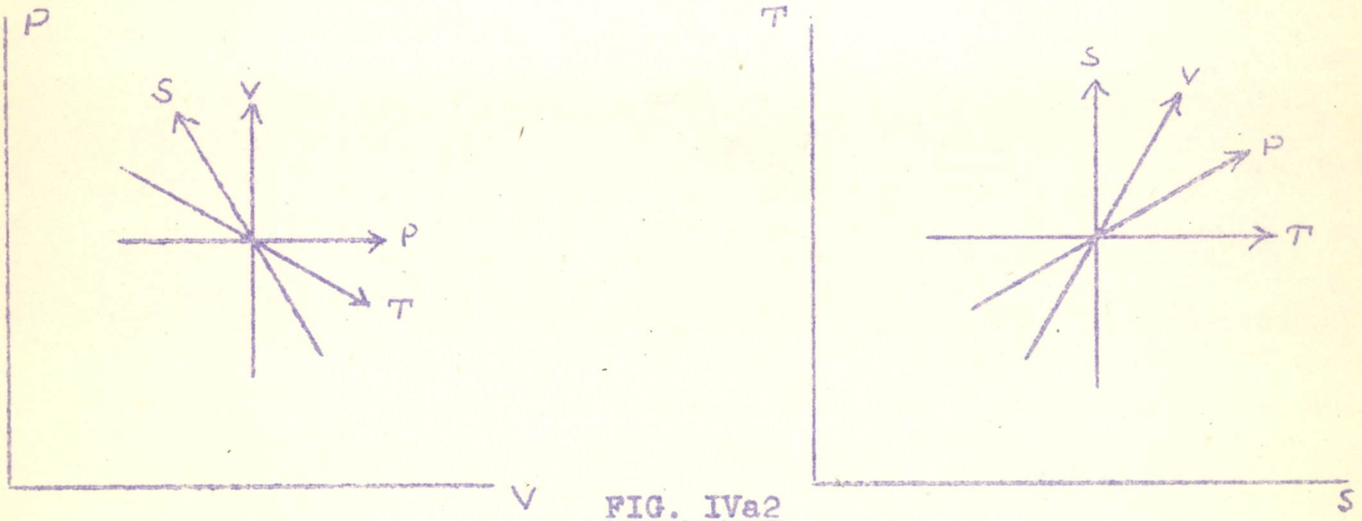


FIG. IVa2

deformation such as to bring the isothermals and adiabatics at right angles in the latter. The topology of a T-S diagram is therefore similar to that of a P-V diagram and the various equilibrium regions between solid and liquid, liquid and vapor, & vapor and solid look much alike. The area under a melting or vaporization isotherm is the latent heat of the process.

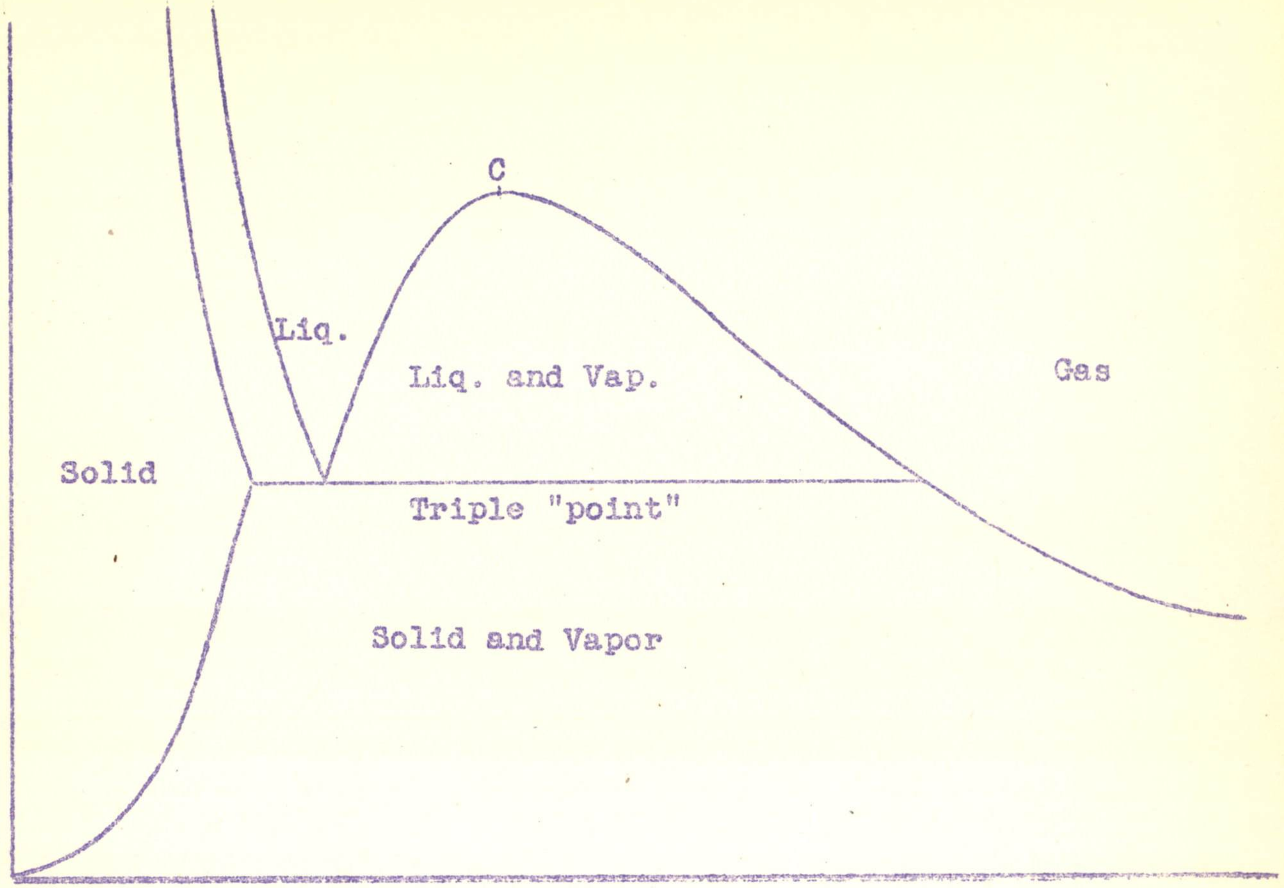


FIG. IVa3

4) The Gibbs Surface

As has been seen with the P-V-T surface, two dimensional diagrams are best considered as projections of an equilibrium surface in a three-dimensional space. Considerable advantage comes of plotting three extensive quantities instead of mixing intensive and extensive ones as is done in the P-V-T surface, and we now have defined three such quantities in the energy U, entropy S, and volume V. Willard Gibbs first proposed using these coordinates and the surface so plotted is named after him. Equation (IVa6) shows that temperature and the negative of pressure are the slopes of a tangent plane to this surface.

Consider the point U_1, V_1, S_1. The equation of the tangent plane is

$$U - U_1 = T_1 (S - S_1) - P_1 (V - V_1)$$

or

$$U - T_1 S - P_1 V = U_1 - T_1 S_1 - P_1 V_1 = G_1 \qquad \text{(IVa13)}$$

G_1 is a constant in this equation and gives the intercept of the tangent plane with the energy axis. Considered as a function of the point of tangency it is called the Gibbs function.

The second derivatives of this surface also have simple meanings:-

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} \qquad \text{(IVa14)}$$

$$\left(\frac{\partial^2 U}{dV^2}\right)_S = \left(\frac{\partial P}{\partial V}\right)_S = \frac{1}{V\kappa_S} \qquad \text{(IVa15)}$$

$$\frac{\partial^2 U}{\partial S \partial V} = \left(\frac{\partial T}{\partial V}\right)_S = \frac{1}{V\beta_S} \qquad \text{(IVa16)}$$

where β_S is a negative quantity which may be called the adiabatic coefficient of volume expansion.

But the particular advantage of these coordinates is the ability to represent non-equilibrium states. If we plot the specific energy u, entropy s, and volume v, per mole or per gram, then the parts of a homogeneous system are represented by the same point as the whole system. The parts of a non-homogeneous system are represented by different points whose center of gravity represents the whole system.

Suppose for instance that n_1 moles of a substance at temperature T_1 are considered together with n_2 moles of the same substance at the temperature T_2. The specific energies are:

$$u_1 = U_1/n_1, \quad u_2 = U_2/n_2 ,$$

the combined specific energy is:

$$u_c = \frac{U_1 + U_2}{n_1 + n_2} = \frac{n_1 u_1 + n_2 u_2}{n_1 + n_2} , \qquad \text{(IVa17)}$$

and similarly for the volumes and entropies as these are also additive. Thus the point c is on the line joining 1 and 2 (Fig. IVa4). Now let the two quantities be physically combined. Their pressure will then rapidly equalise, followed by thermal equilibrium when the point E on the equilibrium surface is reached. If the process is at constant total energy and volume the line CE will be parallel to the entropy axis, and because of the sign of

$$\left(\frac{\partial^2 u}{\partial s^2}\right)_v = \frac{T}{c_v} , \qquad \text{(IVa18)}$$

will be in the direction of increasing entropy.

Saturated liquid and vapor are represented by different points and the equilibrium surface contains the straight line joining these as the liquid and vapor are in equilibrium in any proportions. The triple point is a triangular plane area joining the points representing solid, liquid, and vapor at this pressure and temperature. A non-equilibrium state can generally be divided up into very small parts which are very nearly in equilibrium within themselves and can therefore be represented by points on the surface. But if they are not in equilibrium between each other their center of gravity will not fall on the surface. As the second derivatives (IVa14) and (IVa15) are necessarily positive, the center of gravity lies above the surface. All non-equilibrium states are therefore represented by points above the surface, and an irreversible process is represented by a line passing above the surface. Although the entropy of a non-equilibrium state is not defined by equation (IVa9) it can be computed as the sum of the entropies of the parts of the system if these are close enough to equilibrium.

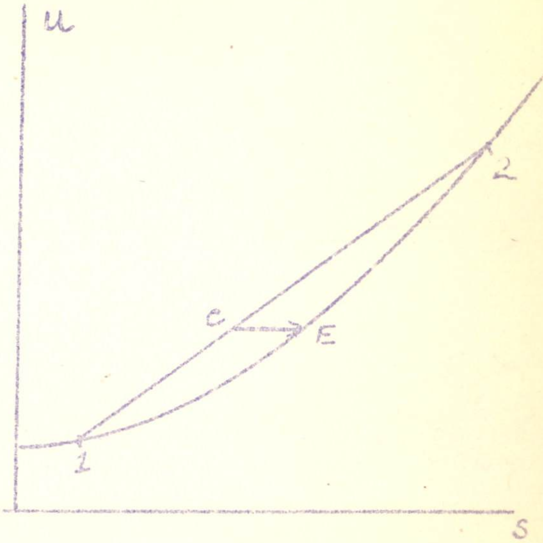


FIG. IVa4.

b. Cyclic Processes

1) Reversible Cycles

Particular importance attaches to reversible cycles, because in a cyclic process the working substance returns to its original state. The net result of the process is then independent of any changes in t. properties of the substance and relate only to the conversions of heat and work. In particular it follows from the First Law that

$$W = Q = Q_2 - Q_1 \qquad \text{(IVb1)}$$

where Q_2 and Q_1 are the quantities of heat absorbed and rejected by the working substance during the cycle and W is the net work done. If the objective is to convert heat into work the efficiency of the process is defined as

$$\eta = \frac{W}{Q_2} = 1 - \frac{Q_1}{Q_2} \qquad \text{(IVb2)}$$

Equation (IVa11) can then be used to relate Q_2 and Q_1 in any particular cycle.

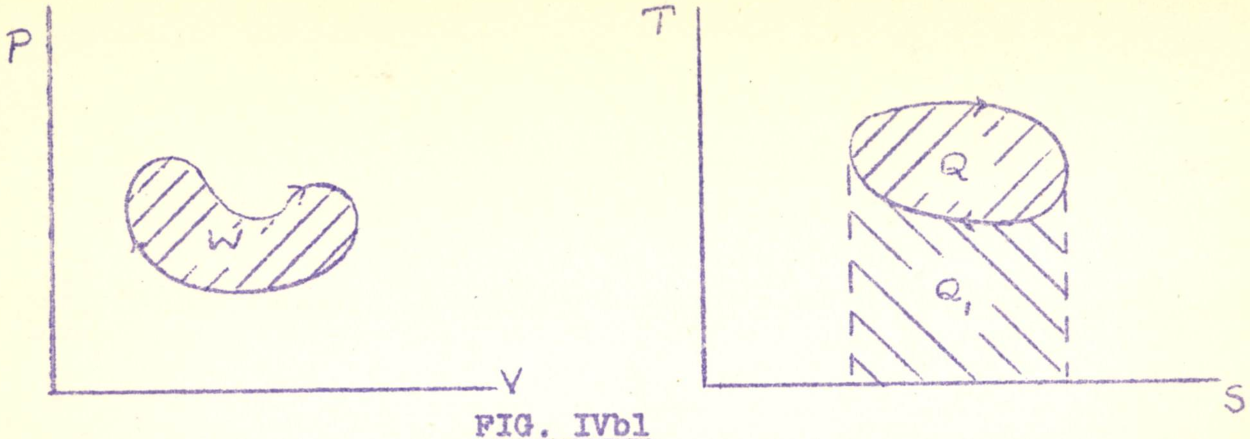


FIG. IVb1

It is immediately clear that the efficiency cannot be one, that is the heat absorbed cannot be entirely converted into work, unless Q_1 is zero, and from figure (IVb1) it is seen that this can occur only if the return path is at the temperature $T = 0$. As the absolute zero is unattainable it follows that:

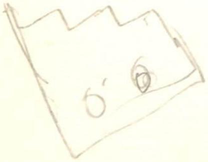
The heat Q cannot be converted into work W without an accompanying amount of heat Q_1 dropping from the higher to a lower temperature. (Kelvin statement: no perpetual motion of the second kind).

Reciprocally, if the cycle is performed in the opposite direction as a refrigerating cycle:

The heat Q_1 cannot be raised from a lower to a higher temperature without the expenditure of an amount of work W. (Clausius statement). The "coefficient of performance" Q_1/W may, however, in this case be greater than one.

If the objective is to deliver heat Q_2 at the higher temperatures the use of a reversible cycle where $Q_2 > W$ is more efficient than the direct conversion of work into heat, as in mechanical friction or in an electrical resistor where $Q = W$. This is the basis for some proposals for the efficient heating of houses.

A special example is the isothermal cycle illustrated in the P-V diagram, figure IIh5. The curved line is a Van der Waal's isotherm, the horizontal line the liquid-vapor equilibrium isotherm. If compressed ? rapidly enough the gas might conceivably be carried through its unstable states and then expanded along the stable isotherm. As the whole cycle is at the same temperature it is represented by a horizontal line on a T-S diagram and $Q_1 = Q_2$. Therefore the work must be zero and the two shaded areas in the figure must be equal, and this is just the construction given previously in figure IIh5.



2) Carnot Cycle

Sadi Carnot (1824) proposed a simple cycle composed of two isothermal and two adiabatic processes and which is therefore represented by a rectangle on a T-S diagram no matter what the working substance. Also as the heat Q_2 is all absorbed at the same temperature T_2 and, similarly, Q_1 is all released at T_1. The heats Q_2 and Q_1 are simply expressed in terms of the entropies S_a and S_b of the two adiabatics.

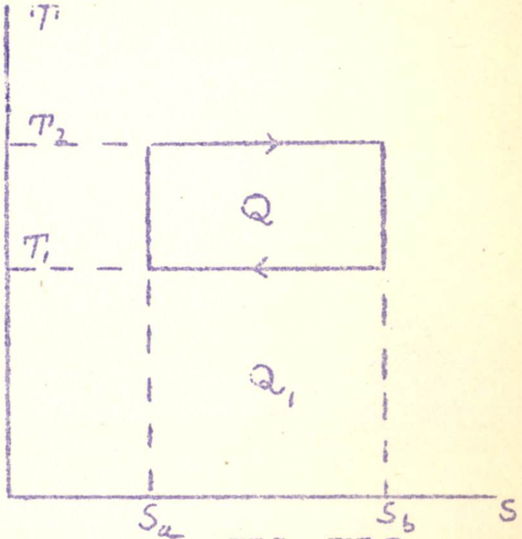


FIG. IVb3

$$\left.\begin{aligned} Q_2 &= T_2\,(S_b - S_a) \\ Q_1 &= T_1\,(S_b - S_a) \end{aligned}\right\} \qquad \text{(IVb3)}$$

$$W = (T_2 - T_1)(S_b - S_a)$$

$$\eta_c = \frac{T_2 - T_1}{T_2} \qquad \text{(IVb4)}$$

The efficiency of a Carnot cycle depends, therefore, only on the temperatures between which it operates and neither on the working substance nor on the entropy difference between the adiabatics.

One application of this, proposed by Lord Kelvin in 1848, is to use the efficiency of a Carnot cycle to measure temperature. At low temperatures the ideal gas thermometer is unavailable, as all gases condense, while the Carnot cycle formula is independent of the substance. In actual practice other consequences of the Second Law than the Carnot Law defines a temperature scale, the integrating denominator of $đQ$, which is independent of any choice of substance.

3) Other Cycles

It is now possible to compare the Carnot cycle with other cycles. Comparing it with other reversible cycles one can say that it is more efficient than any other reversible cycle working between the same extremes of temperature T_2 and T_1. Any reversible cycle can be cut up by adiabatic processes (Fig. IVb4) into smaller cycles which are very nearly Carnot cycles and whose efficiency η_c' is given by (IVb4) but with values T_2' and T_1' appropriate to the small cycle.

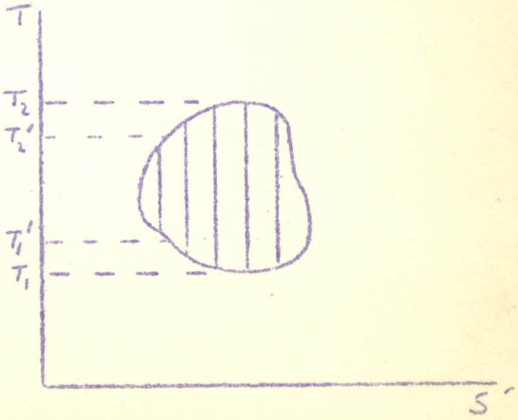


FIG. IVb4

As $T_2' < T_2$ and $T_1' > T_1$ by definition, $\eta_c' < \eta_c$ and therefore the resultant efficiency $\eta < \eta_c$. To have the same efficiency all the heat would have to be taken in at T_2 and given out at T_1, but this would make it a Carnot cycle.

Comparing two cycles, one reversible and the other irreversible, but both taking and surrendering heat at the same temperatures, one can see from (IVa11) that

$$\oint \frac{dQ_{irr}}{T} < \oint \frac{dQ_{rev}}{T}$$

?

Therefore we must have for the heats absorbed $Q_{2\ irr} < Q_{2\ rev}$ or for these rejected

$$Q_{1\ irr} > Q_{1\ rev}$$

or both these inequalities may hold. In any case $(Q_1/Q_2)_{irr} > (Q_1/Q_2)_{rev}$ and therefore

$$\eta_{irr} < \eta_{rev} \qquad \text{(IVb5)}$$

4) The Second Law

In view of these inequalities the statements made in paragraph (Ivb1) can be amplified:

An amount of heat Q cannot be converted into work $W = Q$ without an additional amount of heat

$$Q_1 \geq \frac{T_1}{T_2 - T_1} Q \qquad \text{(IVb6)}$$

falling from the higher temperature T_2 to the lower temperature T_1

The heat Q_1 will not of itself flow from the temperature T_1 to the higher temperature T_2 but requires the expenditure of an amount of work

$$W \geq \frac{T_2 - T_1}{T} Q_1 \qquad \text{(IVb7)}$$

Furthermore our argument can be reversed, as follows:

No violations of the Kelvin or Clausius statements are observed in our experience. If this is universal it follows that all reversible Carnot engines working between the same temperatures have equal efficiencies. Otherwise the more efficient one could be used as a motor to drive the other as a refrigerator. If they are adjusted so the heats Q_2 are equal they will violate the Kelvin statement, or if the works W are equal they violate the Clausius statement. Therefore Q_2/Q_1 is the same for all this class of engines and is equal to T_2/T_1 because this is its value for an ideal gas. Thus

$$\oint \frac{đQ}{T} = 0 \tag{IVb8}$$

for all Reversible Carnot cycles, and therefore for all reversible cycles by the construction of figure IVb4. This is the condition that

$$\frac{đQ}{T} = dS \tag{IVb9}$$

be an exact differential, which therefore follows from the Kelvin or Clausius statements. An irreversible engine need not be as efficient and so, more generally

$$\oint \frac{đQ}{T} \leq 0 \tag{IVb10}$$

c) Irreversible Processes

1) Mechanical Irreversibility

Consider Joule's paddle wheel experiment as a typical example of mechanical irreversibility. There is no heat transfer in this experiment so

$$đQ = 0$$

and $$dU = -đW$$

The work $-đW$ goes into mass motion of the water which, because there are vanes in the vessel to facilitate the process, breaks up into smaller and smaller vorteces and these eventually become invisible. One can imagine the scale of the vorteces continually diminishing until it is of molecular dimensions, when it can be referred to as thermal motion. Part of the kinetic energy may, however, go into potential energy of separation of the molecules. Indeed it is observed that the temperature rises by

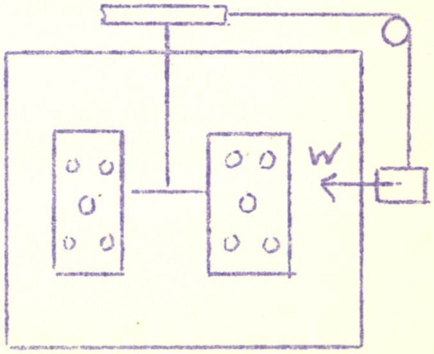


FIG. IVc1

$$dT = dU/C_v$$

(It is easiest to think of the experiment as performed at constant volume although, actually, it is performed at constant pressure).

The same rise in temperature could have been produced by the conduction of an amount of heat

$$\text{đ}Q' = C_v\ dT = -\text{đ}W$$

resulting in an increase of entropy

$$dS = \text{đ}Q'/T = -\text{đ}W/T$$

This entropy came (in large part) from the body which supplied the heat $\text{đ}Q'$, but the same increase of entropy occurs in the paddle wheel experiment, although in this case it does not come from another body but is created. Where? The conversion of the potential energy of the driving weights into the initial kinetic energy in the water does not necessarily involve an increase of entropy as the kinetic energy can be reconverted to potential energy with little loss. It is the breaking up of the vorteces into smaller and smaller ones until they eventually disappear from sight that constitute the creation of entropy. This can be represented schematically by

$$-\text{đ}W \longrightarrow mv^2/2 \longrightarrow TdS \qquad \text{(IVc1)}$$

It is in the dissipation of the vorteces that the possibility is lost of reconverting the kinetic energy back into work. Entropy, therefore, is associated with disordered motion.

The loss of mechanical energy in friction between solid surfaces, or the dissipation of electrical energy in a resistor is entirely similar to the above except that the intermediate stage of mass motion of the medium is missing.

2) Thermal Irreversibility

Another simple way of creating entropy is to put a hot body in contact with a cold one. If a quantity of heat $\text{đ}Q$ passes between them when the hot body is at temperature T_2 and the cold one at T_1 the entropy of the hot body will change by

$$dS_2 = \text{đ}Q/T_2$$

and for the cold body

$$dS_1 = \text{đ}Q/T_1$$

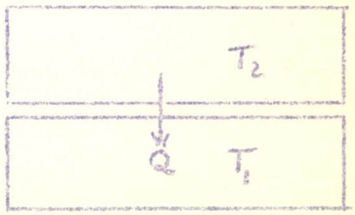


FIG. IVc2

so that the net change is

$$dS = dS_2 + dS_1 = \frac{T_2-T_1}{T_2\ T_1}\,\text{đ}Q \qquad \text{(IVc2)}$$

Conduction always leads to a net increase in entropy. Had we taken the heat $\text{đ}Q$ from the hot body reversibly, that is allowing it to operate a Carnot cycle, we would have obtained an amount of work

$$\text{đ}W' = \frac{T_2-T_1}{T_2}\,\text{đ}Q \qquad \text{(IVc3)}$$

and delivered to the cold body

$$\text{đ}Q' = \frac{T_1}{T_2}\ dQ$$

so that in this case

$$dS' = dS_2 + dS'_1 = 0$$

However there is a relation between the work (IVc3) that we could have obtained, but didn't, and the increase in entropy (IVc2)

$$\text{đ}W' = T_1\ dS \qquad \text{(IVc4)}$$

the loss in ability to do work is always equal to the increase in entropy times the lowest temperature of the system.

3) <u>Internal Irreversibility</u>

The simplest example of internal irreversibility is the free expansion of an ideal gas. In this case

$$\text{đ}W = \text{đ}Q = dU = dT = 0$$

but from equation (IVa3) for the entropy of an ideal gas we find that there has been an increase

$$S_2 - S_1 = nR\ \ell n\ V_2/V_1 \qquad \text{(IVc5)}$$

The process could have been performed reversibly by an isothermal expansion, getting an amount of work

$$W' = \int_{V_1}^{V_2} PdV = nRT \int_{V_1}^{V_2} dV/V = nRT\ \ell n\ V_2/V_1$$

and, of course, supplying an equal amount of heat. Again, the work which could have been obtained, but which has become unavailable in the process, is

$$W' = T\ (S_2-S_1)$$

Examining the details of the free expansion we see that initially parts of the compressed gas do work PdV on other parts to give them kinetic energy $mv^2/2$. There is no entropy change in this process. If the motion of the gas could be kept as a regular pressure wave it might be reflected from the far side of the evacuated vessel and all return to the part originally occupied. But this does not happen and when the accelerated gas hits the further side of the evacuated vessel the motion becomes confused and disordered, and this results in an increase in entropy. The process is again

$$PdV \longrightarrow mv^2/2 \longrightarrow TdS$$

but in this case there is no net increase in kinetic energy as there is no change in temperature. In fact if the experiment is performed with a real gas there will probably be a decrease in temperature and in mean kinetic energy. The entropy is due to the greater randomness of position of the molecules which is simply due to the increased volume within which the molecules are scattered.

3) Insulated Systems

The Clausius inequality

$$đQ \leq TdS$$

shows that for any insulated system, that is one for which

$$\text{one has} \qquad \left.\begin{array}{c} đQ = 0 \\ dS \geq 0 \end{array}\right\} \qquad (IVc6)$$

or the entropy can only increase.

Similarly for a system on which no work is done

$$\text{and} \qquad \begin{array}{c} đW = 0 \\ PdV \geq 0 \end{array} \qquad (IVc7)$$

but one cannot conclude from (IVc7) that the volume can only increase because attractive forces exist which can produce tensions, or negative pressures. Equation (IVc7) merely states that changes in volume will have the same sign as the pressure. The entropy law follows from the non-existence of negative temperatures.

Any system left to itself, that is to which no energy in the form of heat or work is transferred or taken, can only increase in entropy, the maximum being attained when thermal and mechanical equilibrium is attained.

4) Life

Finally there is life itself which deserves a word in this connection. Even the simplest living organism is very highly organized, which means that its entropy is abnormally low. At death rapid irreversible changes take place and the entropy rises to a more normal value. Are the forces which maintain this low entropy violating the Second Law? If life could continue in an "isolated" body they obviously would be; but it cannot. "Life" needs "dead" surroundings and produces order within itself only at the expense of disorder in its environment in complete accordance with the Clausius inequality. Simple plant life reduces its entropy by absorbing the low entropy heat of sunlight and rejecting it at the much higher entropy level of ambient temperature. Animal life feeds on the low entropy products of plant life rejecting it in the high entropy form of carbon dioxide. The irreversibility of life is a good indication that the disorder it produces in its surroundings is always far greater than the order produced within itself.

d. Thermodynamic Formulae

1) Thermodynamic Potentials

The basic laws of Thermodynamics are contained in the relations

$$\begin{aligned} \text{đ}W &\leq PdV \\ \text{đ}Q &\leq TdS \\ dU &= \text{đ}Q - \text{đ}W \end{aligned} \tag{IVd1}$$

containing the inexact differentials for work and heat. These relations are applicable to both reversible and irreversible processes.

It is more convenient, however, to use variables which are functions of the state of the system and have equalities instead of inequalities. This can be done only with the restriction to equilibrium states and reversible processes, and this restriction must be understood in all the equations which are to follow. With this restriction we have already defined a function

$$H = U + PV \tag{IVd2}$$

called the enthalpy. The transformation of U into H by adding the product PV is called a Legendre transformation; it has the effect of interchanging a variable with the corresponding slope, as seen in equations (IVd5) below. Another Legendre transformation, subtracting the product TS, leads to two more such functions: the Helmholtz function

$$A = U - TS \tag{IVd3}$$

and the Gibbs function

$$G = H - TS \qquad \text{(IVd4)}$$

These last two have both been called "free energy" and it is therefore always better to use the names of the men who introduced them U, H, A, and G are called the Thermodynamic Potentials.

2) First Derivatives

From (IVd1) and simple differentiation of (IVd2), (IVd3), (IVd4) one obtains the following equations for the exact differentials

$$\boxed{\begin{aligned} dU &= TdS - PdV \\ dH &= TdS + VdP \\ dA &= -SdT - PdV \\ dG &= -SdT + VdP \end{aligned}} \qquad \text{(IVd5)}$$

From these differentials one readily obtains all the first derivatives of the potentials. There are eight simple ones of the type

$$\left(\frac{\partial U}{\partial S}\right)_V = T \;..........\; \left(\frac{\partial G}{\partial P}\right)_T = V \qquad \text{(IVd6)}$$

in which each potential is differentiated with respect to its "natural" independent variables, those whose differentials appear in the same equation (IVd5) as the potential.

There are eight more in which one of the independent variables is "natural", such as

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \qquad \text{(IVd7)}$$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V = T\left(\frac{\partial S}{\partial T}\right)_V \geq \left(\frac{\text{đ}Q}{dT}\right)_V \qquad \text{(IVd8)}$$

and similarly

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \qquad \text{(IVd9)}$$

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p = T\left(\frac{\partial S}{\partial T}\right)_p \geq \left(\frac{\text{đ}Q}{dT}\right)_p \qquad \text{(IVd10)}$$

and there are eight others, such as $(\frac{\partial U}{\partial P})_T$, in which both independent variables are "unnatural".

There are 312 other first derivatives as each of the eight variables, P, V, T, S, U, H, A, G, may be differentiated with respect to any of the seven others holding any of the remaining six constant. This gives 8 x 7 x 6 = 336 first derivatives. However, they are not independent and it can be shown that there are 521,631,180 relations between them, all obtainable by applying (Ib3) and (Id2)! A few of these relations are of frequent use and will be derived below.

3. Gibbs-Helmholtz Equations

From equations (IVd3) and (IVd5) we have immediately

$$A - U = T(\frac{\partial A}{\partial T})_V \qquad \text{(IVd11)}$$

and similarly from (IVd4) and (IVd5)

$$G - H = T(\frac{\partial G}{\partial T})_P \qquad \text{(IVd12)}$$

These relations are useful to compute U knowing A, or H knowing G, or vice versa, as they do not contain the entropy explicitely.

4. Maxwell's Relations

As the potentials are functions of the state of the system, their differentials must be exact. J. C. Maxwell applied the conditions for exactness to equations (IVd5), obtaining two relations applicable to adiabatic processes:

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

$$= -\frac{T}{C_V}\,\frac{\beta}{\kappa} \qquad \text{(IVd12)}$$

and

$$(\frac{\partial T}{\partial P})_S = (\frac{\partial V}{\partial S})_P = (\frac{\partial V}{\partial T})_P (\frac{\partial T}{\partial S})_P = \frac{TV\beta}{C_P} \qquad \text{(IVd13)}$$

and two which apply to isothermal processes

$$(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V = \frac{\beta}{\kappa} \qquad \text{(IVd14)}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\beta \qquad \text{(IVd15)}$$

5) <u>Energy and Enthalpy Equations</u>

Introducing the last two expressions for the derivatives of the entropy into (IVd7) and (IVd9) respectively give

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T^2\left(\frac{\partial(P/T)}{\partial T}\right)_V \qquad \text{(IVd16)}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P = -T^2\left(\frac{\partial(V/T)}{\partial T}\right)_P = V(1-T\beta) \qquad \text{(IVd17)}$$

Combining these with (IVd8) and (IVd10) gives

$$dU = C_V\,dT + \left(\frac{T\beta}{\kappa} - P\right)dV \qquad \text{(IVd18)}$$

$$dH = C_P\,dT + V(1-T\beta)\,dP \qquad \text{(IVd19)}$$

These equations are used to obtain the energy and enthalpy from measurements of the heat capacities and of the equations of state.

From these we see also that the Joule coefficient

$$\mu = \frac{T\beta - P\kappa}{\kappa C_V} \qquad \text{(IVd20)}$$

and the Joule-Kelvin coefficient

$$\mu' = V\,\frac{1-T\beta}{C_P} = -\frac{T^2}{C_P}\left(\frac{\partial(V/T)}{\partial T}\right)_P \qquad \text{(IVd21)}$$

Referring to the plot of PV/nRT against P for a real gas, it is seen that at the points where successive isotherms cross each other PV/nRT is independent of T at constant P, and therefore at these points the Joule-Kelvin coefficient is zero.

6) <u>TdS Equations</u>

Combining the last two Maxwell relations with (IVd8) and (IVd10) we have what are known as the TdS equations

$$\boxed{\begin{aligned} \text{đ}Q &\leq TdS = C_V\, dT + \frac{T\beta}{\kappa}\, dV \\ \text{đ}Q &\leq TdS = C_p dT - T\, V\beta\, dP \end{aligned}} \qquad \begin{aligned} &(IVd22) \\ &(IVd23) \end{aligned}$$

These equations are useful to obtain the heat absorbed in any process.

Comparing these equations with (IIIc18) and (IIIc19) we see that

$$C_p - C_V = TV\beta^2/\kappa \qquad (IVd24)$$

It is from this equation that C_V generally is calculated from measurements of C_p and the other variables in the equation.

In the case of solids we can use Gruneisen's relation (IVb14) to get the Nernst-Lindemann equation

$$c_p - c_V = AT\, c_p^2 \qquad (IVd25)$$

by which c_V can be calculated from measurements of c_p and T and the determination of A by a single measurement of β and κ.

7) <u>Change of Phase</u>

During a change of phase, which takes place at constant pressure and temperature, it is evident from equations (IVd5) that

$$\left.\begin{aligned} dG &= 0 \\ \text{and} \qquad dH &= TdS \geq \text{đ}Q \end{aligned}\right\} \qquad (IVd26)$$

If the pure phases are denoted by 1 and 2, where 2 is the higher temperature phase

$$\left.\begin{aligned} G_2 &= G_1 \\ H_2 - H_1 &= T\,(S_2 - S_1) = L \end{aligned}\right\} \qquad (IVd27)$$

where L is the latent heat of the transformation.

The first TdS equation

$$\text{đ}Q \leq C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \qquad (IVd28)$$

integrates readily in this case because $dT = 0$ and neither P nor T depend on V. The integral is

$$L = T \frac{dP}{dT}(V_2 - V_1)$$

or

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \qquad \text{(IVd29)}$$

This is called the Clausius-Clapeyron equation. The partial sign has been dropped in the derivative as the ratio of dP to dT in going between two isotherms is the same, in the equilibrium region, whether one takes a constant volume or any other path. In any case dP/dT gives the slope of the line on a P-T diagram which represents the transformation.

Similarly, from (IVd27 and 19),

$$\frac{dL}{dT} = C_{p2} - C_{p1} + (V_2 - V_1)\frac{dP}{dT} - T(V_2\beta_2 - V_1\beta_1)\frac{dP}{dT} = C_{\beta_2} - C_{\beta_1} \text{ for [illegible]}$$

β''

$$= C_{p2} - C_{p1} + \frac{L}{T} - \frac{V_2\beta_2 - V_1\beta_1}{V_2 - V_1} L \qquad \text{(IVd30)}$$

This is Kirchhoff's equation. It may also be written

$$\frac{d(L/T)}{dT} + \frac{V_2\beta_2 - V_1\beta_1}{V_2 - V_1}\frac{L}{T} = \frac{C_{p2} - C_{p1}}{T} \qquad \text{(IVd31)}$$

$\frac{L}{T} = f(T)$

This last is a differential equation for the "latent entropy." L/T. If the equations of state and specific heats of both phases are known, as well as the latent heat at one temperature, it can in principle be integrated for the latent entropy, which may then be substituted in Clapeyron's equation and integrated for the vapor pressure.

e. Applications

1) Ideal Solid

We have defined the ideal solid as one whose equation of state is

$$V \approx V_0(a - bP) \qquad \text{(IVe1)}$$

where a and b are functions of the temperature and

$$\kappa \approx b\, V_o/V \qquad (IVe2)$$

$$\beta \approx (a' - b'P)\, V_o/V \qquad (IVe3)$$

The enthalpy equation (IVd18) is

$$dH \approx C_p\, dT + V_o\, (a - bP - Ta' + Tb'P)\, dP \qquad (IVe4)$$

Integrating first at constant pressure

$$H_1 \approx H_o + \int_o^T C_p\, dT \qquad (IVe5)$$

and then at constant temperature

$$H \approx H_1 + V_o\, (a - Ta')P + V_o\, (Tb' - b)\, P^2/2 \qquad (IVe6)$$

The process of integration may be shown on a P-T diagram. To find the enthalpy at (P,T) we start at the origin and integrate $C_{p\,=\,0}$ along the temperature axis (P = 0) to get H_1. This is the integral (IVe5) which gives the enthalpy at zero pressure. We then integrate $V(1-T\beta)$ at constant temperature to get (IVe6).

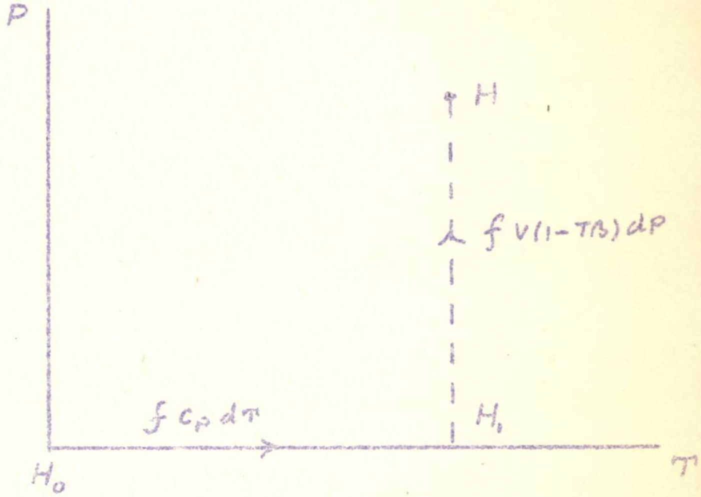


FIG IVe1

Applying the condition for an exact differential to (IVe4) we find

$$\left(\frac{\partial C_p}{\partial P}\right)_T \approx V_o T(b''\, P - a'') \qquad (IVe7)$$

and integrating this

$$C_p \approx C_{po} - V_o\, PT(a'' - b''\, P/2) \qquad (IVe8)$$

where C_{po} represents the heat capacity at zero pressure but arbitrary temperature.

As the second derivatives a" and b" are generally small C_p will not depend greatly on the pressure.

The internal energy U is obtained immediately by subtracting PV from (IVe6)

$$U \approx H_1 - V_o T a'P + V_o (b + Tb') P^2/2 \qquad \text{(IVe9)}$$

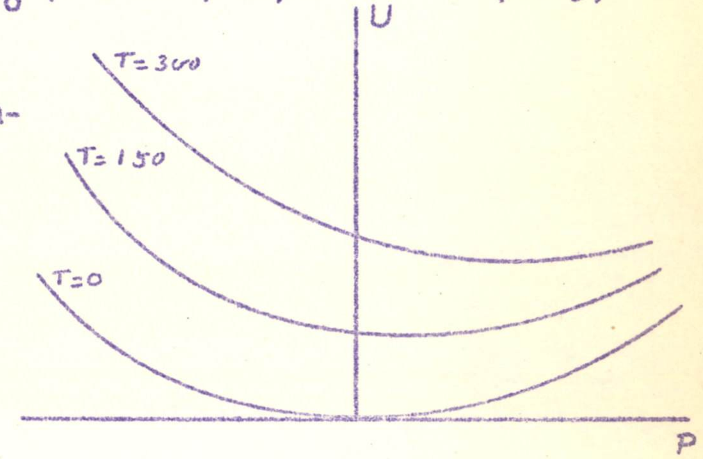


FIG IVe2

It is noted that the internal energy initially decreases on isothermal compression. Of course work is done on the solid during compression, but so much heat has to be taken away to maintain the temperature constant that the internal energy actually decreases until the pressure is large enough for the squared terms to be important.

Using (IVe8) in the second TdS equation one obtains

$$dS \approx \frac{C_{po}}{T} dT - V_o P(a'' - b'' P/2)\, dT - V_o (a' - b'P)\, dP$$

which readily integrates to

$$S_1 \approx S_o + \int_o^T \frac{C_{po}}{T} dT$$

$$S \approx S_1 - V_o P(a' - b' P/2) \qquad \text{(IVe10)}$$

The Helmholtz free energy takes a particularly simple form

$$A \approx A_1 (T) + \frac{1}{2} V_o bP^2$$

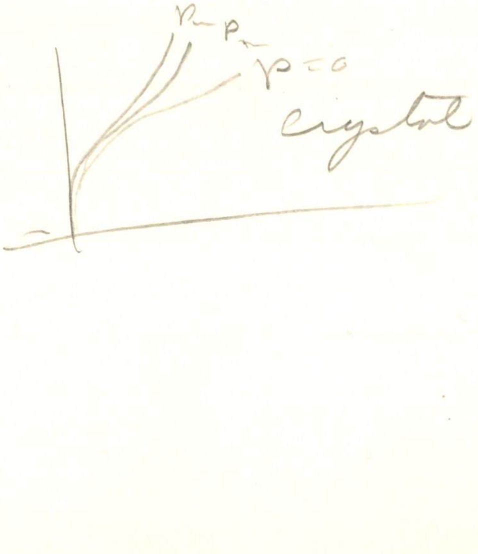
$$A_1' \approx S_1 \qquad \text{(IVe11)}$$

It is a characteristic of this potential that at a given temperature it has a minimum at zero pressure. It is because $\frac{1}{2}\chi V P^2$ is the elastic work done on the solid during an isothermal compression that A is called "free energy".

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{\beta}{\kappa} \to 0$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p = -V\beta \to 0$$

$$\left(\frac{\partial c_v}{\partial V}\right) - -$$



Finally from (IVd24) we have for the difference in heat capacities

$$C_p - C_V \approx V_o\, T\, (a' - b'P)^2/b \qquad \text{(IVe12)}$$

At low temperatures where the thermal coefficient of expansion is small the difference in heat capacities is quite negligible, At normal temperatures, when the thermal coefficient of expansion is sensibly constant, the difference increases linearly with the temperature.

2) The Third Law

It is observed experimentally that both β and C_p for all solids tend towards zero at least proportionately to T as the absolute zero of temperature is approached. It follows then from Maxwell's isothermal relations, as κ does not vanish that the entropy of all solids is completely independent of pressure and volume at absolute zero and increases at most as T^2 with the temperature. Where crystalline solids can be related chemically it is found, from the chemical evidence that the entropy difference between these solids vanishes at absolute zero. It appears therefore that the entropy of all crystalline solids is the same at absolute zero and, as there is always an arbitrary constant in the measurement of entropy, the entropy at absolute zero may be taken as zero. This constitutes the Third Law of Thermodynamics and was discovered by Nernst.

The word "crystalline" above is significant, and this may be illustrated by the properties of glycerine which have been studied. The specific heat of the crystalline solid is plotted in figure (IVe3) up to 291°K at which temperature the crystals melt with a latent heat of 4371 calories per mole. This corresponds to an entropy difference between liquid and crystal $s_\ell - s_c$ = 15.02 cal/mole deg. The specific heat of the liquid is larger than that of the crystal by about 1.5 cal/mole deg. The liquud is easily supercooled and undergoes a rapid but continuous change within a few degrees of 280°K. Below this range it has the rigidity of a solid but has remained amorphous. There is no latent heat in the change, and below it the specific heat of the amorphous solid is much the same as that of the crystal. If one plots the difference of the specific heats divided by the temperature one obtains the curve of Fig. (IVe4). The area under this curve is 10.46 cal/mole deg.

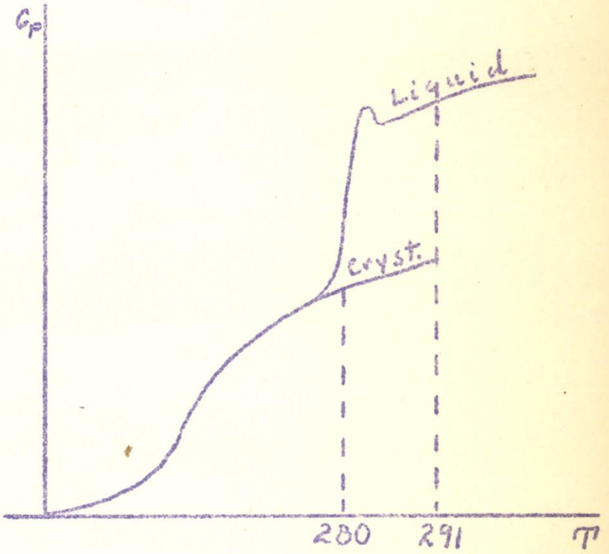
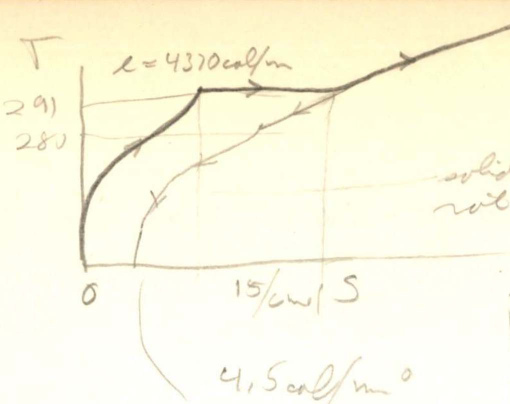


FIG. (IVe3)

for a
glycerin
crystal



C_p liq > C_p sol

$$\boxed{\text{S of all crystals} = 0 \text{ at } 0^\circ}$$

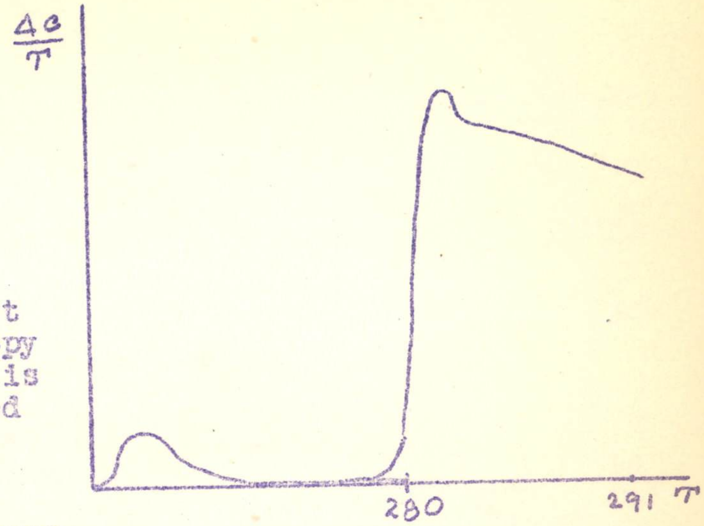


FIG. IVe4

and hence

$$(s_\ell - s_c)_{291} - (s_\ell - s_c)_0 \approx 10.46$$

whence

$$(s_\ell - s_c)_0 \approx 4.56 \text{ cal/mole deg.}$$

If the entropy of the crystal is zero at absolute zero it follows that the entropy of amorphous glycerin at absolute zero is 4.56 cal/mole degree. This is explained by the disordered arrangement of the molecules in the amorphous solid.

The amorphous solid is not, of course, an equilibrium state. If left to itself long enough it will spontaneously crystallize, and as this irreversible change must be accompanied by an increase in entropy the resulting crystal will be hot. That is, there is a latent heat in the change.

3) Van der Waals' Gas

Van der Waals' equation solved for the pressure is

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) \approx NRT$$

$$P \approx \frac{nRT}{V-nb} - \frac{n^2 a}{V^2} \qquad \text{(IVe13)}$$

From this we see that

$$\left(\frac{\partial P}{\partial T}\right)_V \approx \frac{nR}{V - nb} \qquad \text{(IVe14)}$$

and

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V \approx 0$$

The constant volume curves on a P-T diagram are therefore straight lines.

Applying the condition for an exact differential to dS from the first TdS equation one has

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$$T\,ds = du + p\,dV$$
$$C_V dT + p\,dV$$

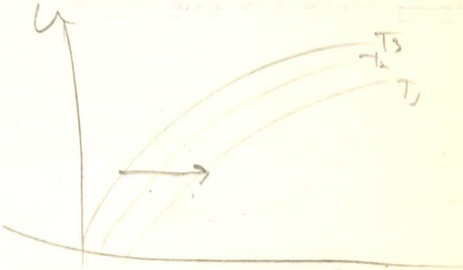
$$\frac{1}{T}\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial T^2}\right)_V \approx 0 \qquad \boxed{\text{(IVe15)}}$$

$$\left(\frac{\partial C_v}{dV}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

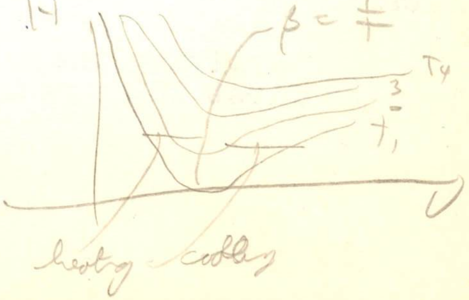
$$\boxed{\begin{array}{c} du = A\,dx + B\,dy \\ \left(\frac{\partial A}{\partial y}\right)_x = \left(\frac{\partial B}{\partial x}\right)_y \end{array}}$$

$$C_v dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

free expansion



throttling



[illegible] $TdS = C_v dT + \left(\frac{\partial P}{\partial T}\right)_V$

So that C_V for a Van der Waals' gas is constant if T is held constant; that is C_V is a function of T only. This is the basic fact from which we can start to derive the Thermodynamic functions of a Van der Waals' gas.

Substituting (IVe14) in the TdS equation

$$dS \approx \frac{C_V}{T}\,dT + \frac{nRdV}{V-nb}$$

which integrates immediately to

$$S \approx \int \frac{C_V}{T}\overset{\text{on } T}{\,dT} + \overset{\text{on } V}{nR}\,\ell n\,(V-nb) + S_o \quad \text{(IVe16)}$$

← diff for ideal gas

$S \approx \int C_v \frac{dT}{T} - nR\ln V + S_0$ — for ideal gas

The Van der Waals' forces which are measured by "a" contribute nothing to the entropy: it is the same as that of an ideal gas whose volume is reduced by nb.

Substituting (IVe14) in the energy equation gives ?,

$dQ = \left(\frac{\partial P}{\partial T}\right)_V dV$

$$\left(\frac{\partial U}{\partial V}\right)_T \approx \frac{nRT}{V-nb} - P = \frac{n^2a}{V^2}$$

$\left(\frac{\partial u}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V - P =$

so that

$$dU \approx C_V\,dT + \frac{n^2a}{V^2}\,dV$$

which integrates to

$$U \approx \int_o^T C_V dT - \frac{n^2a}{V} + U_o \quad \text{(IVe17)}$$

so that here it is only the attractive forces which enter and reduce the energy. In a free expansion, in which V increases but U is constant, it is evident that the integral must decrease, which means that a Van der Waals' gas always cools in a free expansion. The Joule coefficient is

$$\mu \approx n^2a/V^2C_V \quad = \left(\frac{\partial T}{\partial P}\right)_h \quad \text{(IVe18)}$$

The enthalpy is obtained by adding PV to the internal energy and is

$$\left.\begin{aligned} H &\approx \int_o^T C_V dT + \frac{nRTV}{V-nb} - \frac{2n^2a}{V} + U_o \\ &\approx \int_o^T C_V dT + \boxed{PV} - \frac{n^2a}{V} + U_o \end{aligned}\right\} \quad \text{(IVe19)}$$

$$L = H_2 - H_1$$

$$= p(v_2 - v_1) + n^2 a \left(\frac{1}{v_1} - \frac{1}{v_2} \right)$$

$$L = (v_2 - v_1)\left(\underbrace{p}_{\text{external work}} + \underbrace{\frac{na}{v_2 v_1}}_{\text{internal work}} \right)$$

In a throttling process (Joule-Kelvin experiment) the end states have the same enthalpy but the pressure has decreased. It cannot easily be seen from (IVe19) whether this process will result in an increase or decrease of temperature. However it is readily seen from (IVd19) that both enthalpy and temperature can remain constant if

$$T_i \beta = 1 \qquad \text{(IVe20)}$$

$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

Computing β from (IVe13) this equation reduces to

$$P_i V \approx \frac{na}{b}(2 - 3nb/V)$$

or $\qquad$ (IVe21)

$$RT_i \approx \frac{2a}{b}\left(1 - \frac{nb}{V}\right)^2$$

and it may be shown that if P or T are below the values given by these equations the gas cools on expansion and if they are greater it heats. As the volume is always much larger than nb the inversion temperature is nearly independent of V, and therefore of P. Eliminating V between equations (IVe21) one obtains

$$P_i \approx \frac{a}{b^2}\left(1 - \sqrt{\frac{bRT_i}{2a}}\right)\left(3\sqrt{\frac{bRT_i}{2a}} - 1\right) \qquad \text{(IVe22)}$$

which defines the inversion curve on a P-T diagram. The throttling process to obtain cooling and eventual liquefaction is widely used in the Linde Process.

Finally from equation (IVd24) it follows that

$$C_p - C_v \approx \frac{P + n^2a/V^2}{P - n^2a/V^2}\, nR \qquad \text{(IVe23)}$$

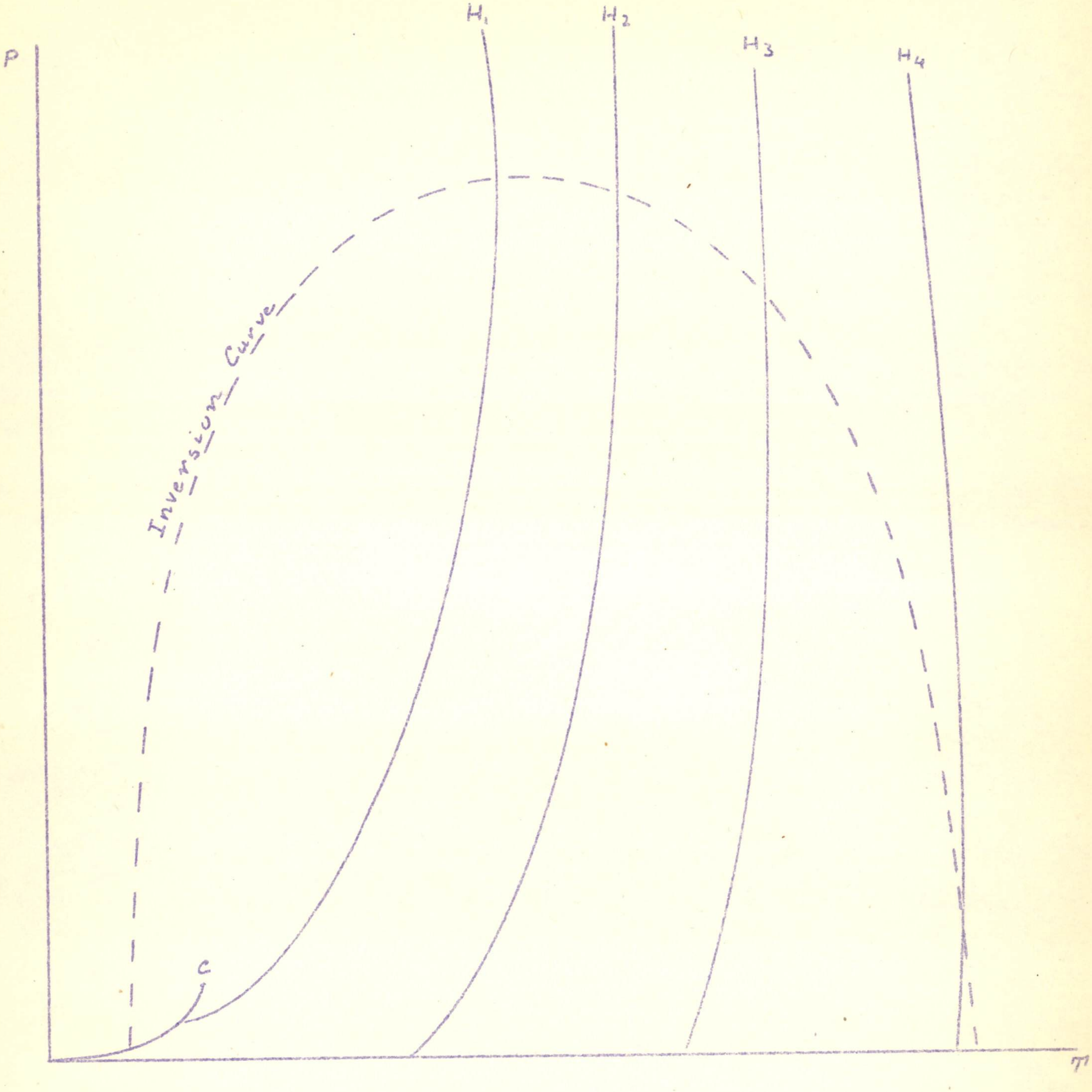


FIG. IVe5

Constant enthalpy curves for a Van der Waals gas.

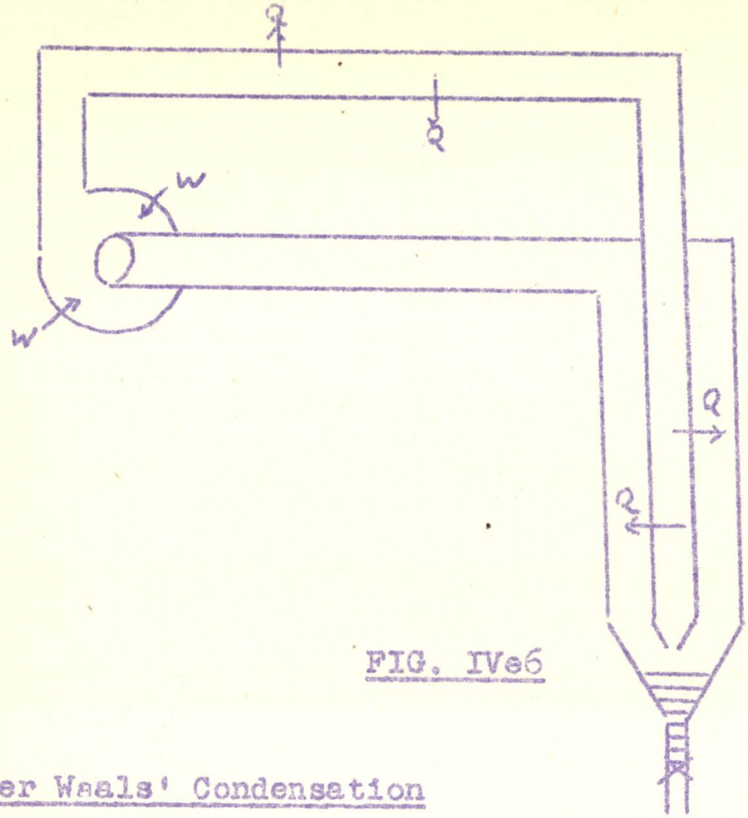


FIG. IVe6

4) Van der Waals' Condensation

Substituting the formula (IVe19) already found for a Van der Waals' gas in (IVd27) we find for the latent heat of condensation

$$L \approx (V_g - V_\ell)(P + n^2\, a/V_g V_\ell) = nRT\, \ell n \frac{V_g - nb}{V_\ell - nb} \qquad \text{(IVe24)}$$

which clearly shows the latent heat to be due to work against external (P) and internal (n^2a/V^2) pressure. Substituting values of P and V near the critical point we find that the internal work is three times the external work, and this ratio becomes larger at lower pressures. Due to the factor $V_g - V_\ell$ the latent heat goes to zero at the critical point, its temperature dependence being shown in Fig. IVe7. Real gases have latent heats considerably larger than that predicted by the Van der Waals' equation as shown in the figure. Clapeyron's equation for a Van der Waals' gas is simply

$$\frac{dP}{dT} \approx \frac{P + n^2a/V_gV_\ell}{T} \qquad \text{(IVe25)}$$

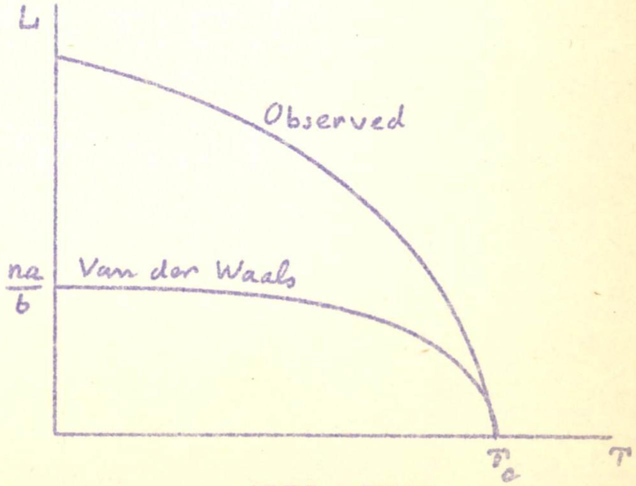
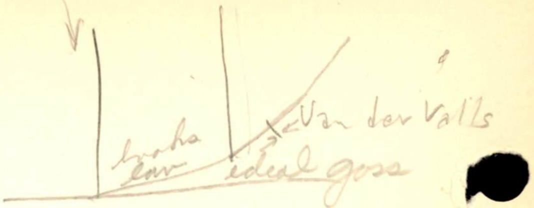


FIG. IVe7

$$\boxed{S_m = \frac{L}{T}}$$ S of melting



$$\frac{dS_m}{dT} = \left(\frac{C_l - C_s}{T}\right)_{sat.}$$

$$\Delta S_m = \frac{L}{T} = (C_l - C_s)_{sat} \ln\frac{T}{T_T} \approx 0$$

$$\frac{L}{T} \approx const = S_m$$

$$\frac{dp}{dT} = \frac{S_m}{V_l - V} = \frac{L}{T(V_2 - V_1)} = \frac{S_2 - S_1}{V_2 - V_1}$$ clapeyron Eqn.

0 (see

from Hooke law $\rightarrow \frac{S_m}{\Delta V_0 (a - bP)}$ assume const. with ΔT.

$$\int \Delta V_0 (a - bP)\, dP \approx \int S_m\, dT =$$

$$\Delta V_0 \left(c + ap - \frac{bp^2}{2}\right) \approx S_m (T - T_T)$$

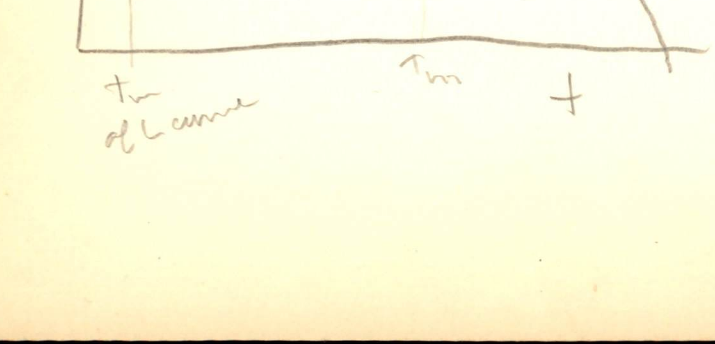
---

for Metals $S_m \sim 2.3$ cal/mol degrees (electrons are free. so only half is melted)

Ionic " " 4

mole. crystal " 4.6

valence " – ?, – don't melt or not data



but the deviation of observation from this formula are so large as to make it of little value.

5) Melting

The latent heats ℓ_m of melting per mole at atmospheric pressure of a few solids is given in the accompanying table. It is seen that they vary by factors up to 200. However the temperatures of melting T_m vary by equally large amounts, and in the same direction, so that the entropy of melting

$$S_\ell - S_s = Lm/T_m \qquad (IVe25)$$

varies remarkably little. It has already been said that entropy measures randomness so it is quite understandable that there should be an increase in entropy in going from a crystal where the molecules are arranged in perfect order to a liquid where they are disordered and that if we deal with the same number of molecules the amount of randomness, and therefore the increase in entropy, should be about the same.

For reference the latent heat of vaporization at the same temperature is also given. It also varies widely, but keeps a nearly constant ratio to the latent heat of melting. At low pressures the latent heat of vaporization represents almost entirely work done against the binding forces in separating the molecules, the work $P(V_g-V_\ell)$ done against the external pressure being negligible. The table shows that a metal absorbs about one thirtieth of its binding energy when it melts. On the other hand a molecular compound requires a seventh of its binding energy to melt it, and this is because the binding of molecular compounds is so weak. In either case, however, the liquid is very much closer in energy to the solid than to the gas.

The coefficient of volume expansion β is quite small for both solids and liquids, so that the last term of Kirchhoff's equation (IVd31) is generally small when this equation is applied to melting. The remainder of the equation integrates to

only roughly true

$$\boxed{\frac{L_m}{T} \approx \frac{L_{mt}}{T_t} + \int_{T_t}^{T} \frac{C_{p\ell} - C_{ps}}{T}\, dT} \qquad (IVe27)$$

where T_t and L_{mt} are the temperature and latent heat of melting at the triple point. As the heat capacity of the liquid $C_{p\ell}$ is always larger than that of the solid C_{ps} the entropy of melting decreases slowly with the temperature.

$$\frac{dL}{dT} = C_p - C_{p_l} + \frac{L}{T} - \cancel{\frac{V_2\beta_2 - V_1\beta_1}{V_2 - V_1} L}$$

Kircoff Eqn.

$V_2 >> V_1$

$PV = nRT$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{T}$$

for gas that obeys ideal gas laws.

$$\frac{dL}{dT} = C_g - C_{p_l}$$

$$L = L_0 + \int_0^T \Delta C_p\, dT$$

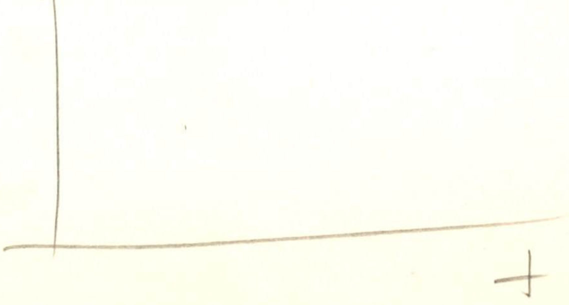
in Clap Eqn.

$$\frac{dP}{dT} = \frac{LP}{TnRT}$$ again using

$$\frac{dP}{P} = \frac{L\,dT}{RT^2}$$ per mole Claps equ. for ideal gas

$$\ln P = -\frac{L_0}{RT} + \int \frac{dT}{nRT}\int_0^T \Delta C_p\, dT = \frac{e}{RT} + \int_0^T \frac{\Delta C_p\, dT}{nRT} - \int_0^T \frac{1}{T}\int \Delta C_p\, dT$$

$$\frac{1}{nRT}\int \Delta C_p\, dT = \cancel{\frac{\Delta C_p}{nRT}} + \frac{1}{T^2}\int \frac{\Delta C_p\, dT}{nR} - \cancel{\frac{\Delta C_p}{nRT}}$$ proof



The meaning of this equation is simple: consider the cycle (Fig. IVe8) which follows the melting curve on both sides, crossing it at the triple point and an arbitrary other point. Equation (IVe27) says that the entropy change on going around this cycle is zero. Looked at in this way it is seen that equation (IVe27) is exact if one introduces C_{Sat}, the heat capacity of the "saturated" solid or liquid, in place of C_p.

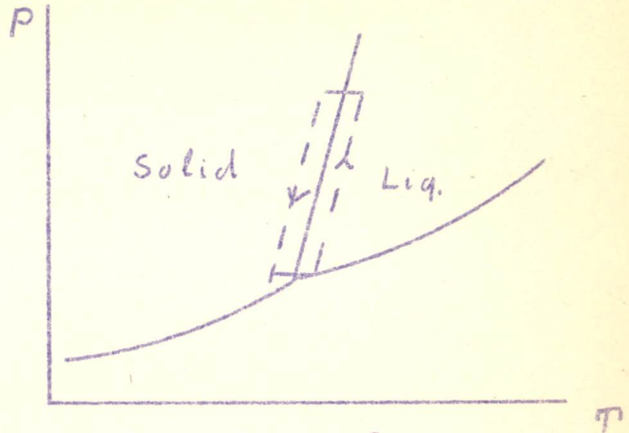


FIG. IVe8

If $Lm/T = \Delta S$ is approximately constant and V_2 and V_1 both obey Hooke's law so that $V_2 - V_1 \approx \Delta V_o(a-bP)$ Clapeyron's equation integrates to

$$\Delta V_o\,(C + aP - bP^2/2) = \Delta S\,(T - T_t) \qquad \text{(IVe28)}$$

and this is the form actually observed for the melting line on a P-T diagram.

6) Sublimation

In the sublimation of a solid the molar volume of the gas is always very large compared to that of the solid, and the same thing is true for the vaporization of a liquid except very near the critical point. In these cases V_1 can be neglected compared to V_2 and V_2 can be given its ideal gas value nRT/P. Furthermore as $\beta_2 = 1/T$ for an ideal gas the last two terms of the Kirchhoff equation (IVd30) cancel so that there remains

$$\frac{dL}{dT} \approx C_{pg} - C_{ps} \approx \Delta C_p \qquad \text{(IVe29)}$$

$$\frac{dP}{dT} \approx \frac{PL}{nRT^2} \qquad \text{(IVe30)}$$

As an example of the approximations involved, if these equations are applied to water at one atmosphere and 100°C Eq. (IVe29) is in error by 3.5 per cent and Eq. (IVe30) by 0.6 per cent. These equations are much more accurately true when applied to sublimation.

These equations may be integrated as follows:

$$L \approx L_o + \int_o^T \Delta C_p\, dT \qquad \text{(IVe31)}$$

$$\frac{dP}{P} \approx \frac{LdT}{nRT^2}$$

$$\ln P \approx -\frac{L_o}{nRT} + \int_0^T \frac{dT}{T^2} \int_0^T \frac{\Delta C_p}{nR}\, dT$$

$$\approx -\frac{L_o}{nRT} + \int_0^T \frac{\Delta C_p}{nRT}\, dT - \frac{1}{T} \int_0^T \frac{\Delta C_p}{nR}\, dT \qquad \text{(IVe32)}$$

Two cases are of particular interest:

α) Above room temperature. Both heat capacities are roughly constant and Dulong and Petit's law is a good approximation for C_{ps}. ΔC_p is then a negative constant

$$\Delta C_p \approx -nRC$$

so that

$$L \approx L_o - nRCT \qquad \text{(IVe33)}$$

and

$$\ln P \approx -\frac{L_o}{nRT} + B - C \ln T$$

where B is an integration constant. This is the vapor pressure law observed empirically.

β) Low temperatures. Here

$$C_{pg} \quad \frac{\gamma}{\gamma - 1}\, nR$$

and C_{ps} is generally small but not a simple function of T. Then

$$L \approx L_o + \frac{\gamma}{\gamma - 1} nRT - \int_0^T C_{ps}\, dT$$

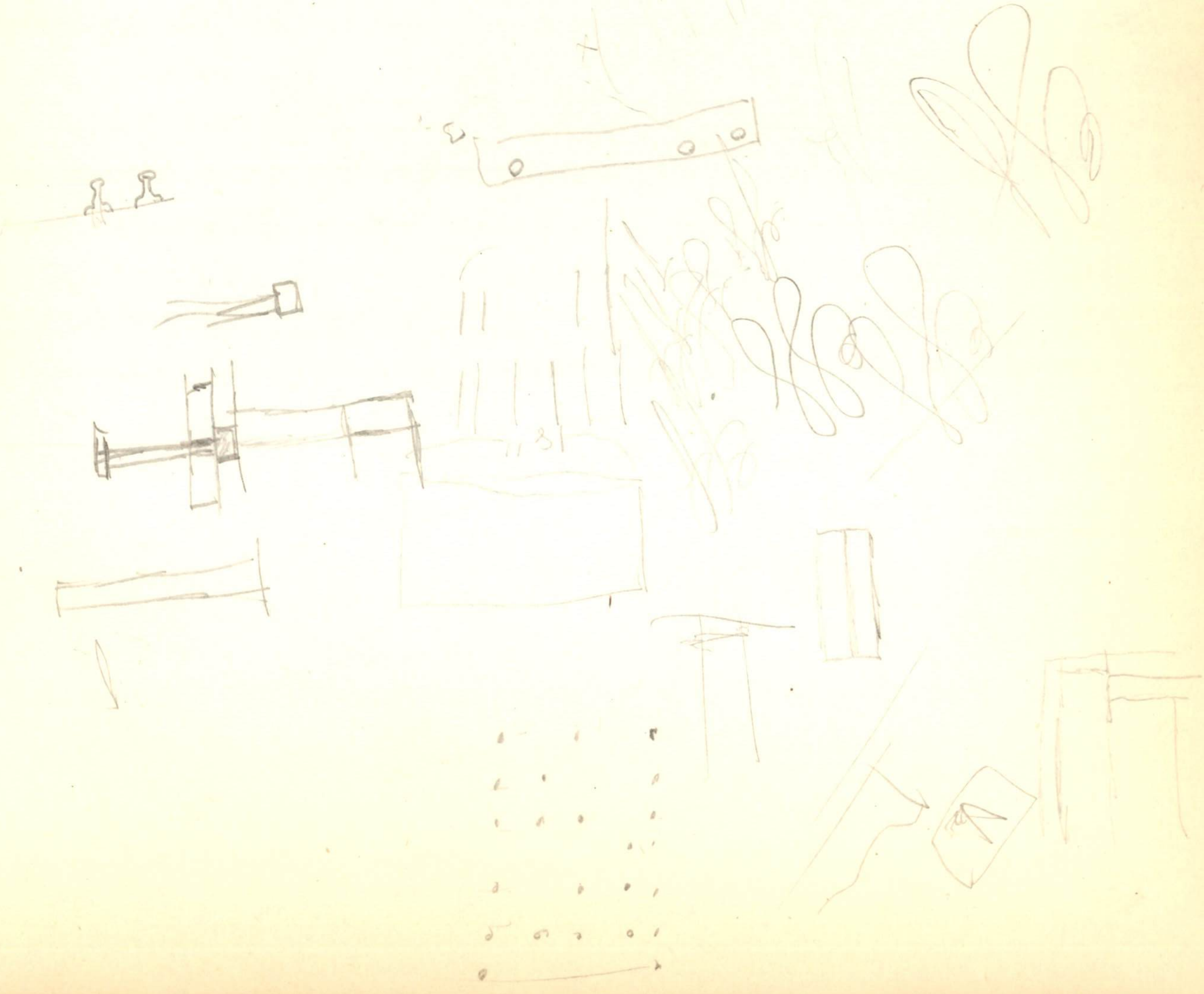
and

$$\ln P \approx -\frac{L_o}{nRT} + i + \frac{\gamma}{\gamma - 1} \ln T - b \qquad \text{(IVe34)}$$

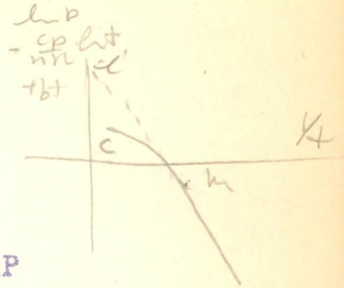
where

$$b = \frac{S_s}{nR} - \frac{1}{T} \int_0^T \frac{C_{ps}}{nR}\, dT$$

and i is called the vapor pressure constant.



These equations enable one to calculate the entropy of the vapor, for



$$S_g - S_s = \frac{L}{T} = \frac{L_o}{T} + \frac{\gamma}{\gamma - 1}\, nR - \frac{1}{T}\int_o^T C_{ps}\, dT$$

$$= \frac{L_o}{T} + \frac{\gamma}{\gamma - 1}\, nR + nRb - S_s$$

$$S_g = \frac{\gamma}{\gamma - 1}\, nR + i\, nR + \frac{\gamma}{\gamma - 1}\, n\, R\, \ell n\, T - nR\ell nP$$

But we already know that for an ideal gas

$$S_g = \frac{\gamma}{\gamma - 1}\, nR\ell nT - nR\ell nP + S_o \qquad \text{(IVe35)}$$

so that

$$S_o = (i + \frac{\gamma}{\gamma - 1})\, nR \qquad \text{(IVe36)}$$

The entropy constant of solids has been fixed by setting the entropy zero at absolute zero, and this has fixed the arbitrary constant in the entropy of the gas. The determination of S_o is important both to verify theory and to determine chemical equilibrium between gases which react. The determination of the vapor pressure constant i is therefore important. It can be done on a log P - 1/T plot, but it is best to calculate b first from specific heat data, and then to plot $\ell n(PT^{\gamma/\gamma-1}) + b$ against 1/T. This plot should be accurately straight, so the best straight line is drawn through the experimental points. The intercept of this line with the $T = \infty$ axis gives the value of i, and the slope gives L_o/nR. Some experimental results for monatomic vapors are given in the following table. It is found that the quantity

$$i_o = i - \frac{3}{2}\,\ell n\,\mathcal{M} - \ell n\, g \approx 7.97 \qquad \text{(IVe37)}$$

where $\mathcal{M}$ is the molecular weight and g is the "statistical weight", a small whole number which is obtained from band spectra, is remarkably constant and close to 7.97 in MKS units. Putting (IVe 37, 36, and 35) together one finds

$$S_o/nR \approx 11.5 + \ell n\, \frac{g}{P}\sqrt{\mathcal{M}^3 T^5} \qquad \text{(IVe38)}$$

$\ln p \doteq -\frac{L_0}{nRt} + \frac{c_p}{nR}\ln t + i - b(t)$

$p = \pi t^{5/2} e^{-L_0/nRt - b}$

$C = \frac{12\pi^4}{5}\left(\frac{t}{\Theta}\right)^3 nR$ for Hg $\Theta = 97K$, $b = 2.13 \times 10^{-15}$

$i_0 = i - \frac{3}{2}\ln \mu - \ln g \approx 7.97$ — $g = 1$ or 2

Element	ℓ_0(cal/mole)	i	mole weight μ	g	i_o
Ne		12.45	20.2	1	7.94
Na		13.32	23.0	2	7.93
Mg	34850	12.61	24.3	1	7.83
Zn	31370	14.31	65.4	1	8.04
Cd	26740	14.98	112	1	7.90
Hg		15.74	201	1	7.79
Tl		16.97	204	2	8.30
				Average	7.97

VAPOR PRESSURE CONSTANT FOR MONATOMIC VAPORS

CHAPTER V

Entropy and Probability

(a) Microstates and Macrostates

The internal energy and the entropy of substances are obtained indirectly from measurements of heat and work by integrating the equations

$$dU = \text{đ}Q - \text{đ}W \qquad \text{(Va1)}$$

and

$$dS \geqslant \text{đ}Q/T \qquad \text{(Va2)}$$

However these definitions in terms of measurements followed by an integration do not give a picture of them, so that it is impossible to visualise what they represent.

In the case of the energy we already have a picture coming from Mechanics. Here we learn first of kinetic energy and then, through an integration, of potential energy and the conservation of the two combined. Knowing matter to be composed of atoms exerting forces on each other one can readily imagine the internal energy to be the sum of the potential and kinetic energies of all the atoms

$$U = \Sigma(\phi + mv^2/2) \qquad \text{(Va3)}$$

One is tempted to assign these two forms of energy somehow to work and heat, but this, it must be said immediately, is doomed to failure, as work and heat are characteristics of a <u>process</u> which completely loose their identity in a <u>state</u>. Nevertheless the atomic picture gives us an understanding of <u>internal</u> energy which one can never obtain from thermodynamics, and the explanation of the specific heats of ideal gases are good examples of its usefulness.

It is our purpose now to derive a formula similar to (Va3) for the entropy. However this is not as intuitive, and there are two reasons for this: In the first place the formula for the entropy derives from Quantum Theory and the concept of Microstates instead of from the more familiar Mechanics. In the second place the entropy, unlike the energy, is a property non-existant in a single particle but which emerges when one has a large number of particles. One must therefore introduce new ideas of Probability and Statistics.

45

Let us first consider the distributions of N particles in a box of volume V leaving their motions aside for the moment. We begin by dividing the volume into cells whose volume a represents the most accurate determination of position we shall want to make. For example, the cells may have the volume occupied by single molecules in a crystal, so that there may be 10^{26} cells in a liter. Let the cells be numbered from 1 to $G = V/a$, let i be the number of any particular cell.

A "microstate" is defined by giving the number N_i of particles in each cell. It does not matter "which" particles are in a given cell for atoms are indistinguishable and it has no meaning to ask them to be named, but we can tell the cells by simple measurements from one corner of the box, and we can count the particles in it. The set of numbers N_i can be represented by $[N_i]$. Thus

$$[N_i] = (0,0,1,0,2,0,0,1) \qquad \text{(Va4)}$$

represents a microstate in which there are 8 cells and 4 particles. The N_i's are called occupation numbers. In general they are small numbers and are frequently zero.

In practice we observe huge numbers of atoms and therefore even greater numbers of cells. Let n be the very least number of atoms whose pressure and temperature can be measured; something of the order of 10^{10} perhaps. Let g be the corresponding number of cells. A "distribution" or "macrostate" will be defined by giving the number n_i in each group of g cells. A macrostate is the most accurate determination desirable of the state of matter in bulk, before the properties we wish to study become lost in the confusion of attempting to keep track of 10^{26} molecules.

An analogy will bring out the reason for introducing macrostates. It is possible to study paintings with a microscope and to learn many things in this way about pigments and the supporting media. However such a study will not reveal the laws of light and shadow and perspective, or even allow a classification into landscapes, interiors, and portraits. These are properties which emerge only when one views the subject from sufficiently far so as to lose sight of the individual pigment particles and see them only in groups. The Thermodynamic properties of pressure, temperature, and entropy are similar to light, shadow, and portrait in that they are properties of the groupings of particles which are best observed when we do not push observation to the limit of detail. We introduce macrostates, therefore, not because we cannot observe more detail but because, at the moment, we are studying the large scale properties of matter. It will of course have to turn out, if the properties we study are to have any meaning, that they do not depend critically on the particular value of the size g of group which we choose.

(b) Probability and Entropy:

We shall start with the postulate that all microstates have the same inherent probability. As a macrostate is less sharply defined than a microstate there will be a great many of the latter corresponding to each one of the former and the first problem is to find how many. This number, W, will be called the thermodynamic probability of the macrostate. It is not, of course, an ordinary probability as it is always a very large number, but it is nevertheless a measure of the relative likelyhood that the particles will have any given distribution rather than another one.

Let us first find the number w_j of microstates within the group g. Let the cells be numbered

$$i_1,\ i_2,\ i_3,\ ----\ i_g$$

and let the molecules be represented by n_j zeros: 0, 0, 0, ---- all identical, as indeed the molecules themselves are. Let us mix the i's and the zeros and let us arrange them in any order. For example:

$$i_1\ i_2\ i_3\ 0\ i_4\ i_5\ 0\ 0\ i_6\ i_7\ i_8\ 0\ ---------- \qquad \text{(Vb1)}$$

and let us adopt the convention that the zeros represent molecules which are located in the cell represented by the next preceding i. Thus the series (Vb1) represents the same state as (Va4). It is necessary for this convention that the first symbol of the series be an i. It can be anyone of the g i's. The remaining symbols can be arranged in any order, so that there are in all

$$g(g + n_j - 1)!$$

sequences such as (Vb1). Each sequence represents a microstate, but there are many repetitions: Permuting the i's was unnecessary as all the microstates can be represented by sequences in which the cells are in the order of their numbers. Permuting the zeros obviously makes no difference. Thus

$$w_j = \frac{g(g + n_j - 1)!}{g!\ n_j!} \qquad \text{(Vb2)}$$

This is a very large number, and it will be convenient to use Stirling's approximation

$$n! = \sqrt{2\pi n}\ (n/e)^n \qquad \text{(Vb3)}$$

$$w_j = g\sqrt{\frac{g+n_j-1}{2\pi g n_j}}\left(\frac{g+n_j-1}{e}\right)^{g+n_j-1}\left(\frac{e}{g}\right)^g\left(\frac{e}{n_j}\right)^{n_j}$$

$$w_j = \frac{e}{\sqrt{2\pi n_j}}\left(\frac{g+n_j-1}{g}\right)^{g+n_j-1/2}\left(\frac{g}{n_j}\right)^{n_j}$$

and taking logarithms

$$\ell n\ w_j = (g+n_j-\tfrac{1}{2})\,\ell n(1+\frac{n_j-1}{g})+ n_j\ \ell n\frac{g}{n_j} - \ell n\frac{\sqrt{2\pi n_j}}{e} \qquad \text{(Vb4)}$$

In this expression we wish to neglect 1 compared to n_j. This imposes a minimum size to the group which is much less severe than the experimental one. Introducing also the notation

$$\bar{N}_j = n_j/g \tag{Vb5}$$

for the average occupation number of the group, we have

$$\ln w_j = g\left[(1+\bar{N}_j)\ln(1+\bar{N}_j)-\bar{N}_j \ln \bar{N}_j\right] \tag{Vb6}$$

This gives the number of ways w_j in which the n_j molecules may be disposed in the g cells of the group.

We now wish to find the number of ways W in which the N molecules may be disposed in the G cells such that each group of g cells has the number n_j appropriate to that group. The set of numbers n_j define the distribution, or macrostate, and W is the number of microstates which correspond to it. But W is just the product of the G/g w_j's

$$W = w_1\, w_2 \cdots w_{G/g} \tag{Vb7}$$

$$\begin{aligned}\ln W &= \sum_1^{G/g} g\left[(1+\bar{N}_j)\ln(1+\bar{N}_j)-\bar{N}_j \ln \bar{N}_j\right] \\ &= \sum_1^{G}\left[(1+\bar{N}_i)\ \ln(L+\bar{N}_i) - \bar{N}_i \ln \bar{N}_i\right]\end{aligned} \tag{Vb8}$$

The first line of (Vb8) is a sum over all the groups of cells g. But as the quantity summed is identical for each cell in a group, it can equally well be summed over the cells and thus do away with the factor g. The last line now does not contain the group size g any more: it has gone out to the extent that 1 could be neglected compared to n_j in formula (Vb4). The vanishing of g as the groups contain more and more particles corresponds to the disappearance of the grains in a painting as one views it from further away.

One further simplification may yet be made. In all cases ordinarily encountered the average occupation numbers are very small. Then

$$\ln(1+\bar{N}_i) \approx \bar{N}_i \tag{Vb9}$$

and

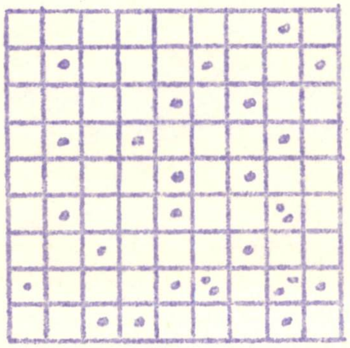
$$\ln W = \sum_1^{G} \bar{N}_i(1-\ln \bar{N}_i) \tag{Vb10}$$

We shall now give the statistical definition of the entropy as

$$\boxed{S = k \ln W} \qquad \text{(Vb11)}$$

where $\boxed{k = 1.381 \times 10^{-23} \text{ Joules/degree}}$

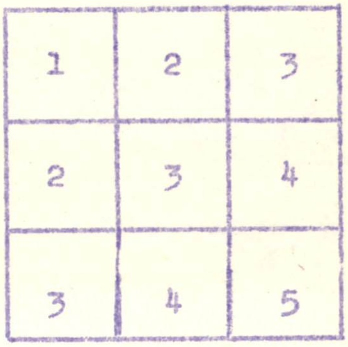
It is not possible to prove that this definition is identical with the thermodynamic one, and all that will be done here is to show that it leads to the same expression for the entropy of an ideal gas



Microstate

$G = 81$

$N = 27$



1	2	3
2	3	4
3	4	5

Macrostate

$g = 9$

Figure Vb

To work out an example in detail consider the microstate with 81 cells and 27 particles shown in figure Vb. Taking groups of 9 cells we find the following values for n_j and for w_j, using the exact formula (Vb2):

$j =$	1	2	3	4	5	6	7	8	9
$n_j =$	1	2	3	2	3	4	3	4	5
$w_j =$	9	45	165	45	165	495	165	495	1287

Taking logarithms we have

$$\ln W = \ln 9 + 2\ln 45 + 3\ln 165 + 2\ln 495 + \ln 1287$$
$$= 45.098$$

$$S = 6.23 \times 10^{-22} \text{ Joules/degree}$$

Dividing the same microstate into groups of 8 cells (with one left over!) the following values of n_j were found:

$$n_j = 1, 1, 3, 2, 3, 3, 4, 2, 4, 4$$

which leads to $\ell n\, W = 42.801$, a 5 per cent difference due to the very small number of particles.

c) The Most Probable Distribution

Different distributions have different probabilities W. To take an extreme example consider the distribution in which all the particles fall in the cells of one group. Then

$$\overline{N}_1 = N/g \quad \text{in that group}$$

$$\overline{N}_1 = 0 \quad \text{in all other groups}$$

and

$$\ell n\, W_1 = N\,(1 - \ell n\, N/g) \qquad \text{(Vc1)}$$

On the other hand consider the macrostate in which the distribution is uniform. Then

$$\overline{N}_1 = N/G$$

and

$$\ell n\, W_u = N\,(1 - \ell n\, N/G) \qquad \text{(Vc2)}$$

Probability favors the uniform distribution, and the ratio is given by

$$\frac{W_u}{W_1} = \left(\frac{G}{g}\right)^N \qquad \text{(Vc3)}$$

This, in general, is a colossal number. Even in the example given in the last section, and for which the condition (Vb9) does not hold,

$$W_1 = \frac{35!}{27!\,8!}\,, \quad W_u = (165)^9,$$

so that

$$\frac{W_u}{W_1} = 38.5 \times 10^{10}$$

When we are considering distributions of 10^{10} particles these relative probabilities become tremendous. A non-equilibrium state, as defined in thermodynamics, is merely one of low probability. If left to itself it is extremely likely ("certain" would be a more "realistic" term) to revert to a more probable distribution and therefore to increase in entropy. The most probable distribution is the equilibrium state.

To find the most probable distribution we seek the maximum of (vb11) by differentiating with respect to the $\bar{N}_i$'s and equating to zero

$$\delta S = -k \sum \ln \bar{N}_i \, \delta \bar{N}_i = 0 \qquad \text{(Vc4)}$$

The $\bar{N}_i$'s represent changes in the numbers of particles in each group due to all possible small changes in the distribution. They are not entirely arbitrary as we are dealing with a fixed number N of particles so that

$$N = \sum \bar{N}_i \qquad \text{(Vc5)}$$

and therefore

$$\sum \delta \bar{N}_i = 0 \qquad \text{(Vc6)}$$

Eq. (Vc6) is called a constraint placed on eq. (Vc4) which restricts the values which can be given to the $\delta \bar{N}_i$'s. Equations (Vc4) and (Vc6) may be solved by the method of Lagrange multipliers: multiplying eq. (Vc6) by an undetermined constant α, and subtracting (Vc4) we obtain

$$\sum (\alpha + k \ln \bar{N}_i) \, \delta \bar{N}_i = 0 \qquad \text{(Vc7)}$$

This equation is satisfied for any $\delta \bar{N}_i$ if

$$\ln \bar{N}_i = -\alpha/k \qquad \text{(Vc8)}$$

$$\bar{N}_i = e^{-\alpha/k} \qquad \text{(Vc9)}$$

and we can satisfy the constraint by substituting (Vc9) in (Vc5)

$$N = \sum e^{-\alpha/k} = \frac{V}{a} e^{-\alpha/k} \qquad \text{(Vc10)}$$

and using this to determine α

$$\alpha = -k \ln Na/V \qquad \text{(Vc11)}$$

Eq. (Vc9) shows that the distribution of maximum entropy is uniform (the $\bar{N}_1$'s are all the same) and substituting from (Vc11) in (Vc9) gives

\# micro in macro

$$\bar{N}_1 = Na/V \qquad \text{(Vc12)}$$

Eq. (Vb10) then gives the maximum value of the entropy.

nR energy/°/atom N = nA

$$S = Nk(1-\ln Na/V) \qquad \text{(Vc13)}$$

This equation agrees with that obtained from Thermodynamics when applied to an ideal monatomic gas

energy/°/mole

$$S = nR \ln (VT^{3/2}) + S_o \qquad \text{(Vc14)}$$

provided k has the value 1.381 x 10^{-23} Joules per degree, and except that it does not contain the temperature, as is to be expected as thermal motions have been specifically neglected.

If two identical volumes of gas are put in communication so as to constitute a single system having 2N particles in a volume 2V, it is seen from (Vc13) that the entropy simply doubles, so entropy as we have defined it is extensive.

On the other hand, if a given amount of gas expands isothermally from V_1 to V_2 there is an increase of entropy.

$$\Delta S = nR \ln V_2/V_1$$

The expansion may take place in any of several ways: it may be "free" as when a gas expands into a vacuum. In this case there is no heat or work involved and the Clausius inequality holds. On the other hand, the gas may expand against a piston, doing work. In this case, heat must be added in order to keep the temperature constant, and if the process is reversible

$$\Delta Q = T \Delta S = nRT \ln V_2/V_1$$

$$\Delta W = \Delta Q$$

The net result of this process has been to convert heat into work. The motions of the particles of the gas have remained unchanged as has their total energy. But their positions are less well specified as they are distributed over a large volume. Heat, which is random motion, is convertible into work, which is ordered motion, only at the expense of increased randomness of position.

d) Entropy of Mixing

Consider now particles of two kinds and let N' of the first kind, and N'' of the second be contained in the volume V. If these particles have no appreciable size and do not attract or repel each other we can go through the argument of the preceding paragraph for each one independently and show that the most probable distribution is that in which each of the two kinds of particles are uniformly distributed in the whole volume and that the entropy of this distribution is

$$\boxed{S = N'k\,(1 - \ln N'a/V) + N''\,k\,(1 - \ln N''\,a/V)} \qquad \text{(Vd1)}$$

Let

$$N = N' + N''$$

$$x = N'/N$$

$$1-x = N''/N$$

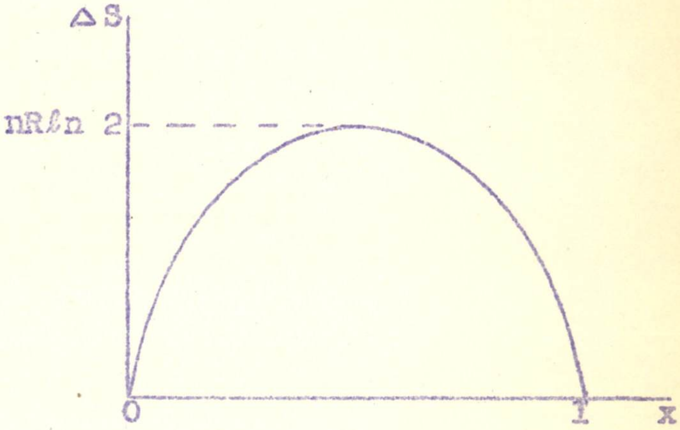
x and 1-x are the mole fractions of two gases whose molecules are in the ratio of N' to N''. Substituting in (Vd1) we obtain

$$S = Nk\left[1 - \ln Na/V - x \ln x - (1-x) \ln (1-x)\right] \qquad \text{(Vd2)}$$

It is seen that the fact that the particles are of two different kinds results in a larger entropy by an amount

$$\boxed{\Delta S = -nR\left[x \ln x + (1-x) \ln (1-x)\right]}$$

This is a positive quantity because the logarithms are negative, and is called the entropy of mixing. It follows if the distributions of the two kinds of molecules are independent of each other, that is that they do not attract or repel.



Entropy of Mixing

Fig. Vd1

To see the meaning of the entropy of mixing imagine a volume V separated by a partition into volumes xV and (1-x)V, and let there be N' particles of the first kind in one part and N'' of the second kind in the other. The entropy is then

$$S = N'k\left(1 - \ln \frac{N'a}{xV}\right) + N''k\left(1 - \ln \frac{N''a}{(1-x)V}\right)$$

$$= Nk\left(1 - \ln \frac{Na}{V}\right) \qquad \text{(Vd3)}$$

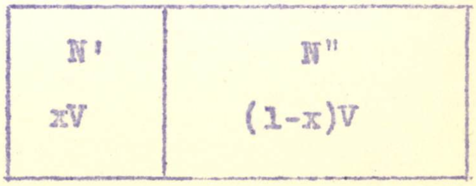


Fig. Vd2

That is, the entropy is the same as though there were N particles all alike in the total volume V. Now if the partition is removed the particles can redistribute themselves (inter diffuse) so as to attain the larger entropy (Vd2). It is therefore probable, though not certain, that they will do so. How probable can be seen by a numerical example. Let the partition divide the volume in equal parts with half a mole on either side. Then the entropy of mixing is

$$\triangle S = Nk \ln 2 = 1{,}375 \text{ cal/deg.mole}$$

This is not a large number. However, if we substitute in equation (Vb11), and call W_m and W_s the probabilities of the mixed and separated states, respectively

$$\ln W_m/W_s = \triangle S/k = N \ln 2$$

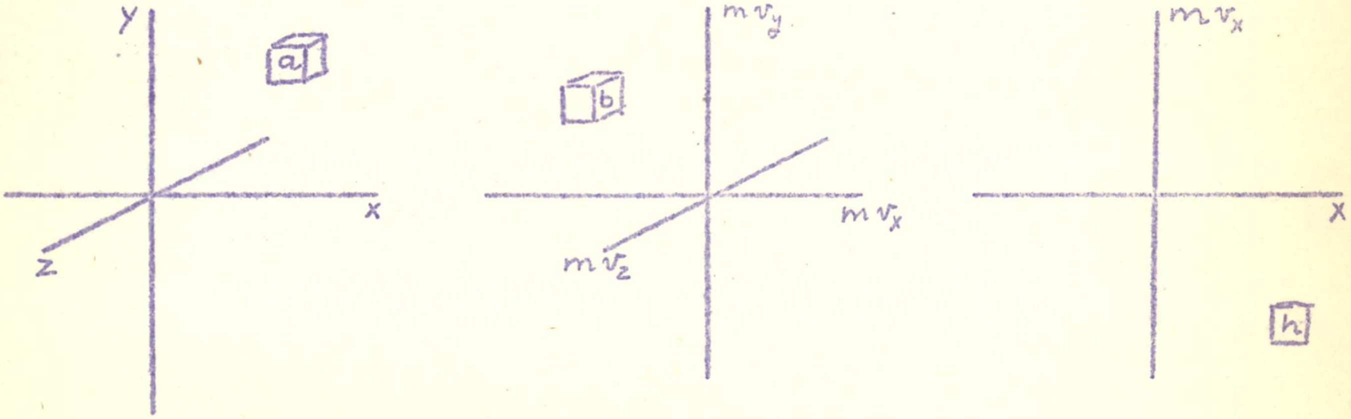
or

$$\frac{W_m}{W_s} = 2^N \approx 10^{10^{23}}$$

The probability of diffusion is therefore overwhelming.

e) Distributions in Phase Space

The theory must now be extended to include the motions as well as the positions of the particles. This is done by extending the notion of a cell so that it specifies, to as high an accuracy as possible, the momentum as well as the position of a particle. This is best visualized by imagining a six-dimensional hyperspace called



Phase Space

Fig. Ve

phase space, whose axes are x, y, z, mv_x, mv_y, mv_z. Projections of this hyperspace can then be represented by drawings, as in figure Ve. Parts 1 and 2 of this figure are the three-dimensional space and momentum projections, and 3 is a two-dimensional projection including one coordinate and the corresponding momentum. There are three projections similar to this one. A cell in this space is a six-dimensional hypervolume $\Delta x \Delta y \Delta z \; m^3 \Delta v_x \Delta v_y \Delta v_z$ whose projections are the cube a in space and the cube b in momentum, or three similar rectangles h corresponding to x, y, and z. Naturally

$$\Delta x \Delta y \Delta z \, m^3 \Delta v_x \Delta v_y \Delta v_z = ab = h^3 \qquad \text{(Ve1)}$$

For a particle to be in this cell its position and momentum must be simultaneously in the cubes a and b.

The quantity h has the dimensions of action, which is already familiar from the Principle of Least Action in Mechanics. It acquires, however, an even greater significance in Quantum Theory where it is shown that there is an absolute experimental limit to the accuracy with which the simultaneous position and momentum of a particle along any axis can be determined, and this limit is defined by the relation

$$\Delta x \, m \Delta v_x \geqslant \underline{h = 6.624 \times 10^{-27} \text{ erg sec.}} \qquad \text{(Ve2)}$$

The cells, which were introduced in ordinary space for the mathematical convenience in defining microstates, have a true physical meaning in phase space. When a microstate is specified the system is as fully defined as it ever can be.

With this new definition of a cell the entire argument of section b carries through as before: the cells are collected into groups which represent the desirable limit of detail so that the Thermodynamic properties emerge. The occupation numbers of the cells, N_i, are replaced by their average values over the groups, $\bar{N}_i$, and the thermodynamic probability W, defined as the number of microstates which correspond to the same macrostate, is found to be given by

$$\boxed{\ln W = \sum \bar{N}_i (1 - \ln \bar{N}_i)} \qquad \text{(Ve3)}$$

The entropy is then

$$\boxed{S = k \ln W} \qquad \text{(Ve4)}$$

The above formulae apply to any macrostate, but we are particularly interested in the equilibrium state, which is that of maximum entropy. Here the development differs from that of section c because we must introduce an additional constraint which prevents the points from spreading out all over momentum space. Besides having a finite number of particles N the system has a finite energy U. Accordingly there are two constraints

$$N = \sum \bar{N}_i \qquad \text{(Ve5)}$$

and

$$U = \sum u_i \bar{N}_i \qquad \text{(Ve6)}$$

where u_i is the energy of a particle in the cell i. For simplicity we shall consider only free particles, so that

$$u_i = m\, v_i^2/2 \qquad \text{(Ve7)}$$

and the results will then apply to an ideal monatomic gas.

The conditions for a maximum are now

$$\delta S = -k \sum \ell n\, \bar{N}_i\, \delta \bar{N}_i = 0 \qquad \text{(Ve8)}$$

$$\delta N = \sum \delta N_i = 0 \qquad \text{(Ve9)}$$

$$\delta U = \sum u_i\, \delta \bar{N}_i = 0 \qquad \text{(Ve10)}$$

Applying the method of Lagrange multipliers we multiply (Ve8) by -1, (Ve9) by α, (Ve10) by β, and add

$$\sum (\alpha + \beta u_i + k\, \ell n\, \bar{N}_i)\, \delta \bar{N}_i = 0 \qquad \text{(Ve11)}$$

For this equation to be satisfied for all variations $\delta \bar{N}_i$ we must have

$$k\, \ell n\, \bar{N}_i = -\alpha - \beta u_i \qquad \text{(Ve12)}$$

or

$$\bar{N}_i = e^{-\frac{\alpha + \beta u_i}{k}} \qquad \text{(Ve13)}$$

where α and β are to be determined by substitution in (Ve5) and (Ve6). This distribution, in which the average occupation numbers decrease exponentially with the energy, is called a Boltzmann distribution. As equation (Ve7) has not been used in deriving this, the Boltzmann distribution is valid for equilibrium almost universally; the only restriction being that of equation (Vb9) which requires the average occupation numbers to be small. Substituting (Ve13) in (Ve3) and (Ve4) gives

$$S = \sum \bar{N}_i\, (k + \alpha + \beta u_i) = (k + \alpha)\, N + \beta\, U \qquad \text{(Ve14)}$$

(f) Integration for α and β

The determination of α and β must be done by substituting (Ve13) in (Ve5) and (Ve6). Performing the summations may be difficult, but if the $\overline{N}_i$ are sufficiently smooth functions of the coordinates of the cell the summation may be replaced by an integration. By simple proportions the number d^6N of particles in the volume element $dx\ dy\ dz\ m^3\ dv_x\ dv_y\ dv_z$ is proportional to the number $\overline{N}_i$ in h^3. Thus

$$d^6N = \frac{m^3}{h^3} e^{-\frac{\alpha+\beta u}{k}} dx\ dy\ dz\ dv_x\ dv_y\ dv_z \qquad \text{(Vf1)}$$

which is immediately integrated over the volume to

$$d^3N = V \frac{m^3}{h^3} e^{-\frac{\alpha+\beta u}{k}} dv_x\ dv_y\ dv_z \qquad \text{(Vf2)}$$

Introducing

$$u = \frac{m}{2} (v_x^2 + v_y^2 + v_z^2) \qquad \text{(Vf3)}$$

$$d^3N = V \frac{m^3}{h^3} e^{-\alpha/k} \left[e^{-mv_x^2/2k}\ dv_x\right] \left[e^{-mv_y^2/2k}\ dv_y\right] \left[e^{-mv_z^2/2k}\ dv_z\right] \qquad \text{(Vf4)}$$

The brackets are functions of one variable only and each one integrated from $-\infty$ to $+\infty$ gives $\sqrt{2\pi k/m}$.

$$\int_0^\infty x^n e^{-ax^2} dx =$$

$1/2 \sqrt{\pi/a}$ for $n = 0$	$1/2a$ for $n = 1$
$1/4 \sqrt{\pi/a^3}$ " $n = 2$	$1/2a^2$ " $n = 3$
$3/8 \sqrt{\pi/a^5}$ " $n = 4$	$1/a^3$ " $n = 5$
$15/16 \sqrt{\pi/a^7}$ " $n = 6$	$3/a^4$ " $n = 7$

Table V

Thus

mass

bolt cns

$$N = V \left(\frac{2\pi mk}{h^2\beta}\right)^{3/2} e^{-\alpha/k} \qquad \text{(Vf5)}$$

planks cns

The energy is given by

$$d^3 U = u\, d^3N = V \frac{m^3}{h^3} u\, e^{-\frac{\alpha+\beta u}{k}} dv_x\, dv_y\, dv_z \qquad \text{(Vf6)}$$

The three components of the energy u lead to three identical integrals, so that

$$U = \frac{3V}{2} \frac{m^4}{h^3} \left[\int v_x^2 \; e^{-mv_x^2/2k}\, dv_x\right] \left[\int e^{-mv_y^2/2k}\, dv_y\right] \left[e^{-mv_z^2/2k}\, dv_z\right]$$

$$= \frac{3Vk}{2\beta} \left(\frac{2\pi mk}{\beta h^2}\right)^{3/2} e^{-\alpha/k} = \frac{3Nk}{2\beta} \qquad \text{(Vf7)}$$

Solving for α and β

$$\beta = \frac{3Nk}{2U} \qquad \text{(Vf8)}$$

$$\alpha = k \ln \frac{V}{N} + \frac{3}{2} k \ln \frac{4\pi mU}{3h^2N} \qquad \text{(Vf9)}$$

(g) Thermodynamic Variables

Substituting for α and β in (Ve14) gives

$$S = N(\alpha + 5k/2) = Nk\left[\frac{5}{2} + \frac{3}{2} \ln \frac{4\pi mU}{3Nh^2} + \ln \frac{V}{N}\right] \qquad \text{(Vg1)}$$

This is an equation connecting the three specific quantities S/N, U/N, V/N. It is therefore the equation of the Gibbs surface for an ideal gas, and we know that the pressure and temperature are the slopes of the tangent plane. Differentiating

$$dS = Nk\left(\frac{dV}{V} + \frac{3}{2}\frac{dU}{U}\right) \qquad \text{(Vg2)}$$

or

$$dU = \frac{2}{3}\frac{U}{Nk}\, dS - \frac{2}{3}\frac{U}{V}\, dV$$

$$= \frac{dS}{\beta} - \frac{Nk}{\beta V}\, dV \qquad \text{(Vg3)}$$

Comparing this with

$$dU = TdS - PdV \qquad \text{(Vg4)}$$

we see immediately that

$$\left.\begin{aligned} \beta &= 1/T \\ U &= \tfrac{3}{2}\,NkT \\ PV &= NkT \end{aligned}\right\} \qquad \text{(Vg5)}$$

Thus the **Lagrange** multiplier β has a physical meaning and we have derived the ideal gas law from statistics alone without any detailed consideration of collisions, although, to be sure, the derivation was not as direct as that of paragraph (IIg6).

On the other hand the determination of the entropy constant i of an ideal gas (Paragraph IVe6) was not easy. It is now already contained in equation (Vg1). Substituting for U and V from (Vg5)

$$S = Nk\left[\frac{5}{2} + \frac{5}{2}\,\ln kT + \frac{3}{2}\,\ln\frac{2\pi m}{h^2} - \ln P\right] \qquad \text{(Vg6)}$$

whence

$$\begin{aligned} i &= \frac{5}{2}\,\ln k + \frac{3}{2}\,\ln\frac{2\pi m}{h^2} \\ &= i_0 + \frac{3}{2}\,\ln \mathcal{M} \end{aligned} \qquad \text{(Vg7)}$$

This is known as the Sackur-Tetrode equation. It is to be noted that the constant h^3 which measures the size of the microcells has cancelled out of the theory almost as completely as the size gh^3 of the macrocells. It does not remain in the energy or the equation of state (Vg5) but enters only in the entropy constant i, a quantity difficult of experimental determination. Taking the value of h from photoelectric measurements one finds

$$\underline{i_0 = 7.862 \text{ MKS}} \qquad \text{(Vg8)}$$

Comparing this with the values obtained from vapor pressure measurements (p.97) we see that it falls within the range of these determinations. We are thus justified in taking the microcells of size h^3, or, more precisely, the definitions of the Thermodynamic probability and entropy given by (Ve3) and (Ve4) are consistent with Nernst's choice of a crystal at absolute zero as the reference point for measuring entropies.

(h) Numerical Check

If the values of α and β given by (Vf5) and (Vf8) are substituted in (Ve13) one obtains for the average occupation numbers

$$\overline{N}_i = \frac{N}{V} \frac{h^3}{(2\pi mkT)^{3/2}} e^{-u_i/kT} \qquad \text{(Vh1)}$$

Let us substitute values for helium at the critical point ($v_c = 61.5$ cm^3/mole, $T_c = 5.19^\circ$K) in this formula. As the formula should apply only to ideal gases this is not a true test of the formula, but the results are significant. At this point $N/V = 0.98 \times 10^{22}$ atoms/cm^3 and

$$\overline{N}_i \approx 0.56\, e^{-u_i/kT}.$$

The cells of energy less than kT are therefore about half occupied, half empty. We are therefore not justified here in taking $\ln(1+\overline{N}_i) \approx \overline{N}_i$. However for any ideal gas either T, V, or $\mathcal{M}$ or all three, are much larger than the values chosen here and therefore the average occupation numbers really are much less than one.

Evaluating g is somewhat more difficult, but suppose one can measure the pressure and temperature of a drop of liquid helium one micron in diameter. N/V for liquid helium is about $.43 \times 10^{22}$ atoms/cm^3 so the drop will contain 10^9 atoms. The number of cells is roughly twice this, so we are quite safe in using Sterling's approximation.

CHAPTER VI

Maxwell-Boltzmann Statistics

(a) Maxwell Distribution

1. The Distribution Function

Substituting for α and β from (Vf5) and (Vf8) in (Vf2) one obtains for the number of particles d^3N in the velocity range $dv_x\, dv_y\, dv_z$

$$d^3N = N\left[\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\right] dv_x\, dv_y\, dv_z \qquad \text{(VIa1)}$$

The quantity in square brackets is called the distribution in velocity. In particular it is a Maxwell distribution. We can distinguish now between "microstate" (Va4), "macrostate" (Vh1), and "distribution" (VIa1) and these are represented schematically, and in only one dimension, in figure VIa1. The vertical lines at the bottom of this figure represent molecules, each one in a cell at the appropriate velocity. The spaces between the lines are empty cells. This is the picture of a microstate. There are no numbers but zeros and ones, and possibly some higher whole numbers, associated with it. The cells are then divided into groups and the average occupation numbers $\bar{N}_i$ computed. These are plotted vertically as the step-function. This is the picture of a macrostate, although in practise the steps are much less coarse than indicated. The midpoints of the steps may now be joined by a smooth curve, and this is the distribution function. It is obtained mathematically by imagining the groups and the steps to become smaller and smaller until the step-function approximates the smooth curve, although this is not possible physically because of the discontinuous nature of the microstate. These steps in converting a microstate to a smooth function have their exact counterpart in radio communication where a pulse frequency modulation signal (the microstate) has to be converted in the receiver to a smooth audio signal.

Expression (VIa1) may be broken into similar factors, each one containing only one component of velocity. Let

$$f(v_x) = \sqrt{\frac{m}{2\pi kT}}\; e^{-mv_x^2/2kT} \qquad \text{(VIa2)}$$

Then $$d^3N = N\, f(v_x)\, dv_x\, f(v_y)\, dv_y\, f(v_z)\, dv_z \qquad \text{(VIa3)}$$

This means that the distribution in v_x is independent of the y and z components of velocities of the molecules. Considering only the components v_x and v_y and plotting the distribution vertically above the $v_x\, v_y$ plane (Fig. VIa2) one obtains a surface with a maximum above the

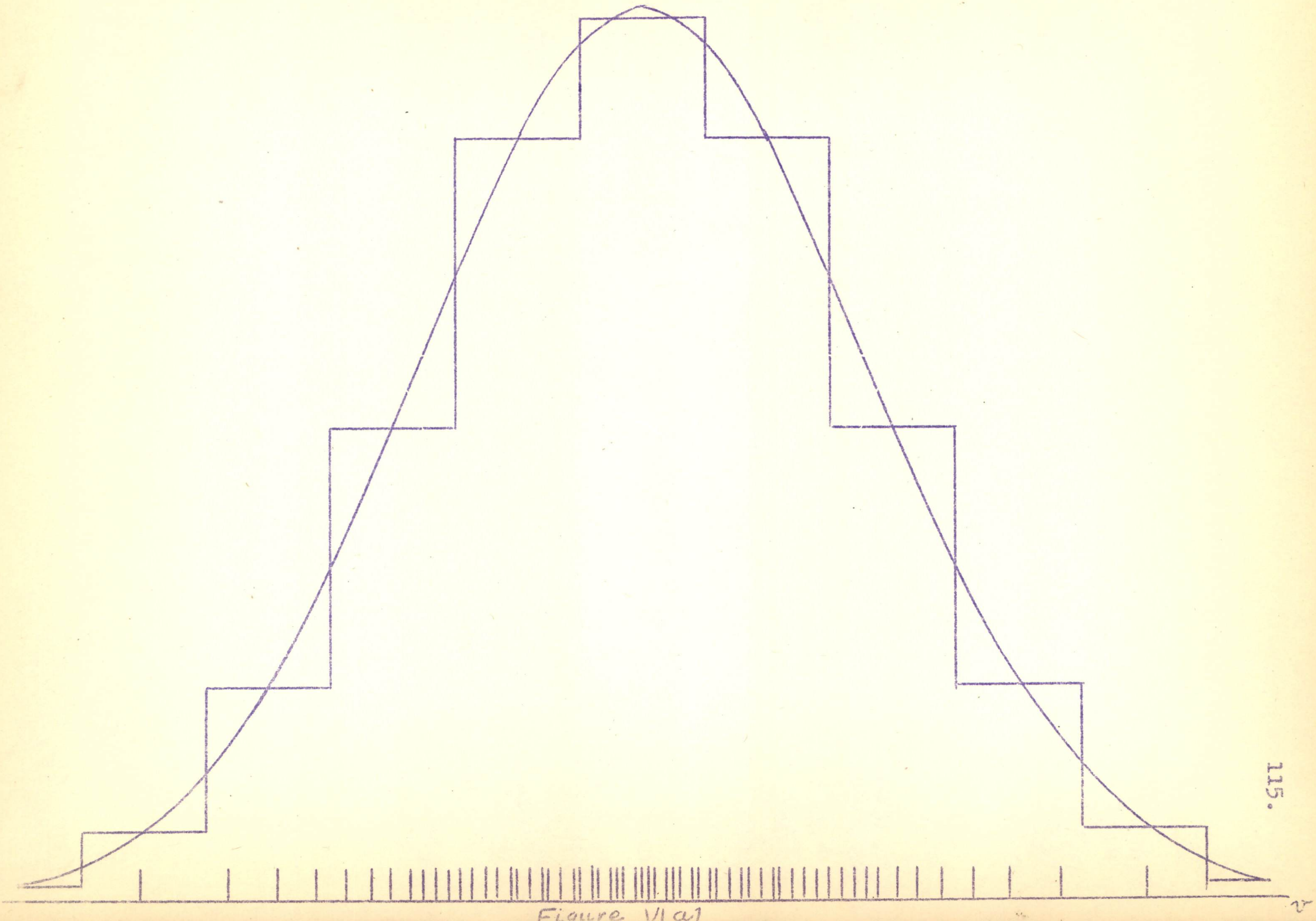


Figure VI a1

origin. Equation (VIa3) states that the section of this surface by any plane perpendicular to v_y, in fact by any vertical plane at all, will give a similar curve. This feature of the Maxwell distribution is expressed by saying that the three components of the velocity are independent. It is an exclusive feature of the Maxwell distribution.

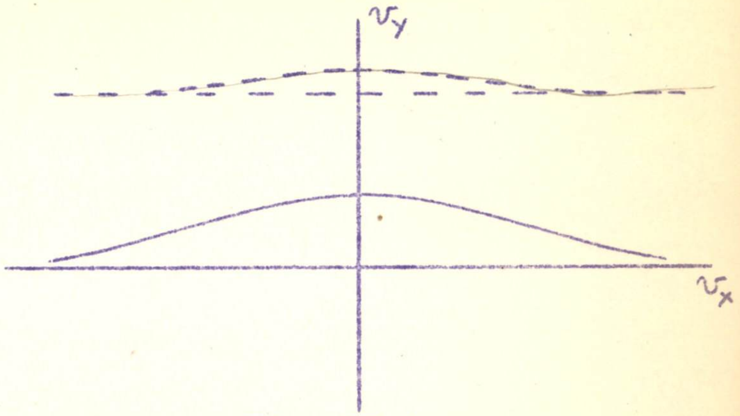


Fig. VIa2

Referring to table Vf it is seen that

$$\int_{-\infty}^{+\infty} f(v_z)\, dv_z = 1 \qquad \text{(VIa4)}$$

Integrating (VIa3) with respect to v_y and v_z one obtains

$$dN = N\sqrt{\frac{m}{2\pi kT}}\; e^{-mv_x^2/2kT}\, dv_x \qquad \text{(VIa5)}$$

This is the distribution in one component of velocity, and it is seen to be similar to the distribution in vector velocity precisely because the components are independent.

Changing to polar coordinates one may write

$$d^3N = N\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\, v^2 \sin\theta\, d\theta\, d\phi\, dv \qquad \text{(VIa6)}$$

which is, of course, the same thing as (VIa1). One may now integrate with respect to θ and ϕ and obtain the distribution in speed

$$dN = N\left[\sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2} e^{-mv^2/2kT}\, v^2\right] dv \qquad \text{(VIa7)}$$

This is also a Maxwell distribution, although it is a different function of the speed than (VIa1) is of the velocity. This is because (VIa1) gives the number of velocity vectors terminating in a small cube $dv_x\, dv_y\, dv_z$ of the same size no matter where located in velocity space, whereas (VIa7) gives the number terminating in a spherical shell of thickness dv, and the volume of this shell increases with its radius v. (VIa7) is plotted in figure (VIa3) and has a maximum at

$$v_p = \sqrt{2kT/m} \qquad \text{(VIa8)}$$

$-\sqrt{\frac{2}{\pi}}\left(\frac{h\nu}{kT}\right)^{\beta/2}\frac{2kT}{h\nu c^2}\,e$

$\cancel{\sqrt{\frac{2}{\pi}}}\ \sqrt{\frac{2h}{kT\pi}}$

[illegible]

E12. Compare the formula for the rate of efflux of gas through a small hole with Torricelli's formula for the flow of fluid through a hole, using the same pressure and density for both cases. Explain why the formulae differ in the direction that they do.

E13. Compute the maximum rate of evaporation of mercury at 0°C and at -20°C. At 0°C the vapor pressure of mercury is 185×10^{-6} mm of mercury and the latent heat is 80.5 cal/gm.

E14. Tungsten at 2500°K will emit 0.28 amp/cm^2 and the work function is 4.5 volts. What is the vapor pressure of the electron gas evaporating from Tungsten and what is the latent heat in calories per mole?

E15. The stratosphere extends from 10 km to 60 km above the earth's surface and the aurora borealis has been observed in the ionosphere up to altitudes of 500 km. Assuming the atmosphere to have a uniform temperature of -53°C calculate the pressure and the molecular densities of nitrogen, oxygen, and hydrogen at these three altitudes. The proportions by volume of these elements in the atmosphere at sea level are:

VI 65

78 per cent N_2, 21 per cent O_2, .01 per cent H_2.

E16. The gravitational potential of a molecule of mass m in the field of the earth is $-mgR^2/r$ where $R = 6380$ km is the radius of the earth. Show that this formula leads to a finite atmospheric pressure at infinity. Calculate the molecular density at infinity using the data of problem E15.

E17. Find the mean forward velocity $\overline{v}_x$ of the particles which escape through a small hole into a vacuum.

E18. Show that the average kinetic energy of the particles which escape through a hole is 2kT.

E19. In a molecular beam experiment the source is a tube at 400°K containing hydrogen at a pressure $p_s = 0.15$ mm of mercury. The tube has a slit 30 x .025 mm which opens on a highly evacuated space in which experiments on the beam can be performed. Opposite the source slit and 1 meter away from it is the detector slit, also 30 x .025 mm in size, and this opens on a small chamber in which the equilibrium pressure p_d can be measured.

a) What is the discharge rate of the source slit in cubic centimeters per second and micrograms per second?

b) At what rate does hydrogen reach the detector slit, in micro-micro gms/sec and in number of molecules/sec?

c) How many molecules which are going to reach the detector are in the space between source and detector at any instant.

d) What is the equilibrium pressure in the detector chamber so that the rate of arrival of hydrogen is equal to its rate of leakage?

$\frac{C_v}{n}$ $C_v = -\left(\frac{\partial (P.E.)}{\partial T}\right)_V +$

$\frac{3}{2}RT$ for mono

$\frac{5}{2}RT$ for bi

$\frac{6}{2}RT$ for poly.

$\frac{C_v}{N}$ C_v for solid $= 3\nu R$ Dulong + Petit's law

$\nu = \#$ atoms/mole

$\frac{C_v}{N\nu} = 3R$ - per generator

This is the most probable speed, whereas the most probable velocity is, of course, zero.

Substituting the energy

$$\left.\begin{aligned} u &= mv^2/2 \\ du &= mv\,dv \end{aligned}\right\} \qquad \text{(VIa9)}$$

in (VIa7) gives the distribution in energy

$$dN = N\left[\frac{2}{(kT)^{3/2}}\sqrt{\frac{u}{\pi}}\,e^{-u/kT}\right]du \qquad \text{(VIa10)}$$

and is shown plotted in (VIa3). This curve looks different from figure (VIa3) because shells of equal energy difference decrease in thickness as the energy increases. The maximum of this curve is at

$$u_p = kT/2 \qquad \text{(VIa11)}$$

which is the most probable energy.

All these curves and functions portray the same Maxwell Distribution.

2. Average Values

The distribution function gives the number of particles having any velocity. It is then easy to get the average value of any quantity X depending in any way on the velocity by applying the formula

$V_{ave} = \frac{1}{N}\int_0^v |V|\,dN$

$$X_{ave} = \frac{1}{N}\int X\,dN \qquad \text{(VIa12)}$$

As examples, the average speed is

$\frac{kT}{\pi m} = \frac{PV}{\pi M}$

$$v_{ave} = \int_0^\infty \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2} e^{-mv^2/2kT}\,v^3\,dv = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8PV}{\pi M}} = \sqrt{\frac{8RT}{\pi M}} \qquad \text{(VIa13)}$$

and the average energy is

$$\overline{u} = \int_0^\infty \sqrt{\frac{m}{2\pi kT}}\,\frac{m^2v^4}{kT}\,e^{-mv^2/2kT}\,dv = \frac{3}{2}kT \qquad \text{(VIa14)}$$

$V_{rms} = \sqrt{\frac{3kT}{2m}}$

This checks with the total energy $\frac{3}{2}NkT$ and gives for the root mean square velocity

$$v_{rms} = \sqrt{3kT/m} = \sqrt{3PV/M} \qquad \text{(VIa15)}$$

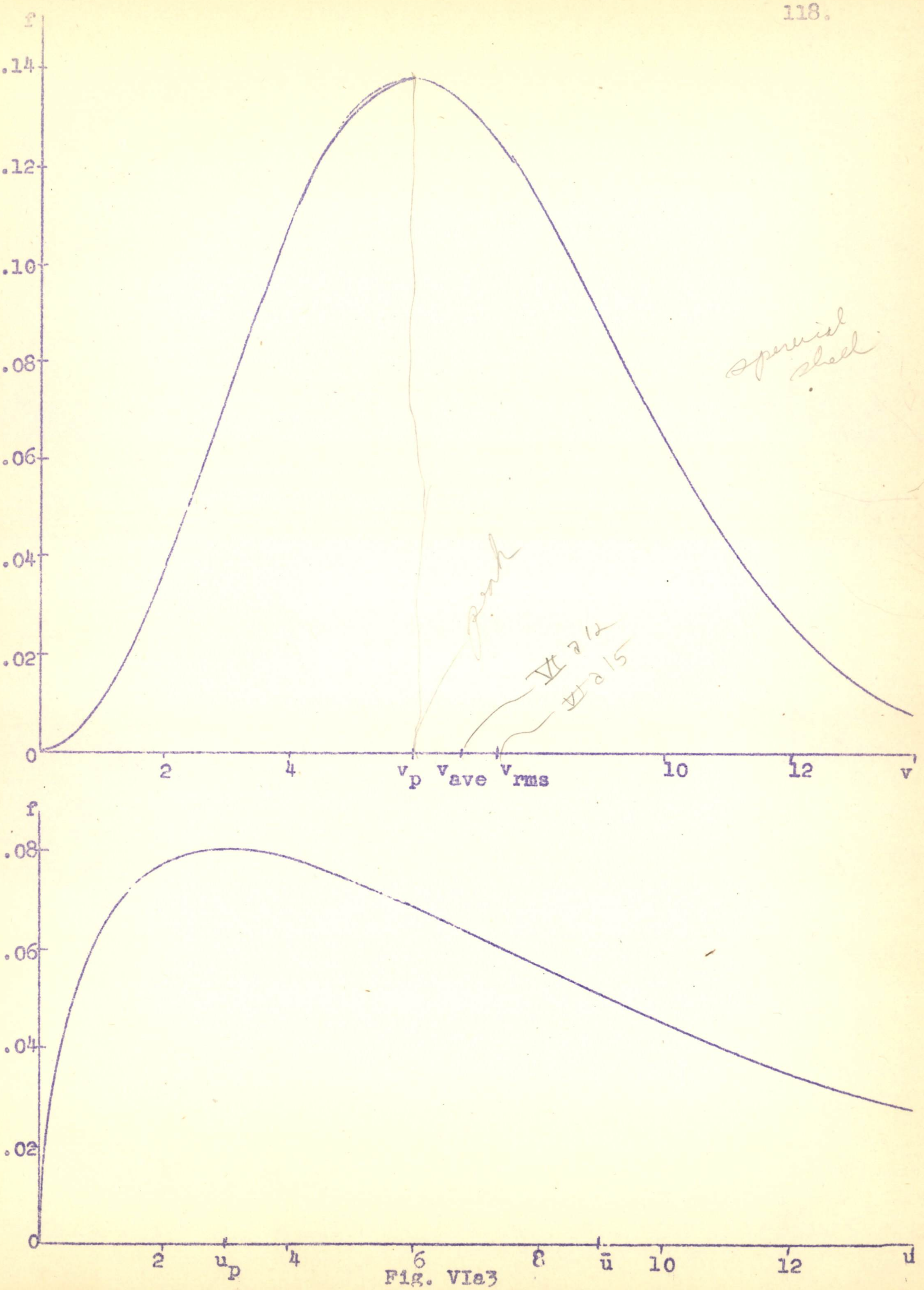

f
.14
.12
.10
.08
.06
.04
.02
0
2
4
v_p
v_{ave}
v_{rms}
10
12
v
spherical shell
peak
VI 212
VI 215
f
.08
.06
.04
.02
0
2
u_p
4
6
8
$\bar{u}$
10
12
u

Fig. VIa3

These value's are indicated_on figure VIa3. Note in particular how much larger the average energy $\bar{u}$ is than the most probable energy u_p. Referring back to the elementary kinetic picture given in section IIg6 we see that the formulae are identical provided the single speed assumed in IIg6 is identified with the r.m.s. velocity. Yet we see how false the postulates made earlier were when we observe, in figure VIa3, how broad the distribution in speed really is.

3. Experimental Verification

There are two direct methods of observation of the velocity distribution of atoms. The first gives the distribution (VIa2) and consists of measuring the profile of spectrum lines. It is known that atoms emit light of various frequencies, but each kind is almost monochromatic. These give the spectral lines. It is also known that the light observed in the x direction from a moving source has its frequency displaced from the emitted frequency by an amount

$$\Delta v = v - v_o = \frac{v_x}{c} v_o$$

Hence the light observed must be spread in frequency due to the velocities of the atoms, and the intensity of the light of frequency v must be proportional to the number of atoms having the velocity v_x. If we plot the intensity I of a single spectrum line, observed with an instrument of high resolution, as a function of frequency, we obtain the profile shown below

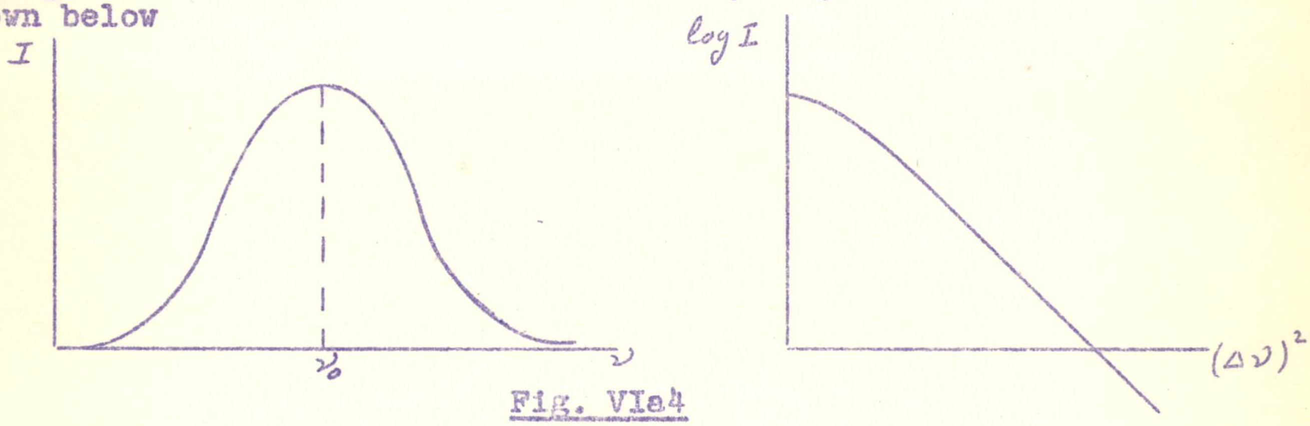


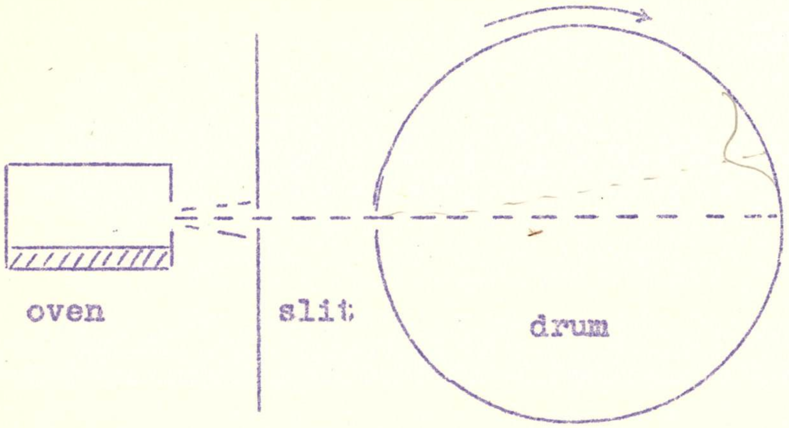
Fig. VIa4

Substituting for v_x in VIa2 we see that the intensity should follow the law

$$I = I_o \exp\left[\frac{-mc^2}{2kT}\left(\frac{\Delta v}{v_o}\right)^2\right]$$

so that a plot of log I against $(\Delta v)^2$ should be a straight line. The observed departures from this law are due to the fact that the emitted light is not strictly monochromatic.

The second method uses a rotating drum as collector in a molecular beam apparatus. A beam of molecules of some metallic vapor,



such as bismuth or cadmium, enters the drum through a slit in one side. If the drum is stationary they strike the opposite wall of the drum where they form a deposit on a glass target. If the drum is rotating it will turn a small angle while the molecules travel the diameter of the drum. Hence the deposit will be spread out according to the distribution (VIa18) appropriate to the particles in a beam.

4. The Random Flow

As the molecules of a gas are by no means stationary one may ask how many cross any area A in the gas per second. The net number is zero, but let us count only those crossing in one direction. This number, per second and per unit area, is called the random flow, or random current density Γ. The same formulae will give the number of particles striking the wall per second, or, if there is a hole in the wall small enough so that the flow of particles through it does not appreciably increase the numbers striking it, the formulae will also give the number of particles issuing from the hole. This is important in the production of molecular beams. These are produced by maintaining a gas pressure P in a chamber used as a source. The source

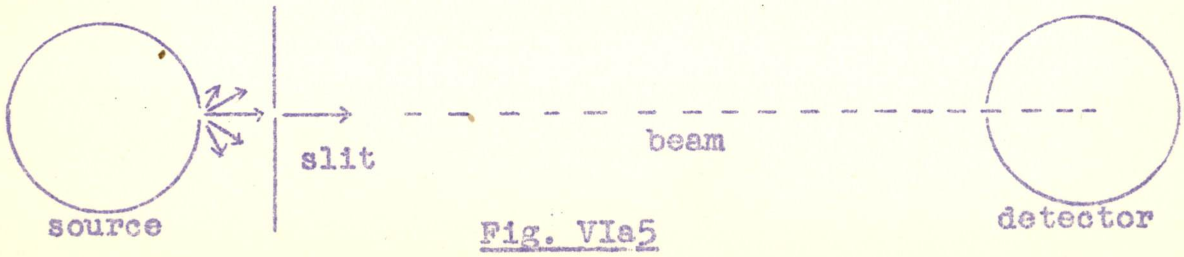


Fig. VIa5

chamber has a fine slit opening through which the molecules escape into a region in which a low pressure is maintained by continuous pumping. Molecules issue from the source slit in all directions, and those going in the desired direction are selected by a system of slits. Various experiments can be performed on the beam, which is then detected by measuring the pressure in a detector cavity.

To calculate the random flow we must first substitute for α and β in equation (Vf1)

$$d^6N = \frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-u/kT}\, dx\, dy\, dz\, dv_x\, dv_y\, dv_z \qquad \text{(VIa16)}$$

Considering first only molecules having a definite vector velocity v. Those striking the area A in the time dt come from a cylindrical volume whose base is A and axis v dt. (Fig. VIa6). Its volume is $Av_x dt$ and this may be substituted for dx dy dz in (VIa16)

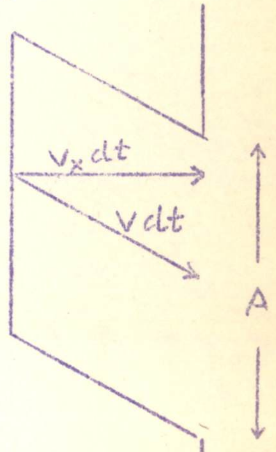


Fig. VIa6

$$d^4N = \frac{NA}{V}\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-u/kT}\, v_x\, dv_x\, dv_y\, dv_z\, dt \qquad \text{(VIa17)}$$

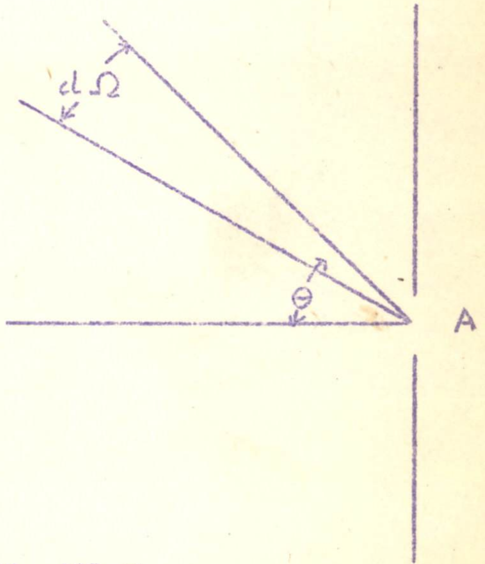
Solid angles can be introduced in this formula by replacing $dv_x\, dv_y\, dv_z$ by

$$v^2 \sin\theta\, d\phi\, d\theta\, dv = v^2\, d^2\Omega\, dv$$

and also setting

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

$$v^3 dv = \frac{2}{m^2}\, u\, du$$



$$d^4N = \frac{NA}{V}\frac{1}{\sqrt{2m}}\frac{1}{(\pi kT)^{3/2}} e^{-u/kT}\, u \cos\theta\, d^2\Omega\, du\, dt \qquad \text{(VIa18)}$$

Fig. VIa7

This formula gives the number of particles issuing from a hole as a function of their energy u and direction θ. It is readily integrated over the energy to give

$$d^3N = \frac{NA}{V}\sqrt{\frac{kT}{2\pi m}}\,\frac{\cos\theta}{\pi}\, d^2\Omega\, dt = \frac{NA}{V}\, v_{ave} \cos\theta\, \frac{d^2\Omega}{4\pi}\, dt \qquad \text{(VIa19)}$$

$$\frac{d^3N}{A\, d^2\Omega\, dt} = \frac{N v_{av}}{V\,4}\,\frac{\cos\theta}{4}$$

m = mass/partical
N = # moles
n =

Integrating now over all directions, we get the random current density
#A 13

#part/A/t

$$\boxed{\Gamma = \frac{1}{A}\frac{dN}{dt} = \frac{N}{V}\frac{v_{ave}}{4}} \rightarrow \frac{N}{4V}\sqrt{\frac{8PV}{\pi M}} \qquad \text{(VIa20)}$$

More precisely, this is the random particle current density. We frequently want the random mass current density Γ_m and this is obtained by multiplying the particle current by the mass m of each particle

$$\boxed{\Gamma_m = \frac{M}{V}\frac{v_{ave}}{4} = \sqrt{\frac{PM}{2\pi V}}} \qquad \text{(VIa21)}$$

For example, substituting the values for air at one bar and 300°K one finds a random flow of 18.5 gm/sec cm^2. It is, of course, this quite appreciable random flow, impinging on the walls, which causes the pressure. It is interesting to compare (VIa21) with Torricelli's formula for the flow of an incompressible fluid through a hole.

$$\frac{dM}{dt} = A'\sqrt{2P\rho} \qquad \text{(VIa22)}$$

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where A' is the area of the "vena contracta", the minimum cross-section of the effluent stream. A' is roughly 0.6 times the area of the hole.

5. Evaporation

Formula (VIa21) may be applied to the gross rate of evaporation from a surface. Consider the surface of a liquid in equilibrium with its vapor. (VIa20) gives the rate at which molecules of the gas impinge on the liquid. Assume that the fraction α of these molecules condense on the liquid and $1-\alpha$ rebound into the gas. Experiments indicate that α is often close to 1. In order to maintain equilibrium the gross rate of evaporation of the liquid must be equal to the rate of condensation, and therefore be

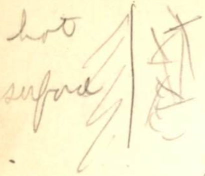
ρ = ρ of vapor

$$\text{Gross Rate of Evaporation} = \alpha\sqrt{P\rho/2\pi} = \alpha P\sqrt{\mathcal{M}/2\pi RT} \qquad \text{(VIa23)}$$

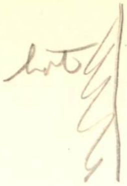
where P and ρ are the pressure and density of the vapor in equilibrium with the liquid.

It is natural to assume that this gross rate is maintained, at a given temperature, even though the external pressure is reduced below equilibrium. (VIa23) is therefore the net rate under zero external pressure.

$\rho = N/V$



$\Gamma_e = \frac{N_e}{V}\frac{v_{av}}{4}$



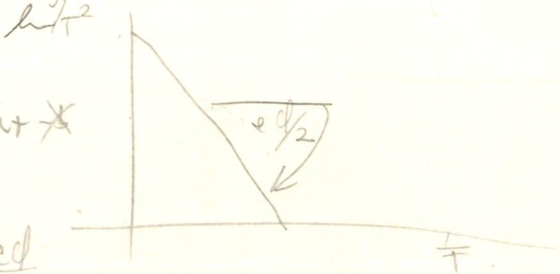
Space Charge Blocked

temperature limited

gross — $\frac{N_{e}}{V}\frac{v_{av}}{4}$ = Rate of em — actual

Rate $= AT^2 e^{-e_w/RT}$

$\frac{e\phi}{kT}$



γ = reflection coeff.

α = accumulation coeff. $\alpha = 1-\gamma$

emissivity $e = a$

$\alpha\,\Gamma_m$ is rate of evaporation $= \alpha\, \overset{\text{vapor pressure}}{p} \sqrt{\frac{M}{2\pi RT}}$

[illegible]

→ $\Gamma = e\sigma T^4$

In the case of solids we can proceed somewhat further. Substituting from (IVe37) in (IVe34)

$$\ell n\, P \; z \; - \frac{\ell_o}{RT} - b + \frac{\gamma}{\gamma - 1}\,\ell n\, T + \frac{3}{2}\,\ell n\, \mu + \ell n\, g + i_o$$

now substituting from (Vg7) for $I_o + \frac{3}{2}\,\ell n\, \mu$ and letting $\gamma = 5/3$ as the theory of (Vg7) applies only to a monatomic gas

$$\ell n\, P \approx - \frac{\ell_o}{RT} - b + \frac{5}{2}\,\ell n\, T + \ell n\, g + \frac{5}{2}\,\ell n\, k + \frac{3}{2}\,\ell n\, \frac{2\pi m}{h^2}$$

or

$$\left.\begin{aligned} P &\approx \Pi\, T^{5/2}\, e^{-b-\ell_o/RT} \\ \text{where} \quad \Pi &= \frac{g}{h^3}\,(2\pi m)^{3/2}\, k^{5/2} \end{aligned}\right\} \qquad \text{VIa24}$$

This can be substituted in (VIa23) to give

$$\left.\begin{aligned} \Gamma_m &= BT^2\, e^{-b-\ell_o/RT} \\ \text{where} \quad B &= 2\pi\, \alpha\, gm^2k^2/h^3 \end{aligned}\right\} \qquad \text{VIa25}$$

This formula has been used, for instance, to obtain the latent heat of vaporization of tungsten, whose vapor pressure is too small to measure but for which the rate of evaporation can be deduced from the loss of weight of tungsten filaments in vacuum tubes. However the most important application of equation (VIa25) has been to the rate of evaporation of electrons from a heated metal. In this application we are interested in the electric rather than the mass current density and so the equation must be multiplied through by e/m. For electrons g is 2 because of the two orientations of the electron's spin, but α is about 1/2 so these two cancel. b is zero and the latent heat per electron is written $e\phi$

where b=0 for electrons

Then

$$\left.\begin{aligned} J &= AT^2\, e^{-e\phi/kT - b} \\ \text{where} \quad A &= 2\pi\alpha\, emk^2/h^3 \\ &= 120\alpha\, \text{amp/cm}^2\, \text{deg}^2 \end{aligned}\right\} \qquad \text{VIa26}$$

and ϕ is of the order of a few volts.

(b) Boltzmann Distribution

1. Independence of Space and Velocity

If there is an external force the total energy u is partly potential, $\phi(x, y, z)$,

$$\textcircled{?} \qquad u = \overset{\text{pot energy}}{\phi} + mv^2/2 \qquad \overset{\text{vel}}{e^{\frac{mv_x}{2kT}} \cdot e^{\frac{mv_y}{2kT}}} \tag{VIb1}$$

Substituting in (Vf1)

$$d^6N = \overbrace{B\,N\,e^{\phi/kT}\,dx\,dy\,dz}^{\text{position}} \cdot \overbrace{\left(\frac{m}{2\pi kT}\right)^{3/2} e^{mv^2/2kT}\,dv_x\,dv_y\,dv_z}^{v} \tag{VIb2}$$

$$\frac{m}{2\pi kT}$$

Where B is a new constant to be determined by normalization. It is first to be observed that the distribution function splits into two factors, one depending on the position, the other on the velocity. This means that the velocity distribution is Maxwellian independently of the position, and reciprocally the spatial distribution is exponential independently of the velocity. Only the parameter T has to be the same in these two distributions. How?

Integrating over the velocity coordinates one obtains

$$dv = dx\,dy\,dz = \int_v^3 \textcircled{?}$$

$$\left.\begin{aligned} d^3N &= B\,N\,e^{-\phi/kT}\,dx\,dy\,dz \\ \text{or} \qquad \boxed{\frac{dN}{dV}} &\boxed{= B\,N\,e^{-\phi/kT}} \end{aligned}\right\} \tag{VIb3}$$

This is called a Boltzmann distribution, the complete function (VIb2) of both position and velocity being a Maxwell-Boltzmann distribution. We shall discuss two applications of these formulae: to particles in a uniform gravitational field, and to small magnets in a magnetic field.

2. Uniform Gravitational Field

In this case

$$\phi = m\,g\,z \tag{VIb4}$$

Consider the column of air above an area A of the surface of the Earth: Integrating (VIb3)

$$N = ABN \int_0^\infty e^{-mgz/kT}\,dz = ABN\ kT/mg$$

so that

$$B = mg/AkT$$

and

$$BN = \frac{Nmg}{AkT} = \frac{W}{AkT} = \frac{P_0}{kT}$$

where W is the weight of the column of air and P_0 is the pressure at the bottom.

Therefore

or

$$\left.\begin{aligned} \frac{dN}{dV} &= \left(\frac{dN}{dV}\right)_o e^{-mgz/kT} \\ P &= P_o\, e^{-mgz/kT} \end{aligned}\right\} \tag{VIb5}$$

This law sufficiently well represents atmospheric pressure as a function of altitude so as to be known as the Law of the Atmosphere. In order to observe it under laboratory conditions, that is over heights of a few centimeters, it would be necessary to observe particles of mass $m \approx kT/g \approx 4 \times 10^{-17}$ gm or about 10^7 atoms. This is not easy. However it is easy to make observable particles of small effective mass by suspending particles of larger mass in a liquid of almost equal density. Thus Perrin, who first performed the experiment, produced grains of 0.4 microns diameter of a resin of density 1.2 gm/cm^3 and therefore of effective density, when suspended in water, of 0.2 gm/cm^3. Accordingly the effective mass was 8×10^{-15} gms. A suspension of these particles does not fall to the bottom of the vessel but retains permanently a Boltzmann distribution which can be observed directly in a microscope, the particle density reducing by 1/2 for every 30 microns vertical displacement.

Of course the particles are not stationary either but are observed to have a rapid Brownian motion.

Returning to the atmosphere, we have seen that the velocity distribution is independent of the height. It is not independent of the distribution in height, however, as both contain the same factor kT. In fact it is a kind of spectrum of the component velocity distribution. Each molecule of vertical velocity v_z can go a height $z = v_z^2/2g$ before reaching the top of its trajectory, and the decrease in density with height corresponds to the decrease in number with v_x^2. A paradox appears here, for if the particles are slowed down by gravity as they move upwards, how is it that the mean kinetic energy stays constant with height? The answer is that only those molecules which had a high velocity in the first place reach the height z at all, this selection of fast molecules exactly balancing the slowing down due to gravity.

The equilibrium atmosphere has a constant temperature. But everyone knows that in our atmosphere, at least up to 12 km and except under unusual conditions, the temperature steadily goes down with altitude. Obviously the atmosphere is not in equilibrium, and the disturbing features are the turbulent winds of the lower atmosphere. If the flow is adiabatic

$$dH = V\, d\, P$$

But from hydrostatics

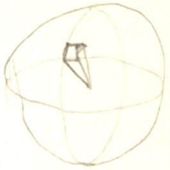
$$dP = -\rho\, g\, dz = -\frac{Mg}{V}\, dz$$

whence

$$dH = -Mg\, dz$$

$$\frac{H - H_0}{n} = -g(h - h_0)$$

$$d^2N = Nc\, e^{-u/kT} \underbrace{\sin\theta\, d\theta\, d\phi}_{d\Omega}$$



or $$H/M + gz = \text{const} \qquad \text{(VIb6)}$$

The enthalpy decreases uniformly with altitude. For an ideal gas in which

$$\text{if} \qquad dH = C_p \, dT$$

it follows that

$$T_o - T = \frac{Mgz}{C_p} \qquad \text{(VIb7)}$$

which, if an effective heat capacity for moist air of 10 cal/mole degree is used, works out to 6.8°C per kilometer rise.

3. Paramagnetism

An application of the Boltzmann formula which is more readily observed in the laboratory is the alignment of the magnetic moments of molecules in a magnetic field. Let $\boxed{\vec{m}}$ be the magnetic moment of a molecule, then its potential energy in a magnetic field B is

$$u = - mB \cos \theta, \qquad m = iA \qquad \text{(VIb8)}$$

where θ is the angle between the vectors $\vec{m}$ and $\vec{B}$. Then if we want the distribution in angle irrespective of the velocity distribution

Ellises convention to balance 2 ds. here

$$d^{2}N = N\,C\,e^{mB \cos \theta/kT} \sin \theta \, d\theta \, d\varphi \qquad \text{(VIb9)}$$

Let

$$\left.\begin{aligned} \boxed{mB/kT = x} \\ \cos \theta = -t \\ \sin \theta \, d\theta = dt \end{aligned}\right\} \qquad \text{(VIb10)}$$

$$d^{2}N = N\,C\,e^{-xt} \, dt \, d\varphi \qquad \text{(VIb11)}$$

Integrating once gives

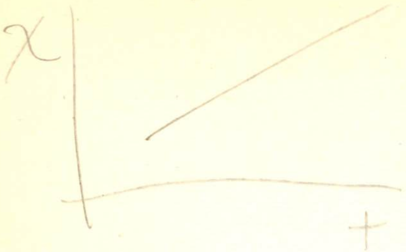
$$dN = 2\pi \, N\,C\,e^{-xt} \, dt = \frac{4\pi e}{x}\left(\frac{e^{x} - e^{-x}}{2}\right) \qquad \text{(VIb12)}$$

and integrating again

$$N = \frac{4\pi N\,C}{x} \sinh x \qquad \text{(VIb13)}$$

This determines the constant C and we can rewrite equation (VIb12)

$$\boxed{dN = \frac{N}{2} \, \frac{x}{\sinh x} \, e^{-xt} \, dt} \qquad \text{(VIb14)}$$



$$\chi = \frac{N m}{V}\frac{m/\nu_0}{3kT}$$

$$dN = \frac{N}{2}\frac{x}{\sinh x}e^{-xt}$$

$$x = \frac{Bm}{kT}$$

$$t = -\cos\theta$$

$$M = \int m\cos\theta\, dN = Nm(\coth x - 1/x) \rightarrow \frac{m^2 N}{3kT}H$$

$$U_m = \sum -m\cos\theta\, B = \int m B t \frac{N}{2}\frac{x}{\sinh}e^{-xt}dt = -BM$$

$$S = k\sum\left(1-\ln \bar{N}_i\right)\bar{N}_i = k\int\left(1-\ln\bar{N}\right)dN$$

$$= k\left(1-\ln\left(\frac{N}{2}\frac{x}{\sinh x}e^{-xt}\right)\right)\frac{N}{2}\frac{x}{\sinh x}e^{-xt}dt + \text{const}$$

$$= k\left(1-\ln\frac{N}{2}+\ln\frac{\sinh x}{x}+xt\right)($$

$$= Nk\left(1-\ln\frac{N}{2}+\ln\frac{\sinh x}{x}\right) - \frac{xk}{m}M + \text{const}$$

$$S_m = nR\ln\frac{\sinh x}{x} - \frac{xkM}{m}$$

$$dS_m = nR$$

note

The total magnetic moment M is given by adding up all the components of the magnetic moments in the direction of the field

$$\overrightarrow{M} = \int_0^N m \cos\theta \, dN = - \frac{Nmx}{2 \sinh x} \int_{-1}^{+1} te^{-xt} \, dt$$

much unimportant integration between these

$$\boxed{= Nm \left[\coth x - 1/x \right]} \frac{\vec{B}}{|B|} \qquad \text{(VIb15)}$$

This formula was found by Langevin in 1905 and the quantity in brackets is called the Langevin function. The initial slope of the function is 1/3 so that for weak fields, or for molecules of small magnetic moments m

$x = mB/kT$

?

$$M = Nm^2B/3\,kT \qquad \text{(VIb16)}$$

and the magnetic susceptibility X is

$$\boxed{\begin{aligned} X &= \frac{Nm^2\mu}{3VkT} = \frac{C}{T} = \frac{M}{HV} \qquad \text{(VIb17)} \\ C &= \frac{Nm^2\mu}{3Vk} = \frac{\mu M_\infty^2}{3nRV} \end{aligned}}$$

$\frac{1}{H} = \frac{\mu}{B}$

χ

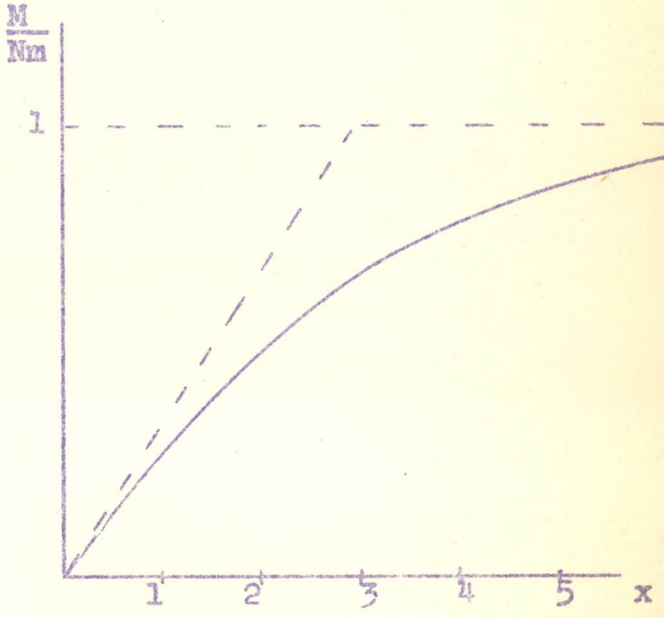


Fig. VIb1

This dependence of the susceptibility of the temperature is called Curie's law and is accurately obeyed by paramgenttic substances down to quite low temperatures.

The magnetic energy of a magnitized substance is found by adding up the energies of the individual molecules in the field

$$U_M = \int_0^N u \, dN \overset{?}{=} +mB \, \frac{N}{2} \frac{x}{\sinh x} \int_{-1}^{+1} te^{-xt} \, dt$$

$$\boxed{= -BM} \qquad \text{(VIb18)}$$

and this is, of course, the well known formula for the energy of a magnet of moment M when oriented in the direction of a magnetic field. The total internal energy is the sum of this term and another part U_p depending on the pressure and volume

$$U = U_p - MB \qquad \text{(VIb19)}$$

$d\varphi = C_{pm}\,dt - B\,dm$

$dU = C_{pm}\,dt - B\,dm - m\,dP$

$dW = -m\,dB$

$\frac{W}{V} = \int H\,dB =$

$B = \mu_0\left(H + \frac{m}{V}\right)$

same $\frac{W}{V} = \int\left(\frac{B}{\mu_0} - \frac{m}{V}\right)dB$

$S = k \ln W$

$dN = \frac{N}{2} \frac{x}{\sinh x} e^{-xt} \, dt$

Similarly the entropy is found by substituting (VIb14) in (Ve4) though there is some difficulty here as (Ve4) is written as a summation over cells and (VIb14) is in differential form. The exact theory shows that the summation can be replaced by an integration provided x is not large, and gives

□S

$$\frac{S}{K} = \int_0^N \left[1 - \ln\left(\frac{Nx}{2\sinh x} e^{-xt}\right)\right] dN$$

$$= \int_0^N \left[1 - \ln\frac{N}{2} + \ln\frac{\sinh x}{x} + xt\right] dN$$

$$= 2N - N\ln\frac{N}{2} + N\ln\frac{\sinh x}{x} - \frac{xM}{m} + \text{const}$$

The first two terms do not depend on magnetic quantities and so can be incorporated in the constant, leaving

$$\left.\begin{aligned} &\boxed{S_M = Nk\ln\frac{\sinh x}{x} - \frac{kxM}{m}} \\ \text{and} \quad &S = S_M + S_p \end{aligned}\right\} \qquad \text{(VIb20)}$$

$x = \frac{mB}{kT}$

This formula fails for large x (extremely low temperatures) where it goes to minus infinity whereas it should go to a negative constant.

The extension of the Tds equations to include magnetic energies is now found by differentiating (VIb20). First it is readily seen that

$$\frac{d}{dx}\ln\frac{\sinh x}{x} = \coth x - 1/x = \frac{M}{Nm} \qquad \text{(VIb21)}$$

so that

$$dS_M = -\frac{kx}{m}\,dM = -\frac{BdM}{T} \qquad \text{(VIb22)}$$

whence

note

$$\boxed{TdS = C_{P,M}\,dT - T\left(\frac{\partial V}{\partial T}\right)_{P,M} dP - \underline{B\,dM}} \qquad \text{(VIb23)}$$

both const.

One of the ways of producing extremely low temperatures, around 1/200 of a degree Kelvin, is through the use of the entropy of a paramagnetic salt. The process is as follows: First a magnetic field is applied to the salt while it is in thermal contact with liquid helium. In this process the pressure and temperature are constant. Therefore, by equation (VIb23), the entropy must decrease as the magnetization increases. This is readily understandable as the magnetization represents an ordering of the magnetic moments in the direction of the field and therefore a decrease in the randomness. Accordingly heat is given off in an amount

$$\boxed{Q \leqq - \int_0^M BdM \ , \quad đQ \leqq - BdM} \qquad \text{(VIb24)}$$

and causes the liquid helium to boil. The work done by the electric circuits in producing the field B within the volume V is

$$-W = V \int_0^B HdB = V \int_0^B \left(\frac{B}{\mu_0} - \frac{M}{V}\right) dB$$

$$= \frac{VB^2}{2\mu_0} - \int_0^B MdB \qquad \text{(VIb25)}$$

how?

Hence

$$\boxed{U_B = Q - W = \frac{VB^2}{2\mu_0} - MB} \qquad \text{(VIb26)}$$

which differs from (VIb18) in including the energy of the field B.

Let us now insulate the paramagnetic salt. The entropy is then constant provided all changes are made reversibly. The field is then reduced slowly, and at constant pressure. The magnetic moments resume their random orientation and, becoming disordered, must produce order elsewhere. The only disorder available is in the thermal motions of the molecules and these are, accordingly, reduced. From (VIb23)

$$\int C_p dT = \int BdM \qquad \text{(VIb27)}$$

should an inadequate amount of entropy be available so that T_f as computed by (VIb27) came out negative, the magnetic moment M would simply not go to zero as B went to zero, leaving a remanent magnetization.

There remains the problem of determining the value of the absolute temperature which has been reached by demagnetization. So long as Curie's law (VIb17) holds the temperature can be computed from measurements of susceptibilities. But at extremely low temperatures Curie's law fails and then the temperature must be determined directly from the Second Law. This is best seen on a T-S plot, fig. VIb2, on which the initially unknown plot of T vs S at zero field is shown. Consider two experiments starting from the same initial point O at the known temperature T_o, but using different fields B_1 and B_2 to reach the unknown temperatures T_1 and T_2. The heats $-Q_1$ and $-Q_2$ given off during magnetization are measured by the amounts of helium evaporated and determine the entropy difference

$$S_1 - S_2 = \frac{Q_1 - Q_2}{T_o}$$

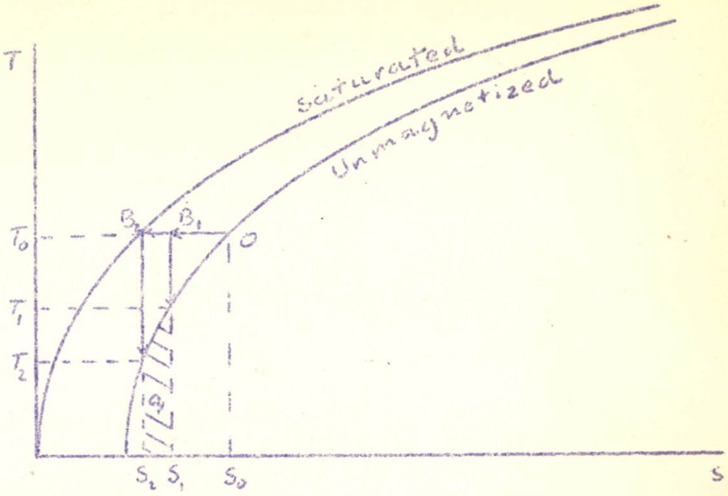


Fig. VIb2

After the second experiment let us supply a small amount of heat q, by means of the absorption of γ-rays for example, so as to bring the salt back to T_1. This point can be determined by a measurement of susceptibility quite independently of Curie's law. Then, if T_1 and T_2 are nearly the same

$$\frac{T_1 + T_2}{2} = \frac{q}{S_1 - S_2} = T_o \frac{q}{Q_1 - Q_2} \qquad \text{(VIb28)}$$

The average absolute temperature is thus determined over any small temperature interval desired.

(c) Equipartition of Energy

1) The Theorem

It can be shown that if particles of different masses are mixed they will tend to assume the same average kinetic energy 3/2 kT each, because this distribution has the greatest number of complexions and therefore greatest entropy. The same result can be derived by considering elastic collisions between particles of masses m_1 and m_2. It can then be shown that the particle of least energy will in the average gain a fraction $\frac{8}{3} \frac{m_1 m_2}{(m_1+m_2)^2}$ of the energy difference before the collision. In the average, therefore, the energy difference between groups of particles which collide becomes less as time goes on.

This equal sharing of energy between particles is a special case of a much more general theorem called the Equipartition of Energy, which states that in any complicated system kinetic energy will be shared equally between all the degrees of freedom of the system, kT/2 for each degree of freedom.

Departure from Equipartition

H2 < 100°K, c_v = 3 cal/mol

so light its an exception

Degress of Trans

M	D	P	
0	2	3	Rotation
0	1	—	Trans
.			

Monoatomic 3 trans cal/mole/degree
Diatomic 3 trans ✱ 2 rotation = C cal/mole

Breakes down when
{1. low T
{2. small m
{3. Ridgid

The equipartition theorem says nothing about potential energy but the laws of mechanics give the ratio of potential to kinetic energy for any type of force. Two cases are of importance: in "free" translations and rotations there is no potential energy and therefore the total energy is kT/2 per degree of freedom. For "bound" particles there is an elastic restoring force giving simple harmonic motion for which the average potential energy is equal to the average kinetic energy and therefore the average energy is kT per degree of freedom. For other types of forces the ratio of potential to kinetic energy may depend on the amplitude of the motion and thus give a total energy which is not simply proportional to the temperature.

2) Specific heats

Let us apply the Equipartition theorem to a system of N molecules each of which has f "free" degrees of freedom and b "bound" degrees of freedom. Then

$$\boxed{U = (f/2 + b)\, NkT} \qquad \text{(VIc1)}$$

and

$$\boxed{C_v = (f/2 + b)\, nR} \qquad \text{(VIc2)}$$

Applying this formula to ideal gases for which

$$C_p = \gamma C_v = \boxed{C_v + nR} \qquad \gamma = \frac{c_v + nR}{c_v} = \frac{c_p}{c_p - nR}$$

and hence

$$f + 2b = \frac{2}{\gamma - 1} \qquad \frac{12}{10} \qquad 1.2 = \frac{\ }{.2} \qquad \text{(VIc3)}$$

one can obtain the combination f + 2b directly from measurements of γ. The experimental results for a number of gases is shown below. It is seen that the quantity (VIc3) very frequently comes close to a whole number which corresponds in all cases to the three directions of translation plus, for diatomic molecules, two axes of rotation and, for triatomic and polyatomic molecules, three axes of rotation. In general the interatomic vibrations which might have been expected are not observed except for the heavier polyatomic molecules, and in these cases they do not come out whole numbers. In fact for the diatomic molecules, except chlorine, the energy difference between the cells in phase space for vibration is so large that at normal temperatures all the molecules are in the cell of lowest energy and vibration does not contribute at all to the specific heat or the entropy. Going back to the diatomic molecules we find the same thing happening with respect to rotation although only at temperatures around -200°C.

Turning to solids, where the atoms are all bound to the points of a crystal lattice, one may expect each atom to be able to vibrate in three directions and therefore have 3kT of energy. This gives for the

SPECIFIC HEATS OF GASES

Gas	T°C	γ	$\frac{2}{\gamma-1}$	Trans.	Rot.	Vibr.
Monatomic Gases						
He	18°	1.63	3.19	3		
Ne	19°	1.642	3.13	3		
A	0°	1.667	3.00	3		
Kr	19°	1.689	2.87	3		
Xe	19°	1.666	3.00	3		
Hg	310°	1.666	3.00	3		
Diatomic Gases						
H_2	16°	1.407	4.90	3	2	
H_2	-181°	1.597	3.37	3	.4	
N_2	-20°	1.400	5.00	3	2	
N_2	-161°	1.468	4.27	3	1.3	
O_2	20°	1.399	5.01	3	2	
NO		1.394	5.08	3	2	
Cl_2		1.333	6.00	3	2	.5
HCl		1.40	5.00	3	2	
Triatomic Gases						
H_2O		1.305	6.56	3	3	.3
CO_2		1.300	6.67	3	3	.3
NO_2	150°	1.31	6.45	3	3	.2
N_2O		1.324	6.18	3	3	.1
Polyatomic Gases						
CH_4		1.313	6.4	3	3	.2
CH_3Cl		1.279	7.2	3	3	.6
CH_2Cl_2		1.219	9.0	3	3	1.5
$CHCl_3$		1.154	13.0	3	3	3.5
$C\ Cl_4$		1.130	15.4	3	3	4.7

H-S-H

SPECIFIC HEATS OF SOLIDS

Solid	T°C	Cal/g.°C C_p	Cal/mole°C C'_p	Cal/g.a.°C C'_p	
Molecular Compounds					
I_2	20	.0523	13.6	6.65	low becaus of H_2
H_2O (ice)	0	.480	8.64	2.88	
$C\,Cl_4$	-40	.201	30.9	6.18	
Ionic Compounds					
Na Cl	0	.204	11.9	5.95	
Zn S	0	.116	10.8	5.4	
Zn O	0	.114	9.3	4.6	
$Ca\,F_2$	0	.204	15.9	5.3	
$Ca\,CO_3$	0	.182	18.2	3.6	
$NH_4\,Cl$	0	.358	19.7	3.3	
Metallic Compounds					
Na	20	.298		6.85	
Al	20	.215		5.82	
Fe	20	.107		6.00	
Cu	20	.092		5.86	
Zn	20	.0925		6.04	
W	20	.0330		6.08	
Pb	20	.0304		6.30	
Valence Compounds					
Diamond	20	.118		1.42	very ridgid
Graphite	20	.168		2.01	
Quartz	20	.174	10.4	3.48	

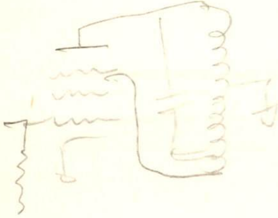
Voltmeter

$$\tau = -K\theta$$

$$\frac{1}{2} I\omega^2 = \frac{1}{2} kT$$

$$PE = \frac{1}{2} K\theta = \frac{1}{2} kT$$

$$\theta_{rms} = \sqrt{\frac{kT}{K}}$$



specific heat 3R per gram atom, which corresponds to Dulong and Petit's law. The following table gives some experimental values and it is seen that Dulong and Petit's law is in general quite well, though not accurately, observed. The most notable exceptions are the valence compounds and the reason here again is the size of the energy differences between cells in phase space, and is well explained by Debye's theory of specific heats. It is found that these substances obey Dulong and Petit's law at higher temperatures.

3) Fluctuations

The equipartition theorem applies not only to molecules but also to systems of macroscopic dimensions. Thermal motion was first noticed by a botanist, Robert Brown, in 1827 as he observed the constant motion of pollen particles suspended in water. Colloidal gold suspensions are readily made with particles of diameters of the order of 5×10^{-6} cm and these can be seen by the light they scatter. As their mass is about 10^{-15} grams their r.m.s. velocity is readily calculated from

$$\boxed{m\overline{v^2} = 3kT} \qquad \text{(VIc4)}$$

to be about 10 cm/sec.

The ultimate sensitivity of a galvanometer is limited by the thermal motion of the mirror. If K is the torsion constant of the suspension, the potential energy of the mirror when turned through the angle θ is $1/2\ K\theta^2$. As this is a one-dimensional motion with an elastic restoring force

$$\boxed{\begin{array}{c} 1/2\ I\overline{\dot\theta^2} = 1/2\ K\overline{\theta^2} = 1/2\ kT \\ \text{or} \quad \left.\begin{array}{l} \theta_{r.m.s.} = \sqrt{kT/K} \\ \dot\theta_{r.m.s.} = \sqrt{kT/I} \end{array}\right\} \end{array}} \qquad \text{(VIc5)}$$

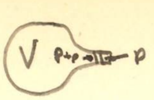
Superimposed on the steady deflection produced by the current being measured, there will be a random thermal motion whose angle and angular velocity are given by (VIc5), and deflections smaller than this amount can therefore not be read. Reducing I and K to improve the sensitivity only increases the thermal motion. The type of motion will depend on the amount of damping of the instrument: if it is more than critically damped the motion will be irregular and jittery; if it is undamped the mirror will swing with its proper frequency and with an amplitude which varies with time but stays in the neighborhood of $\sqrt{kT/K}$.

Thermal motions will produce fluctuations in the density of any medium, though they are particularly noticeable in the case of a gas. This is most easily shown by considering a large amount of gas within which a small amount, n moles, are separated by an imaginary surface. This will normally enclose a volume V but, due to fluctuations its volume may be V + v and therefore the internal pressure is P + p due to 1 volume element

$$\left\{\begin{array}{l} V \approx \lambda^3 \\ \left(\frac{\delta\rho}{\rho}\right)^2 = \frac{kT}{\rho\lambda^3} \approx H \propto E \quad \text{scattered} \quad \longrightarrow \\ \left(\frac{\delta\rho}{\rho}\right) = \sqrt{\frac{kT}{\rho\lambda^3}} \sim \text{Energy scattered} \end{array}\right.$$

$$\text{light} = \Sigma \nearrow$$

$$\text{"} \sim \frac{1}{\lambda^4}$$



Ply does harmonic motion
or $\frac{1}{2}KT = KE$
$\frac{1}{2}KT = PE$

$$-v = V\kappa p \qquad \text{(VIc6)}$$

The external pressure is assumed to remain P. The net work done in producing the compression -v is

$$W = -\int_0^v p\,dv = \int_0^v \frac{v\,dv}{V\kappa} = \frac{1}{2}\,\frac{v^2}{V\kappa} \qquad \text{(VIc7)}$$

and applying the equipartition theorem $\frac{1}{2}kT = PE = \frac{v^2}{2V\kappa}$

$$\overline{v^2} = V\kappa kT \qquad \text{(VIc8)}$$

$\overline{\left(\frac{v}{V}\right)^2} = \frac{\kappa}{V}kT = \overline{\left(\frac{\delta\rho}{\rho}\right)^2}$ change in density

or, as the relative change in density is minus v/V, the relative change in volume

$$\overline{(\delta\rho/\rho)^2} = \overline{(v/V)^2} = kT\kappa/V \qquad \text{(VIc9)}$$

Fluctuations in density are therefore greatest when small volumes of a highly compressible substance are observed. The compressibility of a gas near the critical point becomes very large and therefore one may expect large fluctuations of density. These produce the opalescence which is observed in gases near the critical point.

In the case of an ideal gas, where $\kappa = 1/P$

$$\overline{(\delta N/N)^2} = \overline{(\delta\rho/\rho)^2} = kT/PV = 1/N \qquad \text{(VIc10)}$$

or 𝍸

$$\underset{\text{\# fluctuating points}}{\overline{(\delta N)^2}} = N \qquad \text{(VIc11)}$$

in large # where sterling approx

the mean square fluctuation in the number of molecules in any volume is equal to the number of molecules in that volume. The temperature has disappeared from this equation and we find a relation which is well known in the theory of the random distribution of particles.

The blue color of the sky and the correspondingly red color of the sun at sunset is due to the scattering of sunlight by the air. This would not take place if the molecules of the air were uniformly spaced but, as was pointed out by Lord Rayleigh in 1871, is due to fluctuations in the refractive index and therefore in the density of the air in volumes of the order of a wave-length of light cube. For blue light and at normal temperature and pressure there are about nine million molecules in such a cube, and therefore the r.m.s. fluctuation is three thousand molecules. The numbers of molecules in neighboring cubes differ by about this amount and this irregularity produces the scattering which is observed. The percentage fluctuation (VIc10) is proportional to 1/V and therefore to $1/\lambda^3$, and the number of scattering centers observed in any direction is proportional to $1/\lambda$ so that the net scattering varies as $1/\lambda^4$, which is Rayleigh's law for scattering, and explains the preponderance of blue in the scattered light.

d) Johnson Noise

The Equipartition Theorem is not, of course, limited to mechanical energy. A short-circuited inductance carries a random thermal current given by

$$1/2\ L\ \overline{I^2} = 1/2\ kT = 2 \times 10^{-14} \text{ ergs at } 300^\circ K$$

or

$$I_{r.m.s.} = \sqrt{kT/L} \qquad \text{(VIc12)}$$

and similarly a short-circuited condenser has a random potential

$$V_{r.m.s.} = \sqrt{kT/C} \qquad \text{(VIc13)}$$

This works out to 20 micro volts if $C = 10\ \mu\mu f$

These random currents and potentials are called "Thermal" or "Johnson" noise in a communications circuit and as they are frequently the limiting factor on the amplification which can be applied to an electric signal it is important to know their frequency distribution. In a resonant circuit (condenser shorted by an inductance) the answer is simple; the circuit oscillates at its resonant frequency with an r.m.s. amplitude given by (VIc12) or (VIc13).

To get the frequency distribution in a damped circuit we use the device of considering a very long lossless transmission line, of length ℓ, similarly terminated at both ends. This system has many modes of oscillation, each one corresponding to a standing wave of

$$\begin{aligned} &\text{wave-length} && \lambda = 2\ell/n \\ &\text{and of frequency} && \nu = nc/2\ell \end{aligned} \qquad \text{(VIc14)}$$

where n is a whole number. In a frequency interval $\Delta\nu$ there are

$$\Delta n = \frac{2\ell}{c} \Delta\nu \qquad \text{(VIc15)}$$

modes of oscillation. Each of these modes of oscillation is a degree of freedom of the system and therefore has in the average, 1/2 kT of kinetic energy $1/2LI^2$ and 1/2 kT of potential energy $1/2\ CV^2$. The mean energy in the frequency internal $\Delta\nu$ is therefore

$$\overline{U}_\nu\ \Delta\nu = kT\Delta n = \frac{2\ell}{c} kT \Delta\nu \qquad \text{(VIc16)}$$

and the mean energy density is

$$\overline{U}_\nu \triangle\nu = \frac{2kT}{c}\triangle\nu \qquad \text{(VIc17)}$$

Each standing wave can be decomposed into two travelling waves, one going each way, and the power in one of these waves is its energy density multiplied by c, so that

$$P_\nu \triangle\nu = kT\triangle\nu \qquad \text{(VIc18)}$$

This is the basic formula for the power spectrum of Johnson noise. Its derivation is Nyquist's theorem.

At the end of the line there is generally a reflection coefficient r so that $(1-r)\,kT\triangle\nu$ is absorbed and $rkT\triangle\nu$ reflected. As a full $kT\triangle\nu$ comes from the end of the line, the termination must be emitting $(1-r)\,kT\triangle\nu$ and as only resistances absorb power the emission must come from the resistances also. The fraction $(1-r)$ is both an absorption and an emission coefficient and it can be calculated from circuit theory. If a line of real impedance Z is terminated by a pure resistance R

$$1-r = \frac{4RZ}{(R+Z)^2} \qquad \text{(VIc19)}$$

and it is readily verified that $r = 0$ if the load is matched to the line $R = Z$. The absorbed power is then

$$P_a = \frac{4RZ}{(R+Z)^2}\,kT\triangle\nu = \overline{i_a^2}\,R$$

and

$$\overline{i_a^2} = \frac{4Z}{(R+Z)^2}\,kT\triangle\nu$$

The emissive power of a resistance is best pictured by imagining a source of electromotive force E contained in it. As the emitted power is

$$P_e = P_a = \overline{i_e^2}\,Z$$

$$i_e^2 = \frac{4R}{(R+Z)^2}\,kT\triangle\nu$$

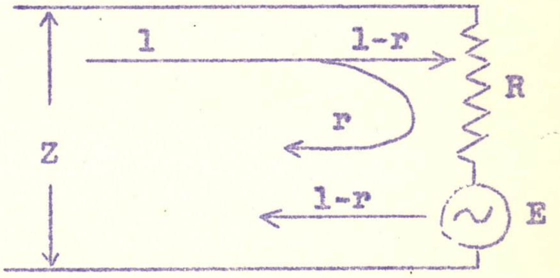


Fig. VIc1

The emission voltage is

$$V_e = i_e Z = E - i_e R$$

Hence

$$\overline{E^2} = \overline{i_e^2}\,(R+Z)^2 = 4RkT\triangle\nu \qquad \text{(VIc20)}$$

This formula was derived by Nyquist also. As it does not contain any parameters of the line it represents an inherent property of resistances.

Suppose, for instance, that we are interested in frequencies from 1 to 6 megacycles. From (VIc18) we see that a line will carry 2 x 10^{-8} microwatts of thermal power in this frequency range in each direction, and from (VIc20) we see that a half megohm resistor contains a 200 microvolt e.m.f. uniformly spread over the same frequency range.

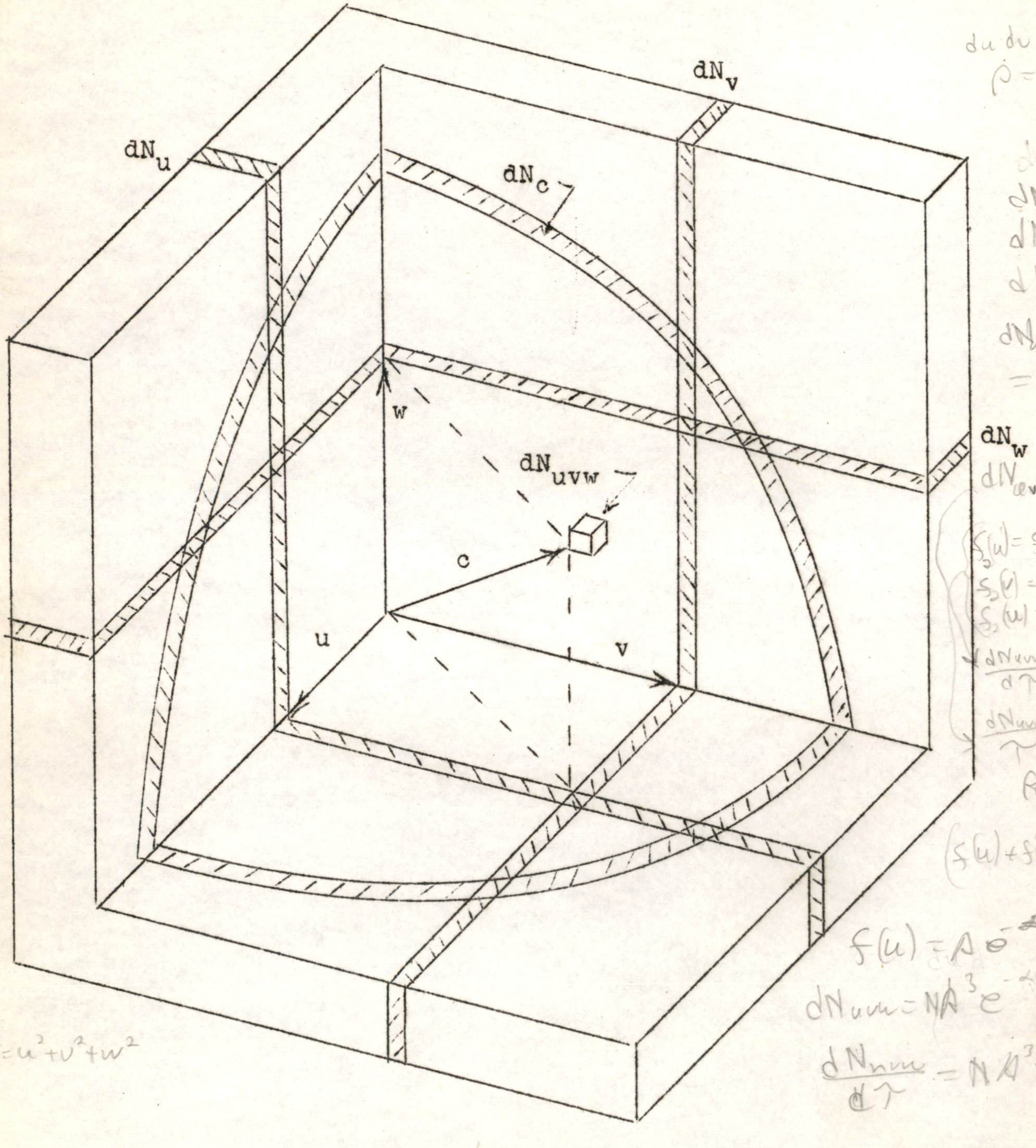


Diagram of velocity space.

$du\,dv\,dw = d\tau$

$\rho = \frac{dN'_{uvw}}{d\tau}$

$dN_u = N f(u)\,du$

$dN_v = N f(v)\,du$

$dN_w = N f(w)\,dw$

$dN_{uv} = dN_v\, f(u)\, du$

$= N f(u) f(v)\, du\, dv$

$dN_{uvw} = N f(u) f(v) f(w)\, du\, dv\, dw$

$f_2(u) = f(u) + \frac{df(u)}{du}\Delta u$

$f_2(v) = f(u)\ f(u)\,\Delta u$

$f_2(w) =$

$\frac{dN_{uvw}}{d\tau} = N f(u) f(v) f(w) = \rho$

$\frac{dN_{uvw}}{\tau} = N f_2(u) f_2(v) f_3(w)$

$\rho_1 = \rho_2$

$(f(u) + f'(u)\Delta u)(f(v) + f'(v)\Delta v)$ etc

$f(u) = A e^{-\alpha u^2}$

$dN_{uvw} = NA^3 e^{-\alpha u^2} e^{-\alpha w^2} e^{-\alpha u^2}\, d\tau$

$\frac{dN_{uvw}}{d\tau} = NA^3 e^{\alpha c^2}$

$c^2 = u^2 + v^2 + w^2$

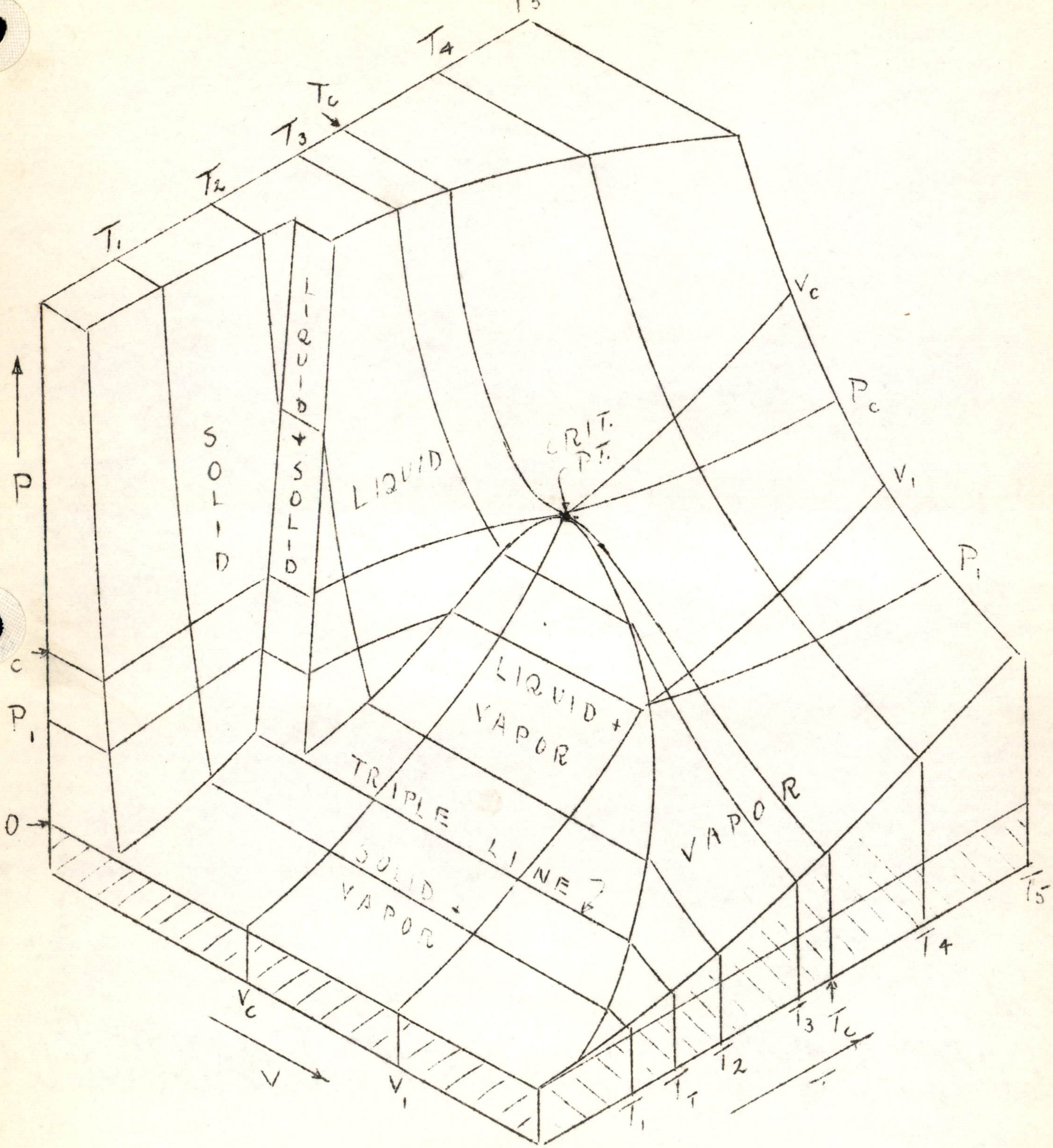
$w = V_z$

$u = V_y$

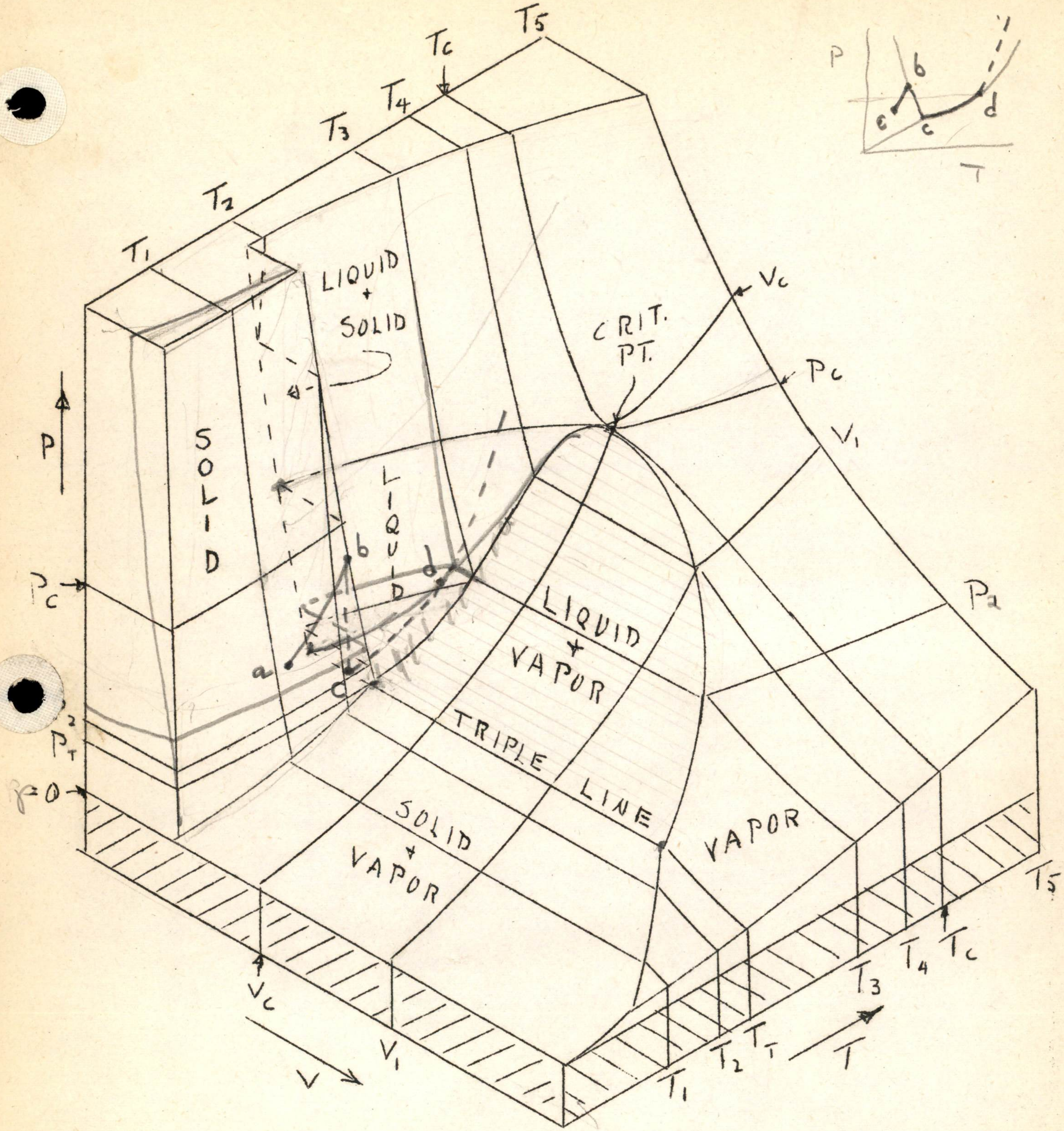
$v = V_x$

$$N = \int dN_c = \int_0^V Ac\,dc = \frac{AV^2}{2} \qquad \frac{dN_c \times c}{N_0}$$

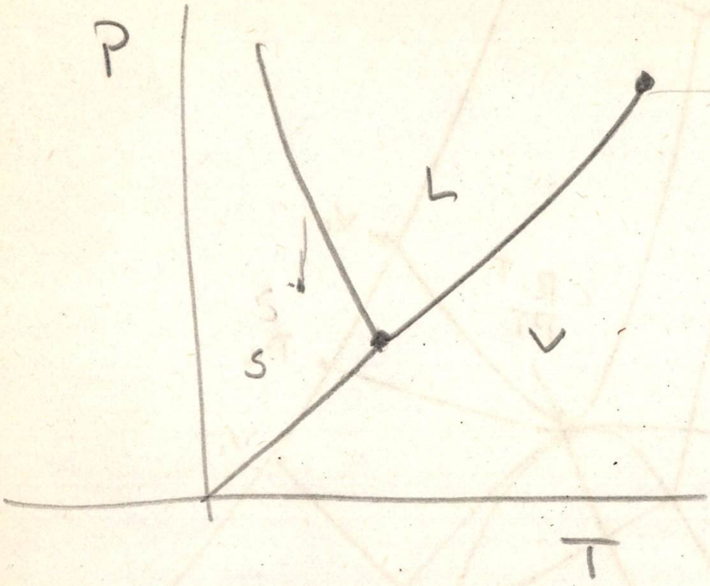
$$\bar{c} = \frac{1}{N}\int_0^V Ac^2\,dc = \frac{1}{N}\frac{2N}{V^2}\frac{V^3}{3} = \frac{2}{3}V$$



Schematic diagram of P-v-T surface for a substance that contracts on freezing.



Schematic P-v-T diagram for a substance that expands on freezing.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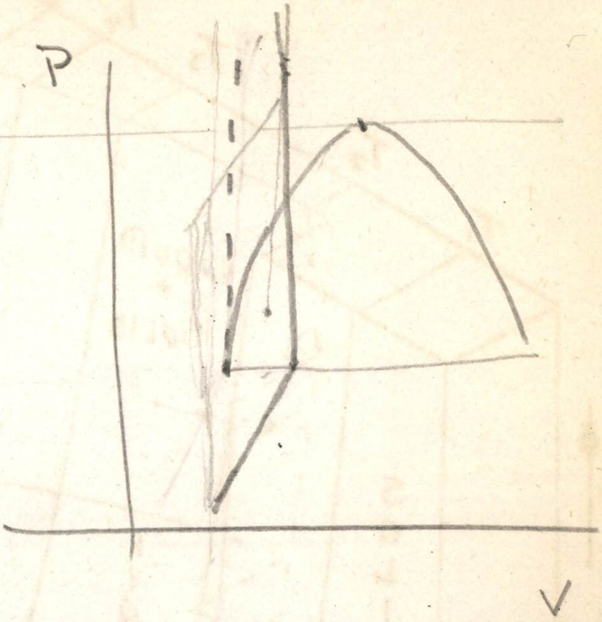

P
V

Mr. Hill

Wed. - 1-4
Fri. 1-4
20A-120

NOTES ON ELECTRONICS

Course 8.08
M.I.T. Spring Term, 1949

Chapter I. Introduction

This set of notes is written as an introduction to that part of electronics which deals with the physical properties of electrons, and to some extent with the physical properties of other fundamental charged particles. This branch of the broad field of electronics is sometimes referred to as Physical Electronics. We can define physical electronics as the science which deals with the motion of electrons in electromagnetic fields; the interaction of electrons with each other, with other charged particles, and with radiation; and the emission of free electrons from matter, in particular, from metals.

Matter is made up of molecules which in turn are made up from the atoms of the chemical elements. All atoms consist of a heavy positively charged core, the nucleus, and a sufficient number of electrons surrounding the nucleus to just annul the net charge of the atom. An atom or a molecule may become ionized (charged) by the gain or loss of one or more electrons. All fundamental particles contain a charge which is numerically equal to the charge on the electron, or to a small integral multiple of this charge, and this charge may be both positive and negative in sign.

The position of the atom in the Periodic Table determines the amount of positive charge carried by its nucleus; the number of negatively charged electrons surrounding this positive core is then just equal to the atomic number of the atom. While the total charge carried by the external electrons is just equal and opposite to the charge of the nucleus, most of the mass of the atom resides in the nucleus. The nucleus of the lightest atom, hydrogen, which is called the proton, is 1837 times the mass of the electron. The heaviest natural atom, Uranium, is some 238 times more massive than hydrogen. All nuclei are made up of protons and neutrons; the neutron being an uncharged particle nearly equal in mass to the proton. Here the masses of all nuclei are nearly integral multiples of the proton mass, or the hydrogen atom mass.

When the atoms of a substance form a metallic solid some of the outermost electrons become detached from their atoms and are then free to move about in the metal. These free electrons are the carriers of electric current in metals, and it is from their number that thermionic and photoelectric electrons arise.

The particles with which we shall deal mostly are: (1) the electron, (2) the proton, (3) the deuteron, which is the nucleus of heavy hydrogen, and contains one neutron and one proton, (4) the α-particle which is the nucleus of helium, and (5) the positive and negative ions of various atoms and molecules.

All fundamental particles are characterized by four definite properties, (1) mass, (2) charge, (3) inherent angular momentum (spin), and (4) inherent magnetic moment. Any of the last three quantities may be zero, but in general the values of each must be specified to help in our understanding of the particle. Modern physics has not progressed far enough to tell us much about the size of these particles, but order of magnitude calculations can give upper and lower limits to the size.

These notes can be divided into the following general sections,

(1) Motion of Charged Particles in Electric and Magnetic Fields.

(2) Relativistic Motion

(3) High Energy Charged Particle Accelerators.

(4) Space Charge Effects.

(5) Kinetic Theory of Gases.

(6) Elements of Atomic Theory and Collision Processes in Gases.

(7) Gaseous Discharges.

(8) Fermi-Dirac Statistical Mechanics.

(9) Emission of Electrons from Metals.

The general reference text will be Millman and Seely, "Electronics" and the material covered will be similar in content to Millman and Seely (M and S) Chapters I-X, XV, although the order of the treatment will be different. Page references to M. and S. will be given throughout these notes.

These notes will use rationalized m.k.s. units throughout, except where otherwise specified, and will try to conform to the most widely used notation of physical and electrical engineering texts. Millman and Seely use the so-called practical system of units and their notation departs from the norm to a considerable extent. Table I serves to compare the Millman and Seely notation with that of these notes, but we can scarcely hope that this table is complete. The student should feel responsible for the conciliation of the two systems of units and notation.

TABLE I

Principle Differences in Notation and Units Between Millman and Seely and these Notes

Quantity	Millman-Seely Symbol	Millman-Seely Unit	Notes Symbol	Notes Unit	Conversion Factor
force	f	dyne	F	newton	1 newton = 10^5 dynes
electric field	F	volt/cm	E	volt/m	1 volt/m = 10^{-2} volt/cm
Potential	E	volt	V	volt	
mass	m	gram	m	kg.	1 kg = 10^3 grams
distance	(various)	cm	(various)	meter	1 m = 10^2 cm
Magnetic Induction	B	Gauss	B	weber/m^2	1 weber/m^2 = 10^4 gauss
Energy	E no symbol	electron-volts joules	U,w	joules	1 joule = 6.25 x 10^{18} e.v.

Chapter II. Motion of Charged Particles, in Electric and Magnetic Fields

2.1 The Electrostatic Field

In order to formulate the laws of force between electromagnetic fields and charged particles we will begin with a summary of the special case in which the fields do not vary with time. The electric field, we know, arises from the presence of free charges, which attract or repel each other according to Coulomb's Law

$$F = \frac{+qq'}{4\pi\varepsilon r^2} \qquad (2.1.1)$$

+ tend to increase r

Here F is the force between the two charges measured in newtons, q and q' are the respective charges measured in coulombs, r is the separation measured in meters, and ε is a constant of the medium in which the charges are immersed, and for homogeneous isotropic media ε is a scalar quantity. In the rationalized m.k.s system of units ε in empty space is equal to $\frac{1}{36\pi} \times 10^{-9}$ farads/meter, and is designated ε_0. Since we will be dealing only with empty space, or nearly empty space, in this course, ε_0 will be used throughout.

It is an experimental fact that charge consists of two kinds, labelled positive and negative, and that no net charge is ever created or destroyed. All matter is made up of both kinds of charges, and one may separate negative charge from a neutral body, but one will always leave the body with a positive charge equal numerically to the negative charge removed. It is also an experimental fact that like charges repel each other and that unlike charges attract each other. The symbol q for charge, then, implies that an algebraic sign must be used when the symbol is to be replaced by a number. The positive sign in equation (2.1.1) indicates that when q and q' are of like sign the force is positive, tending to increase r, and when q and q' are of unlike sign the force is negative, tending to decrease r.

The electric intensity vector E due to a single charge may now be defined. Let us imagine a single charge q isolated in space. If we placed any other charge q' in this space we know q will exert a force on q' no matter where in space we put q'. We can think of this process as being due to an electric field due to q which completely fills this space, i.e., a vector field since the force is always directed along the line joining q and q'. However, since q' will also give rise to a field it is necessary for the sake of definition that q' be very small compared to q so that its effect on the field is negligible. In symbols then, the electric field due to a single point charge is

$$E = \underset{q'\to 0}{L} \frac{F}{q'} = \frac{q}{4\pi\epsilon_o r^2} \quad . \tag{2.1.2}$$

With this definition the force on any charged particle q in an electrostatic field is always,

$$F = Eq \tag{2.1.3}$$

providing q does not disturb the charges giving rise to E.

The electric field due to an assemblage of charges is the vector sum of the fields of the individual charges. In order to completely describe phenomena in material media it is necessary to introduce another vector, namely, the electric displacement vector D which is related to the electric intensity vector by

$$\underline{D = \epsilon_o E \ .} \tag{2.1.4}$$

As a direct consequence of (2.1.4) and Coulomb's Law, with ϵ_o replacing ϵ, we can formulate Gauss' Law, which states that the flux of D over any closed surface is equal to the net charge q contained in the volume of which the surface is a boundary. In symbols

$$\underset{\text{closed}}{\iint} D \cdot dS = q \tag{2.1.5}$$

where the dot • signifies that the component of D normal to the surface is to be multiplied by the element of area dS before the integration is performed. The sign convention states that D • dS is positive if the component of D normal to the surface is directed outwards.

2.2 The Electrostatic Potential

The electrostatic field is conservative and can, therefore, be derived from a scalar potential function. That is to say that if only electric forces are acting the work done by these forces on a charged particle will serve to raise the kinetic energy of the particle by the amount of the work done. More precisely we say that the electric field vector is the negative gradient of the scalar potential, V,

$$E = - \text{grad } V \qquad (2.2.1)$$

in cartesian coordinates

$$E_x = - \frac{\partial V}{\partial x}$$

$$E_y = - \frac{\partial V}{\partial y}$$

$$E_z = - \frac{\partial V}{\partial z}$$

The necessary and sufficient condition that a field be conservative is that the line integral of the field vector around any closed path be zero, or,

$$\oint E \cdot ds = 0 \qquad (2.2.2)$$

Physically this means that there is no net work done (per unit charge) as we move a charge around a closed path, which is of course essential if energy is to be conserved.

The potential itself is not uniquely determined, since it arises from an integration of E, and must contain an arbitrary

constant. However, we can define the difference of potential between two points A and B as the negative of the work done per unit charge in moving a charge from point A to point B. Hence,

$$V_B - V_A = -\int_A^B E \cdot ds \quad . \qquad (2.2.3)$$

This integration is independent of the path taken from A to B because of the condition (2.2.2). We may, if we wish, so choose the point A that V_A may conveniently be set equal to zero. This is equivalent to stating a boundary condition which enables us to evaluate the arbitrary constant in (2.2.3). We may use the following method to choose the point A. The field in many problems can be expressed as,

$$E \propto \frac{1}{r^n}$$

where n may have any finite value. If n is greater than 1 we choose A at infinity, and if n is less than 1 we choose A at zero. For the special case where n is equal to 1 neither zero nor infinity are good points, but some finite point appropriate to the situation must be chosen.

Since the potential is scalar function, most electrostatic problems are more readily solved by computing the potential, rather than by computing the three components of the field directly. After the potential has been ascertained the field is readily obtained by differentiation.

The potential due to a point charge, q, at a distance r from the charge, is,

$$V = \frac{q}{4\pi\epsilon_0 r} \qquad (2.2.4)$$

where the potential at $r = \infty$ has been set equal to zero.

The potential of an assemblage of point charges is simply the algebraic sum of the individual potential.

The electromotive force in an electric field is defined as the line integral of E. It is equal, therefore, to the work done by E per unit charge, and is hence the negative of the potential difference. The net e.m.f. around any closed path in an electrostatic field is zero, equation (2.2.2). Where time varying fields are present equation (2.2.2) does not hold as we shall see later.

2.3 Poisson's Equation

If instead of considering the field due to point charges we wish to evaluate the field or potential due to distributed charges, it is convenient to restate Gauss' Law, equation (2.1.5), in differential form.

Let us consider a small element of volume in space, dx dy dz, in which an electric charge density ρ exists. The charge density ρ need not be a constant, but can vary from point to point; however, the total charge contained in any small volume dx dy dz is just ρ multiplied by dx dy dz.

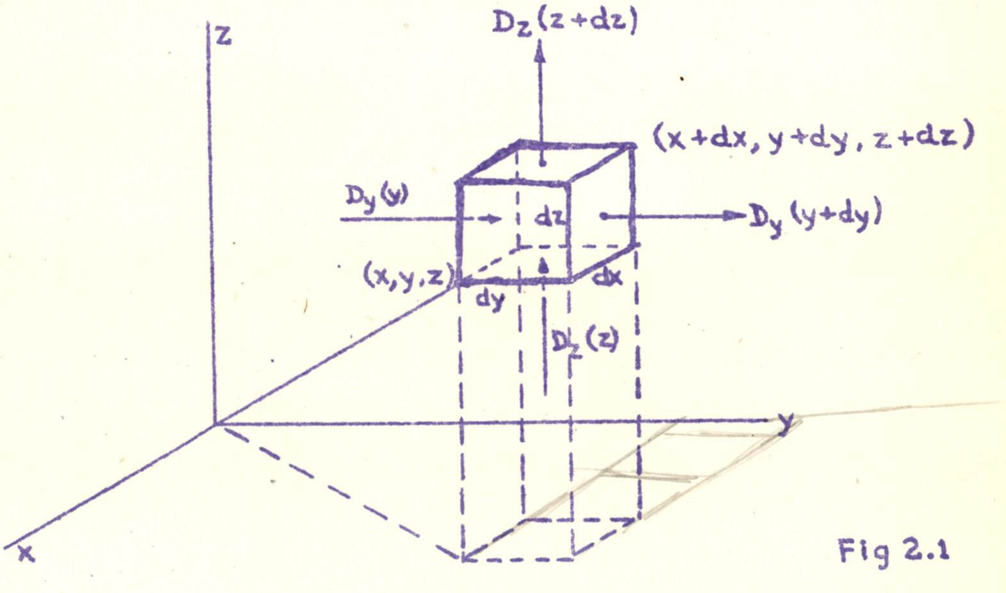


Fig 2.1

Let us apply Gauss' Theorem to the small volume element in Fig. 2.1. Since a charge is contained inside the volume there must be a non-zero integral of the normal component of D over the bounding surface. Since the volume is very small, the surface integral of D_y is evidently, $[D_y(y+dy) - D(y)]\,dx\,dz$ where dx dz is the area normal to D_y, and where we have used the sign convention that an outward drawn normal leads to a positive surface integral.

Similarly the surface integral over the dx dy surfaces is $[D_z(z + dz) - D_z(z)]\, dx\, dy$, and over the dy dz surfaces is $[D_x(x + dx) - D_x(x)]\, dy\, dz$. Combining and equating to the charge enclosed, we have,

$$[D_x(x + dx) - D_x(x)]dydz + [D_y(y + dy) - D_y(y)]dxdz + [D_z(z + dz) - D_z(z)]dxdy = \rho\, dx\, dy\, dz$$

dividing through by dx dy dz we have

$$\frac{D_x(x + dx) - D_x(x)}{dx} + \frac{D_y(y + dy) - D_y(y)}{dy} + \frac{D_z(z + dz) - D_z(z)}{dz} = \rho$$

Now the terms on the left hand side of the above equation are by definition $\frac{\partial D_x}{\partial x}$, $\frac{\partial D_y}{\partial y}$ and $\frac{\partial D_z}{\partial z}$ respectively in the limit as dx, dy and dz approach zero. Hence,

$$\frac{\partial D_x}{\partial x} + \frac{\partial D_y}{\partial y} + \frac{\partial D_z}{\partial z} = \rho$$

Combining with Equation (2.1.4) this becomes

$$\frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z} = \frac{\rho}{\epsilon_0} \qquad (2.3.1)$$

If now we use the three component equations of the set (2.2.1), we have Poisson's equation,

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = -\frac{\rho}{\epsilon_0} \qquad (2.3.2)$$

For the special case where the charge density at the point in question is zero, the reduced form of (2.3.2) is called LaPlace's equation.

In many practical problems the geometry of the system has cylindrical symmetry. For such cases it is advantageous to make use of cylindrical polar coordinates r, φ and z. We can express Poisson's equation in terms of such coordinates by following much the same procedure as for cartesian coordinates. In Fig. 2.2 we have a set of cylindrical polar coordinates shown in their relationship to x, y, z coordinates and now our element of volume is $r\,d\varphi\,dr\,dz$.

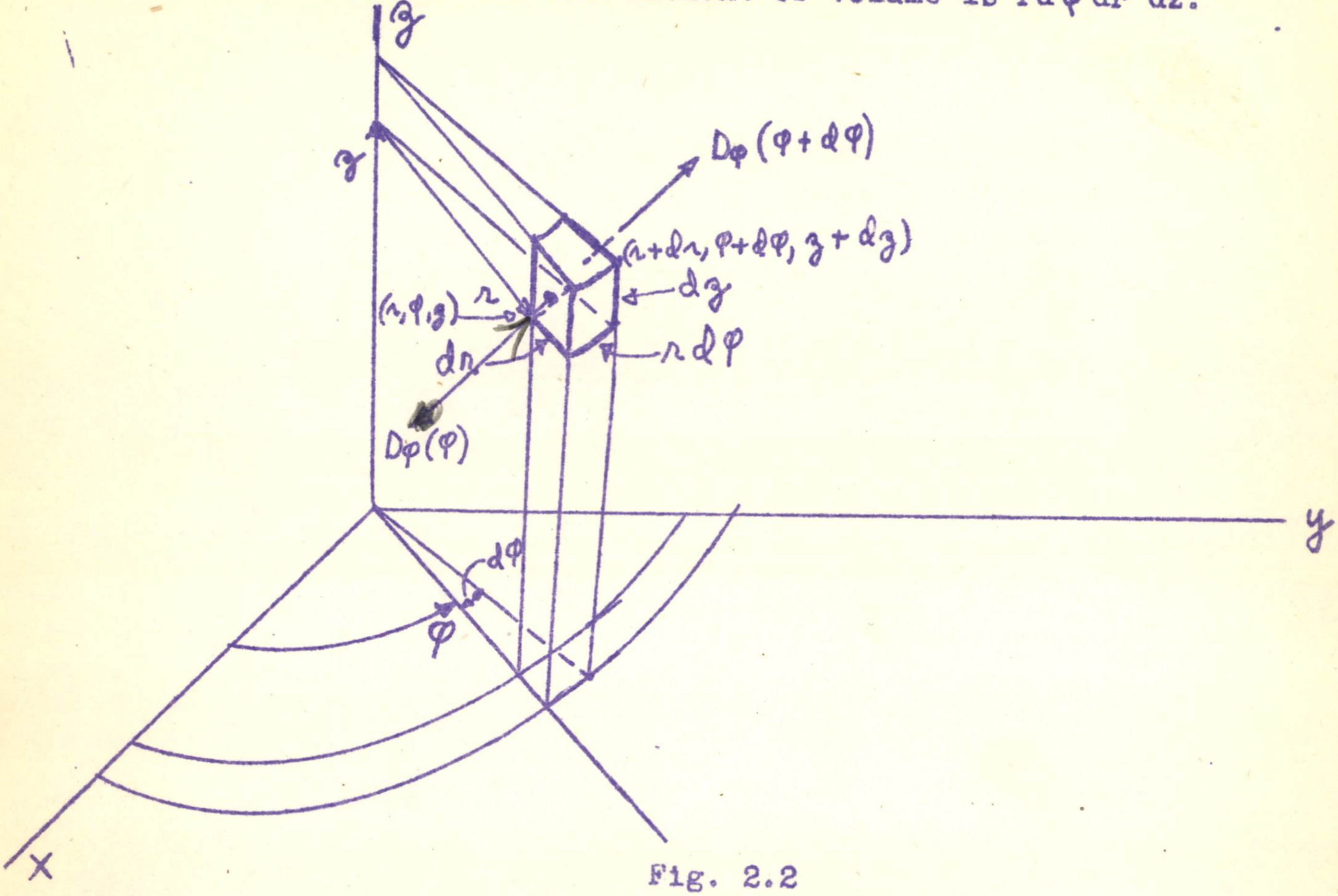


Fig. 2.2

Furthermore, the size of the volume elements, and the size of four of the surfaces which bound it, depend on the position of the volume element, since one side, $r\,d\varphi$, is proportional to r. Since the volume element depends on r alone of the coordinates, this difference will be important only for the surfaces perpendicular to r in the application of Gauss' Theorem which then yields,

$$[(r + dr)D_r(r + dr) - r\,D_r(r)]d\varphi dz + [D_\varphi(\varphi + d\varphi) - D_\varphi(\varphi)]\,drdz$$

$$+ [D_z(z + dz) - D_z(z)]\,rd\varphi dz = \rho\,rd\varphi\,dr\,dz$$

from which it follows,

$$\frac{1}{r}\,\frac{\partial(rD_r)}{\partial r} + \frac{1}{r}\,\frac{\partial D_\varphi}{\partial \varphi} + \frac{\partial D_z}{\partial z} = \rho$$

and since in cylindrical polar coordinates,

$$D_r = -\epsilon_0 \frac{\partial V}{\partial r}$$

$$D_\varphi = -\epsilon_0 \frac{1}{r}\,\frac{\partial V}{\partial \varphi}$$

$$D_z = -\epsilon_0 \frac{\partial V}{\partial z}$$

we have

$$\frac{1}{r}\,\frac{\partial}{\partial r}\left(r\,\frac{\partial V}{\partial r}\right) + \frac{1}{r^2}\,\frac{\partial^2 V}{\partial \varphi^2} + \frac{\partial^2 V}{\partial z^2} = -\frac{\rho}{\epsilon_0} \qquad (2.3.3)$$

2.4 <u>The Motion of Charged Particles in Electrostatic Fields</u>

[Millman and Seely: pp. 18-25, pp. 63-69, pp. 71-86]

2.4.1 <u>Work and Energy</u>

A charged particle of mass m and charge q suffers a force of Eq in an electrostatic field. (We are tacitly assuming that the charge q is not large enough to affect the distribution of charges which give rise to the field E.) By Newton's second law, we have,

$$\frac{d(mv)}{dt} = qE \quad . \qquad (2.4.1)$$

If we wish we can compute the work done on a particle in moving through an electrostatic field of force. We take the scalar product of each side of equation 2.4.1 with ds, the element of length along the path, and integrate from the initial point A to the final point B.

$$\int_A^B \frac{d(m\vec{v})}{dt} \cdot \vec{ds} = \int_A^B q\vec{E} \cdot \vec{ds} \qquad (2.4.2)$$

The left hand side of the equation may be rewritten, providing the mass m is constant, as

$$\int_A^B m \frac{dv}{dt} \cdot ds = \int_A^B m \frac{ds}{dt} \cdot dv = \int_A^B mv \cdot dv .$$

Upon integration equation (2.4.2) becomes,

$$\frac{1}{2} m v_B^2 - \frac{1}{2} m v_A^2 = \int_A^B q\vec{E} \cdot d\vec{s}$$

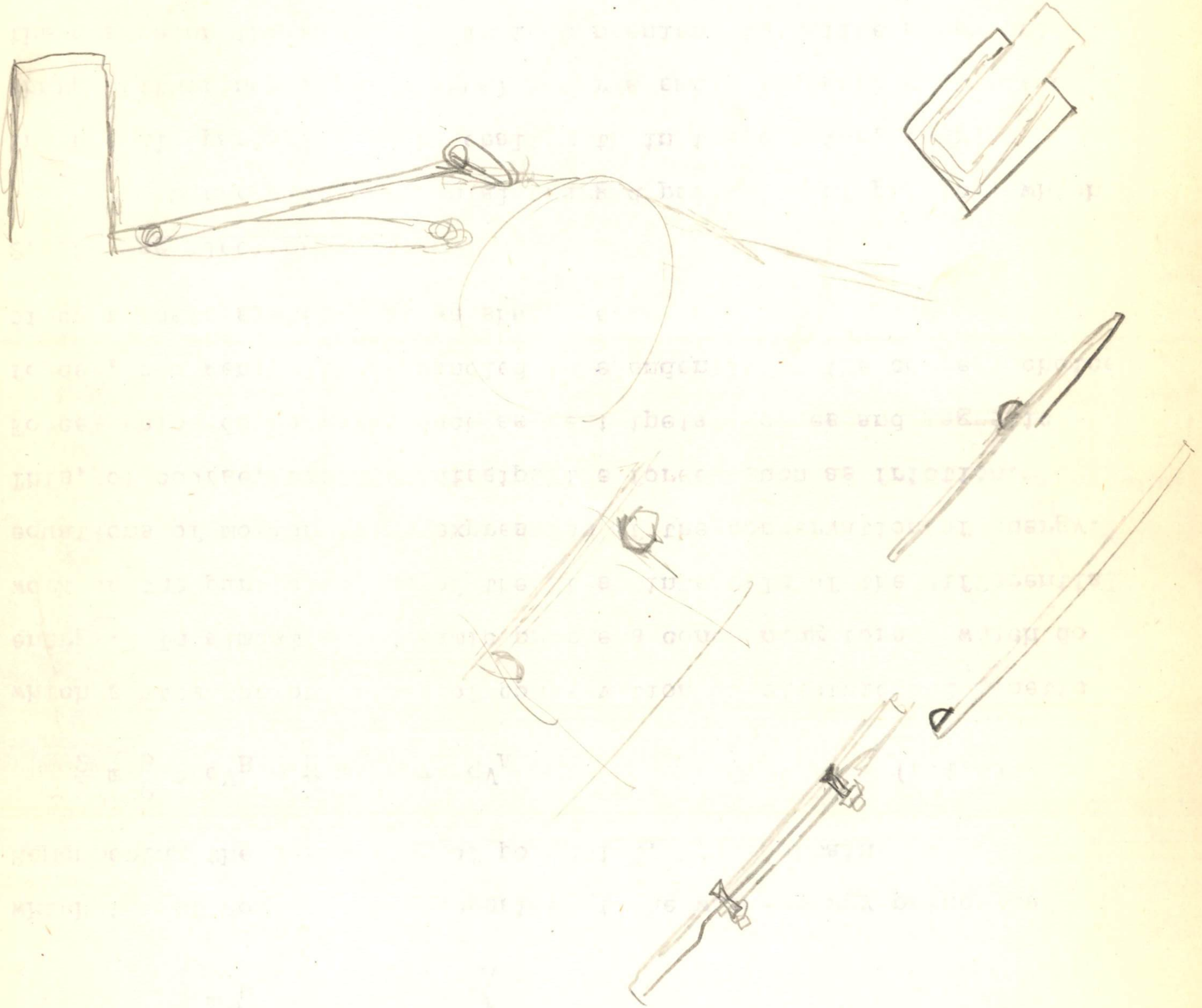
which is, of course, an expression of the work-energy principle. Remembering the definition of potential, V, we obtain

$$\boxed{\frac{1}{2} mv_B^2 + qV_B = \frac{1}{2} mv_A^2 + qV_A} \qquad (2.4.3)$$

which states the principle of conservation of electric and kinetic energy. In almost all dynamic problems concerning forces which do work on the particle, one of the first integrals of the differential equations of motion is an expression of the conservation of energy. This, of course, excludes dissipative forces such as friction. Forces which do no work, such as centripetal forces and magnetic forces, can generally be handled independently by the correct choice of coordinate systems, as we shall see.

2.4.2 The Electron Volt

Since all fundamental charged particles of physics, which include all particles to be dealt with in these notes, carry a charge either numerically equal to or a small integral multiple of the charge on the electron, it is convenient to define a new unit of energy in terms of this charge. This energy unit is called the electron volt, and is defined as the energy acquired by an electron in falling through a potential difference of one volt. We may write equation (2.4.3)



1ev = 1.6x10^{-19} joules

$$\frac{1}{2} mv_B^2 - \frac{1}{2} mv_A^2 = e(V_B - V_A) \quad ,$$

where we have set q = - e the electronic charge. This equation states that the electron increases its kinetic energy by an amount equal to its numerical charge times the increase in potential; an electron tends to move to points of higher potential. For particles of numerical charge + e the sign of the right hand side is reversed since positive charges tend to move to points of lower potential. In either case the particles are said to have gained 1 electron volt (1 ev) of energy if the difference in potential is 1 volt. To change from joules to electron-volts we need only divide the number of joules by the electronic charge in coulombs in order to obtain the number of electron volts, since,

change in kinetic energy = change in Potential Energy

or

$$\frac{\text{change in kinetic energy}}{\text{electron charge}} = \text{change in potential in volts} =$$

$$= \text{energy change in e - v.}$$

If the particles are doubly or triply charged, that is if they have charges equal numerically to two or three electronic charges, then the energy change in ev is numerically 2 or 3 times the potential charge in volts. It is customary, though not precise, to speak of 1400 volt electrons, or electrons of 1400 volts energy, meaning of course electrons of energy 1400 ev.

2.4.3 The Electrostatically Deflected Cathode Ray Tube

An interesting application of the motion of electrons (or charged particles) in electric fields is met with in the Cathode Ray Tube. This tube in its simplest form is illustrated in Fig. 2.3. A cathode K emits electrons which are accelerated along the axis of the tube by means of a potential V_A applied to

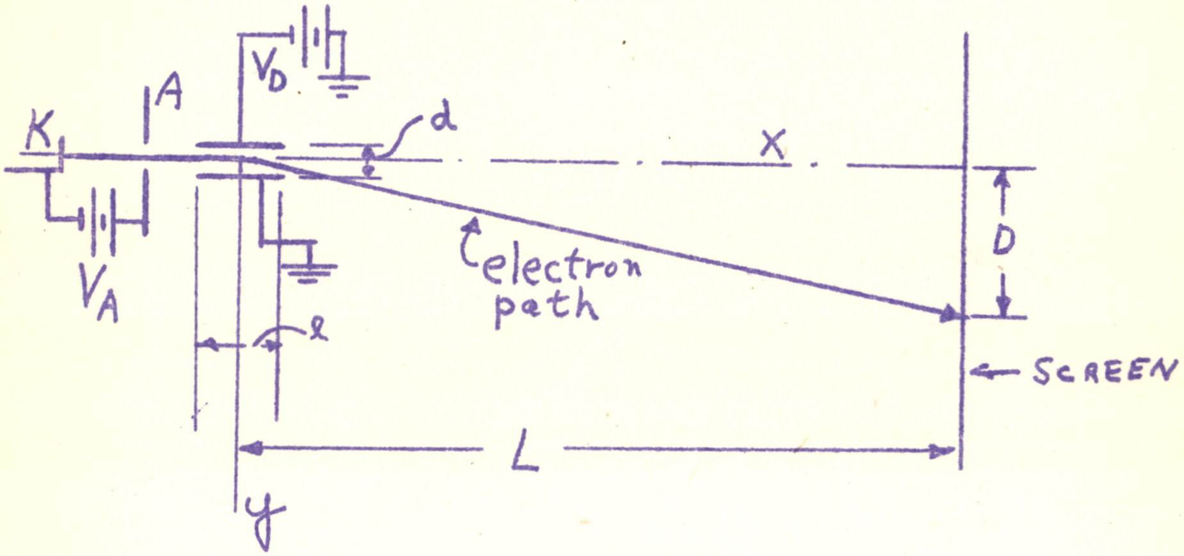


Fig. 2.3

an accelerating electrode A. We will assume that by means of a suitable focussing system, not shown, that the electrons emerge from A in a well focussed, pencil-like beam. After leaving the anode the electrons next enter a region of constant electric field which is at right angles to their direction of motion. This constant electric field can be approximated by applying a deflecting potential V_D across two flat deflecting plates, shown here in section, whose separation d is somewhat smaller than the length ℓ of either plate. The motion of the electrons in the region between the deflecting plates is similar to the motion of a baseball thrown horizontally in the earth's gravitational field. Since the electric field is uniform, the electrons will move in a parabola until they leave the deflecting region, at which time they will be travelling at an angle θ, to their original direction. After leaving the deflecting field the electrons travel in a straight line, through field free space, until they strike a fluorescent screen, and are thus observed at a distance L from the center of the deflecting plates. We desire to calculate the deflection D on the screen.

Let us choose a coordinate system such that x is measured vertically downwardz from the center of the deflecting region. The electrons acquire a velocity v_{xo} in passing from cathode to anode. If they leave the cathode with negligibly low velocities, we have, from conservation of energy,

$$\frac{1}{2} m v_{xo}^2 = e V_A, \text{ or } v_{xo} = \sqrt{2 \frac{e}{m} V_A} .$$

On entering the deflecting region at time t = o, the electrons are subjected to a force in the y-direction equal to ~~eE_y~~ eE_y. Assuming that the deflecting plates behave like a parallel plate condenser, large in ~~line or~~ linear dimensions compared to the plate separation, and neglecting fringing of the field near the edges, we have,

$$E_y = \frac{V_D}{d}$$

and by Newton's second law

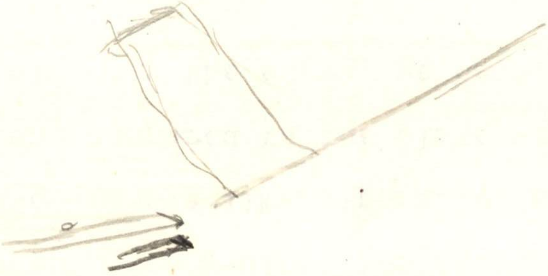
$$m \frac{dv_y}{dt} = e \frac{V_D}{d}$$

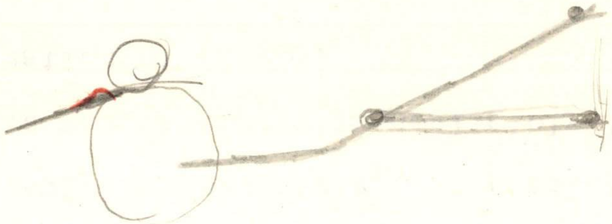
or

$$v_y = \frac{e}{m} \frac{V_D}{d} t \quad , \quad v_y = o \text{ when } t = o$$

and

$$y = \frac{1}{2} \frac{e}{m} \frac{V_D}{d} t^2, \quad y = o \text{ when } t = o$$





Since there is no force in the x direction

$$v_x = \text{constant} = v_{xo}$$

$$x = v_{xo}t - \frac{\ell}{2} \quad , \quad x = -\frac{\ell}{2} \text{ when } t = o$$

The time of flight t_f through the deflecting region can be found by setting $x = \frac{\ell}{2}$, hence $t_f = \frac{\ell}{v_{ox}}$.

The y deflection y_f during this time is then

$$y_f = \frac{1}{2}\frac{e}{m}\frac{V_D}{d}\frac{\ell^2}{v_{xo}^2} \ .$$

The y directed velocity at time t_f is

$$v_{yf} = \frac{e}{m}\frac{V_D}{d}\frac{\ell}{v_{xo}}$$

After leaving the deflecting region the electrons are traveling at an angle θ to the axis, given by,

$$\tan\theta = \frac{v_{yf}}{v_{xo}} = \frac{e}{m}\frac{V_D}{d}\frac{\ell}{v_{xo}^2} \ .$$

The further deflection due to traveling a distance $L - \frac{\ell}{2}$ to the screen at this angle is just,

$$(L - \frac{\ell}{2}) \tan\theta \ .$$

To this deflection we must add y_f to get the total deflection D.

$$D = y_f + (L - \frac{\ell}{2}) \tan\theta$$

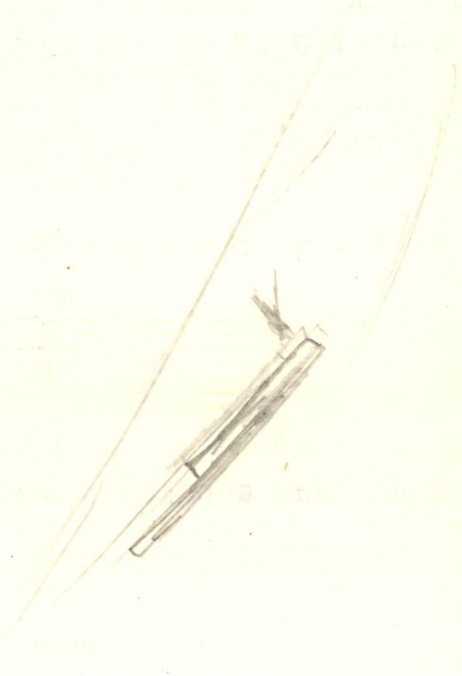
$$D = \frac{1}{2}\frac{e}{m}\frac{V_D}{d}\frac{\ell^2}{v_{xo}^2} + (L - \frac{\ell}{2})\frac{e}{m}\frac{V_D}{d}\frac{\ell}{v_{xo}^2}$$

from which,

$$D = L\frac{e}{m}\frac{V_D}{d}\frac{\ell}{v_{xo}^2}$$

remembering $v_{xo}^2 = 2\frac{e}{m}V_A$

$$\boxed{D = \frac{1}{2}\frac{\ell L}{d}\frac{V_D}{V_A}} \qquad (2.4.4)$$



This result is somewhat startling in that the magnitude of the deflection does not depend at all on the kind of charged particle. Of great practical importance is the fact that the deflection is proportional to the deflecting voltage, and hence the electrostatic CRT is a linear instrument. A little geometrical work serves to show that all electrons seem to come from the central point in the space between the deflecting plates, which is therefore referred to as the "virtual" cathode.

We have thus far neglected errors due to the non-uniformity of the field; in practice the plates are never large compared to their separation; and to the fringing of the field at the edges of the deflecting plates. The errors thus introduced can be corrected for by modifying the geometrical factor Ll/d in equation (2.4.4) a small amount; for small deflections the linearity of the instrument is preserved.

Cathode Ray Tubes have many and varied uses including television screens, radar presentation screens, and a large variety of uses as measuring instruments in the laboratory. The most common use is as the well-hnown cathode ray oscilloscope. In this tube a second pair of deflecting plates are introduced along the axis, but rotated by 90° to the first pair in order to produce a deflection at right angles to that produced by the first pair. If the separation of deflecting plate pairs is short compared to the mean distance to the screen our formula (2.4.4) will still hold approximately. We are now enabled to get a two-dimensional picture of voltage or voltage and some of other suitable variable.

A common use of such an instrument is the measurement of

A.C. voltage vs. time. Up till now we have assumed that the electronic field is static. However, as far as the electron is concerned we need only require that the voltage varies but little during the time that one electron is in the deflecting field. This means that the transit time of a particular electron must be short compared to the period of oscillation of the electric field or voltage. If we require that the transit time of the electron be no greater than 1% of the period, then

$$\frac{\ell}{v_{xo}} = \frac{\ell}{\sqrt{2\frac{e}{m}V_A}} = .01T = \frac{.01}{f_{max}}$$

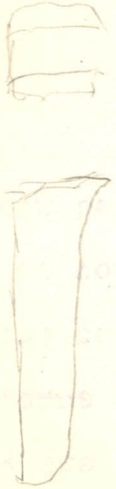
$$f_{max} = \frac{.01}{\ell}\sqrt{2\frac{e}{m}V_A}$$

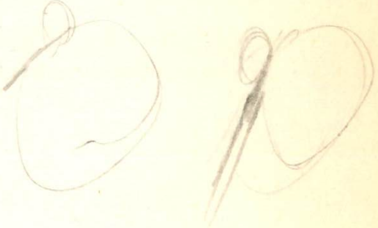
for $\ell = .02$ meters, $V_a = 1{,}000$ volts

$$f_{max} = 9.4 \text{ mc/sec.}$$

Hence, the measurement of voltages varying at frequencies up to $\sim 10^7$ cps puts no stringent conditions on the instrument.

Such a measurement is carried out by putting the voltage to be observed on the vertically deflecting plates, and a voltage varying linearly with the time on the horizontally deflecting plates. The horizontal deflection is proportional to the time and the vertical deflection is proportional to the signal voltage. The trace on the fluorescent screen then represents the signal voltage as a function of time. We must, of course, repeat the linear sweep at definite intervals, and these intervals must be synchronized with the signal voltage. This latter adjustment is easily made at the moderate frequencies we are considering here.





2.4.4 Motion of Charged Particles in Electric Fields Varying Slowly with the Time.

If the electric field of force is varying slowly with the time we can handle dynamical problems by much the same methods used for electrostatic fields. By slowly, we mean fields for which the wavelength λ is long compared to the dimensions of the space in which the field exists. Since $\lambda = \frac{c}{f}$ this puts an upper limit on the frequency of the electric field, where c is the velocity with which electromagnetic disturbances are propagated. If this condition is not met the magnetic forces associated with the time varying electric field must be taken into consideration.

For example, consider a particle of charge q in the unifrom (in space) field between two large condenser plates. We may allow the field, $E = \frac{V}{d}$, to vary with the time, but at a given instance it is constant throughout the region in question. If $V = V_o \sin \omega t$, Newton's second law requires

$$\frac{d}{dt}(mv_x) = q\,\frac{V_o}{d}\sin \omega t$$

where x is the coordinate along the field direction. If x = o, $v_x = o$ when t = o, the first integral of this equation is,

$$v_x = \frac{1}{\omega}\,\frac{q}{m}\,\frac{V_o}{d}\,(1 - \text{cost}\ \omega t)$$

and

$$x = \frac{1}{\omega^2}\,\frac{q}{m}\,\frac{V_o}{d}\,(\omega t - \sin \omega t) \qquad (2.4.5)$$

This result shows that no matter what the value of the constants, ωt will eventually predominate over $\sin \omega t$, and the particle will be cleared from the space between the plates. It is easy to show that there is one and only one value of the initial velocity which will enable the particle to oscillate between the plates and not be swept out by the field.

2.5 The Magnetostatic Field

It is well known experimentally that there are forces between moving electric charges which are completely independent of the electrostatic forces described in Section 2.1. Since an electric current consists of an assemblage of moving charges, it follows that there are similar forces between currents and between currents and moving electric charges. These forces are called magnetic and may be uniquely described if we introduce a field vector, B. This vector B, the magnetic induction vector, can be considered as arising from the currents, and we can describe the mutual forces between currents and moving charges as interactions between the field B and these moving charges or currents. This is similar to the electrostatic case where the field E arises from charges (stationary) and the electric force on another charge is considered as due to an interaction between E and the charge in question.

The magnetic force on a moving charge can then be written as

$$F = q\, v \times B \qquad (2.5.1)$$

where v is the velocity of the charge. The magnetic force on a small circuit element ds is, by analogy,

$$dF = i\,ds \times B \qquad (2.5.2)$$

When dealing with material media it is necessary to introduce another vector, the magnetic intensity H. This vector is related to the magnetic induction by,

$$H = \frac{B}{\mu},$$

where μ is the permeability of the medium. For free space which is our chief concern μ is designated by μ_0 and is equal to $4\pi \times 10^{-7}$ henries per meter.

Ampere's rule enables us to compute the magnetic intensity due to a current element, and is

$$dH = \frac{i \, ds \times r}{|r^3|} \quad ,$$

where r is the vector drawn from the current element ids to the point at which the field is to be evaluated. Another general theorem applicable to the understanding of magnetic fields is Ampere's circuital law, which states,

$$\oint H \cdot ds = i \qquad (2.5.3)$$

or in words, the line integral of H around any closed path is equal to the algebraic sum of the currents linked by the path.

If we compare eq. (2.5.3) with eq. (2.2.2) we see that the condition for the establishment of a scaler magnetic potential is not fulfilled in general, and hence no magnetic potential can be uniquely defined. That is to say the magnetic field is not conservative. This does not imply that the general principle of conservation of energy is violated, but rather that magnetic forces do no work on moving charges. An inspection of eq. (2.5.1) shows that the magnetic force is always at right angles to the direction of motion, and hence no work is ever done on moving charges by magnetic fields.

If, however, we restrict ourselves to paths of integration which do not link currents we can set up a scalar magnetic potential, V_m, and this is often convenient for the solution of field problems. This potential is defined in a similar manner to the electric potential, and strictly speaking, of course, it is the potential difference which is determined.

$$H = - \text{grad } V_m \qquad (2.5.4)$$

It is also convenient in many problems to introduce the concept of magnetic dipole or magnetic moment. A small circuit elememt for instance behaves like a dipole in a uniform magnetic field, in that there is no net force, but there is a net torque tending to turn the circuit element. This torque is

$$T = m \times B \qquad (2.5.5)$$

where m is the dipole moment and is equal to iA where A is the area of the circuit element. This equation (2.5.5) assumes that the field B does not vary appreciably over the area of the circuit element. The sense of the vector m is arbitrarily taken as the direction of advance of a right handed screw whose perimeter is turned in the direction of the positive current flow.

2.6 Motion of Charged Particles in Magnetostatic Fields

[M. & S. pp. 31-40, 69-71]

Let us consider a particle of charge q moving in a magnetic field B. Eq. (2.5.1) tells us that a force will be exerted on the particle which is at once perpendicular to B and to the velocity of the particle. If B is uniform and if the particle is initially moving parallel to B there will be no force whatsoever. If, however, the initial speed v of the particle is at right angles to B then there will be a force numerically equal to qv_oB which remains at right angles to both B and the velocity. This force is then centripetal in nature and does not increase the speed of the particle. It can and does change the direction of motion. Newton's second law for this case is then

$$\frac{mv^2}{R} = qvB \qquad (2.5.6)$$

or

$$\omega = \frac{v}{R} = \frac{q}{m} B \qquad (2.5.7)$$

The angular velocity for a given particle and magnetic field is thus constant. This fact is made use of in the cyclotron, a device for accelerating charged particles, as we shall see later.

If the initial velocity has components both perpendicular and parallel to the field B then the motion will be helical in form. Let us assume that a charged particle is injected into a region of uniform magnetic field with an initial velocity v_o which makes an angle θ with the magnetic induction vector B. Then the initial velocity along the direction of the magnetic field is $v_o \cos \theta$ and is unaffected by the field B. The velocity at right angles to B is initially $v_o \sin \theta$, and we may think of this component of velocity interacting with the magnetic field so that eq. (2.5.7) becomes

$$\frac{v \sin \theta}{R} = \frac{q}{m} B$$

and the projection of the motion in a plane at right angles to B is circular; the net motion being helical.

This situation has an important practical application;

namely, magnetic focussing. For instance ~~if~~ suppose we have a beam of electrons which emerge from a cathode, or electron gun, which are not sharply focussed in a pencil-like beam, but are in a slightly divergent beam of ½ angle θ_0. Let us assume that all the electrons have the same speed v_0 and that θ_0 is small, so that, the component of velocity along the axis of the beam is,

$$v_0 \cos \theta_0 \cong v_0$$

and the component perpendicular to the axis is

$$v_0 \sin \theta_0 \ .$$

Here we are considering the extreme case of the electron making the greatest angle, θ_0, with the beam axis. What follows will apply equally well to the electrons which are less divergent. These electrons will proceed down the tube with equal drift velocities, v_0, regardless of the particular value of θ, but with different components of transverse velocity. However, the angular velocity about the axis of the beam will be the same for all electrons regardless of the value of θ, i.e.,

$$\omega = \frac{v_0 \sin \theta}{r} = \frac{e}{m} B$$

Hence after a time (the period) equal to $T = \frac{2\pi}{\omega}$ all the electrons will be back on the axis of the beam, and this point is a focal spot. The distance from the cathode to the first focal spot is just the pitch of the helix, and is,

$$\boxed{p = v_0 T = \frac{2\pi v_0}{e/m \ B}}$$

If the electrons have acquired their velocity by falling through a potential difference V_A this expression becomes

$$\boxed{p = \frac{2\pi}{B}\sqrt{\frac{2V_A}{e/m}}}$$

Theoretically it is possible to have an infinite number of such focal points, and indeed in some applications, the beam goes through many focal points before traversing the entire length of the vacuum tube in question. The pitch of the helix, which is the separation of the focal points, is inversely proportional to B. If one wishes to limit the maximum sideways deflection that any given electron can have, one would increase B and hence decrease p, and for a given length of beam this process will increase the number of focal points. One example of the type of application is met with in the travelling wave tube. In this application it is necessary for a beam of electrons 20 to 30 cm in length to be confined in a pencil beam a few millimeters in diameter. Thus far only magnetic focussing methods have been successfully used for this purpose. The travelling wave tube is a very interesting example of the interaction of electrons and high frequency waves, but its general theory is beyond the scope of these notes.

Another application of the motion of electrons in magnetic fields is the magnetically deflected cathode ray tube. In Fig. 2.3, we can imagine that the electric deflecting plates are removed, and that a uniform magnetic field B, perpendicular to the plane of the paper, occupies the region of length ℓ. Then the electrons after entering the region occupied by the magnetic field B will be deflected in the arc of a circle. Fig. 2.4 shows a simplified view of the situation.

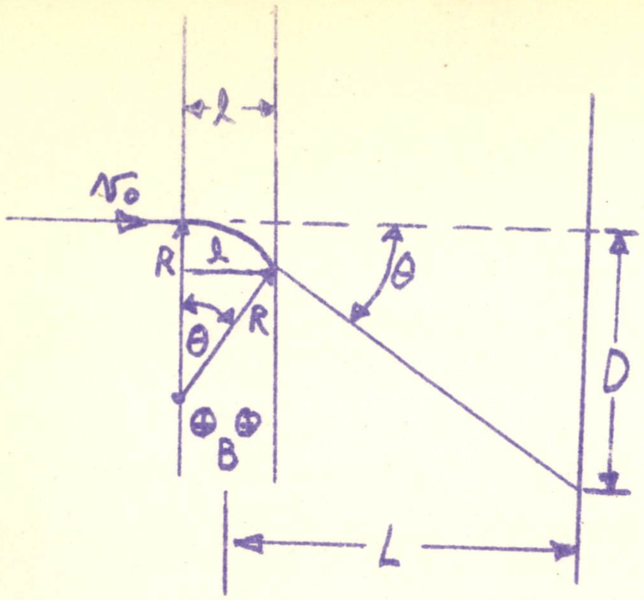


Fig. 2.4

By inspection,

$$\sin \theta = \frac{\ell}{R}$$

for small θ

$$\sin \theta \cong \theta \cong \tan \theta$$

and for $L \gg \ell$

$$D \cong L \tan \theta = L \frac{\ell}{R}$$

$$R = \frac{v_o}{e/mB}$$

$$\boxed{D = \frac{L \ell B}{v_o} \frac{e}{m} = L \ell B \sqrt{\frac{e/m}{2 V_A}}}$$

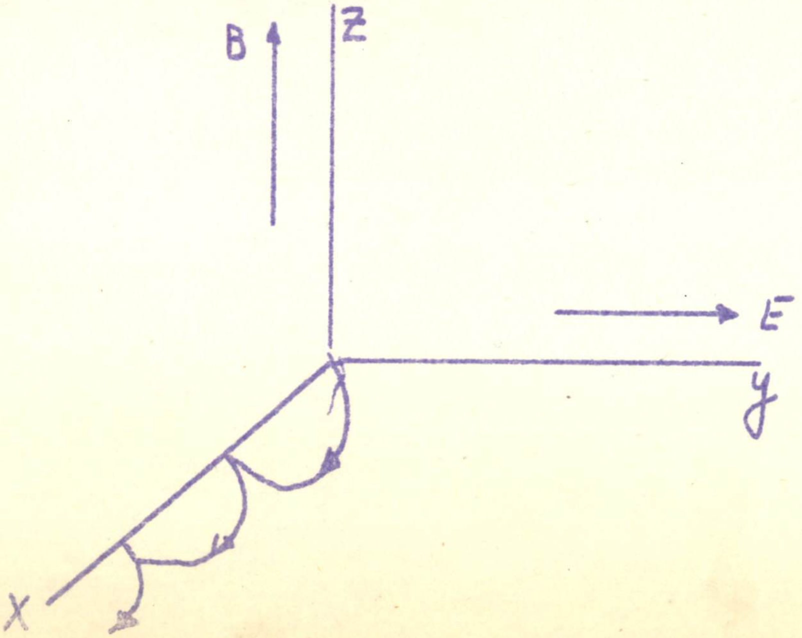
The deflection is proportional to B which in turn is proportional to the currents producing it, so this tube is a linear instrument. It is not as widely used as the electrostatic

CRT, but is useful in cases where one wishes current rather than voltage sensitivity.

2.7 Motion of Charged Particles in Combined Electric and Magnetic Fields. (M. + S. pp. 40 - 48, 86, 87)

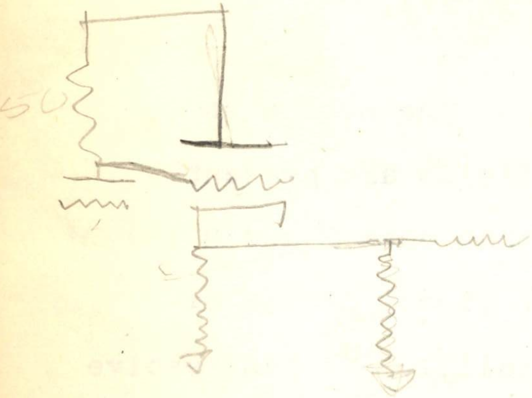
We are now in a position to discuss the motion of particles when both electric and magnetic fields are present. For our immediate purposes we will assume that both E and B are uniform in space and constant in time. First, let us examine the case where the two fields are parallel. We can resolve the velocity vector into two components, one parallel to the fields and one at right angles. The parallel component will be accelerated or decellerated by the electric field, but will not be influenced by the magnetic field. The perpendicular component will remain constant in magnitude, since it will not react with E, but will change continuously in direction under the influence of B. Hence, the projection of the motion in a plane perpendicular to the fields is a circle, and the entire path of the motion might be described as a helix of variable pitch.

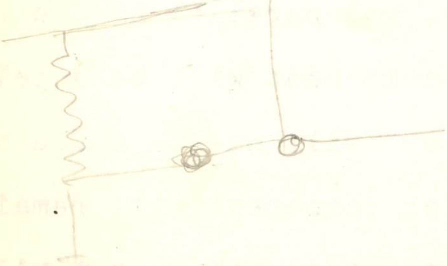
Let us next examine the case where E and B are at right angles to one another as shown in Fig. 2.5



200

.1





The equations of motion are

$$\frac{dv_x}{dt} = \frac{q}{m} v_y B$$

$$\frac{dv_y}{dt} = \frac{q}{m} E - \frac{q}{m} v_x B$$

$$\frac{dv_z}{dt} = 0$$

Let us adopt the abbreviations

$$\omega = \frac{q}{m} \beta \qquad a = \frac{q}{m} E$$

we then have

$$\frac{dv_x}{dt} = \omega v_y \qquad \frac{dv_y}{dt} = a - \omega v_x \qquad \frac{dv_z}{dt} = 0$$

if we differentiate the second of these equations and substitute from the first, we have

$$\frac{d^2 v_y}{dt^2} + \omega^2 v_y = 0$$

The solution of this equation is

$$v_y = C_1 \cos \omega t + C_2 \sin \omega t$$

where C_1 and C_2 are arbitrary constants. If we now assume that initially $v_x = v_y = v_z = 0$, then $C_1 = 0$, and

$$v_y = C_2 \sin \omega t$$

differentiating

$$\frac{dv_y}{dt} = C_2 \omega \cos \omega t$$

initially $\frac{dv_y}{dt} = a$ and hence $C_2 = \frac{a}{\omega}$ and,

$$\boxed{\left.\begin{aligned} v_y &= \frac{a}{\omega} \sin \omega t \\ y &= \frac{a}{\omega^2}(1 - \cos \omega t) \end{aligned}\right\}} \qquad (2.7.1)$$

11 6
12 7
13 8
14
9 crowd
15
10
16 11
17 nonactive
18 12

6
7
8
9
10

for crossed fields

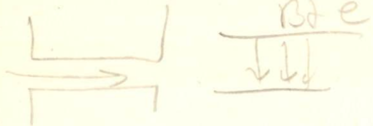
$$y = \frac{v_y}{\omega}\sin\omega t + \left(\frac{a}{\omega^2} - \frac{v_x}{\omega}\right)(1-\cos\omega t)$$

$$x = \frac{v_x}{\omega}(1-\cos\omega t) - \left(\cancel{\frac{a}{\omega^2}} - \frac{v_y}{\omega}\right)\sin\omega t + \frac{a}{\omega}t$$

if the particle is at the origin at t = o .

now,
$$\boxed{\begin{aligned} \frac{dv_x}{dt} &= \omega v_y = a \sin \omega t \\ v_x &= \frac{a}{\omega}(1 - \cos \omega t) \\ x &= \frac{a}{\omega^2}(\omega t - \sin \omega t) \end{aligned}} \quad (2.7.2)$$

The expression for x and y above are the parametric equations of a cycloid. The path of the motion is sketchediin Fig. 2.5 for a positive particle. The solution of the case in which v_x, v_y and v_z are not zero is left to the problems.

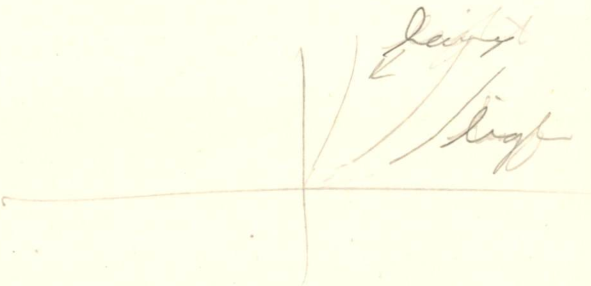


electric $y = \frac{1}{2}\frac{\ell L}{d}\frac{V_b}{V_A}$

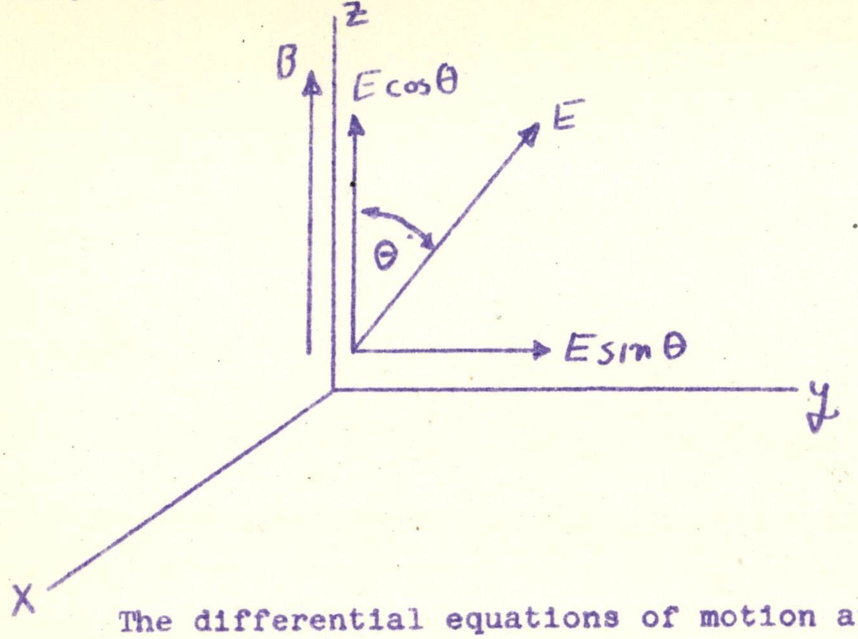
mag $X = L\ell B\sqrt{\frac{q/m}{2V_A}}$

$X^2 = \ell^2 L^2 B^2 \frac{q/m}{2VA}$

$y = \frac{V_b}{L\ell d B^2}\frac{1}{q/m}X^2$



Now let us examine the case where E and B make an arbitrary angle θ with each other as in Fig. 2.6.



The differential equations of motion are;

$$\frac{dv_x}{dt} = \frac{q}{m} B v_y$$

$$\frac{dv_y}{dt} = (E \sin\theta)\frac{q}{m} - \frac{q}{m} B v_x \qquad (2.7.3)$$

$$\frac{dv_z}{dt} = \frac{q}{m} E \cos\theta$$

The equations for the x and y coordinates are precisely the same as those at the top of page 29 with the exception that E sin θ has been substituted for E. Therefore if we make the same substitution in eqs. (2.7.1) and (2.7.2), remembering that a now equals $q/m\ E \sin\theta$, we have the solutions of the first two of eqs. (2.7.3) if the initial x and y velocities are zero. The solution of the final equation of (2.7.3) is just the usual expression for acceleration in a uniform field. Hence, the projection of the motion in the plane x and y is cycloidal, and the motion parallel to the z-axis is that of uniform acceleration. This result is evidently true for any finite value of θ, however small.

2.8 The Measurement of q/m

In all of the equations concerning motion of charged particles in electric and magnetic fields, which we have so far considered, the ratio of charge to mass has always occurred, but never the charge or mass alone. The ratios q/m for various fundamental particles make up one of the great sets of experimental knowledge in physics. These data, combined with the measurement of the electronic charge and the further knowledge that all other charges are equal to or are small integral multiples of the electronic charge, have been the most exact source of our knowledge of the mass of fundamental particles, atoms, and molecules. Not only was the first discovery of the existence of isotopes of the atomic elements made by such means, but also the whole science of "mass spectroscopy" has been built up through the measurement of the ratio of charge to mass.

The first measurements of q/m were made by J. J. Thomson about 1900, and led to his discovery of the isotopic constitution of the elements. In Thomson's apparatus parallel electric and magnetic fields were set up in the same region in space, and electrons or positive ions which had previously fallen through a potential difference were injected into this region at right angles to the fields. This is just as though a CRT were equipped with a set of electrostatic deflecting plates and a set of magnetic deflecting coils. The deflection produced by the electric field will be at right angles to the deflection produced by the magnetic coils (since the fields are parallel) and we may use the expression for the deflections in the two kinds of cathode ray tubes.

Calling the deflection on the screen produced by the electric field, y, and by the magnetic field, x, we have

$$y = \frac{1}{2} \frac{L\ell}{d} \frac{V_D}{V_A}$$

and

$$x = L\ell B\sqrt{\frac{q/m}{2V_A}}$$

Now we can find the curve on the screen due to a particular kind of particle by eliminating V_a between the two equations above. Squaring the second,

$$x^2 = \frac{1}{2}\frac{L^2\ell^2B^2 q/m}{V_A}$$

and dividing this into the first equation we have,

$$\frac{y}{x^2} = \frac{V_D}{L\ell dB^2\ q/m}$$

Hence, all particles of the same q/m will lie on a parabola on the screen; different points on the parabola corresponding to different values of V_A. The initial slope of the parabola will be proportional to the mass; hence the parabolas of the heavier particles will lie closer to the y axis, i.e., the direction of the fields. Fig. 2.7 shows the case for positive and negative ions. The parabolas above and to the right of the axes are due to positive particles; the curves below and to the left are due to negative particles.

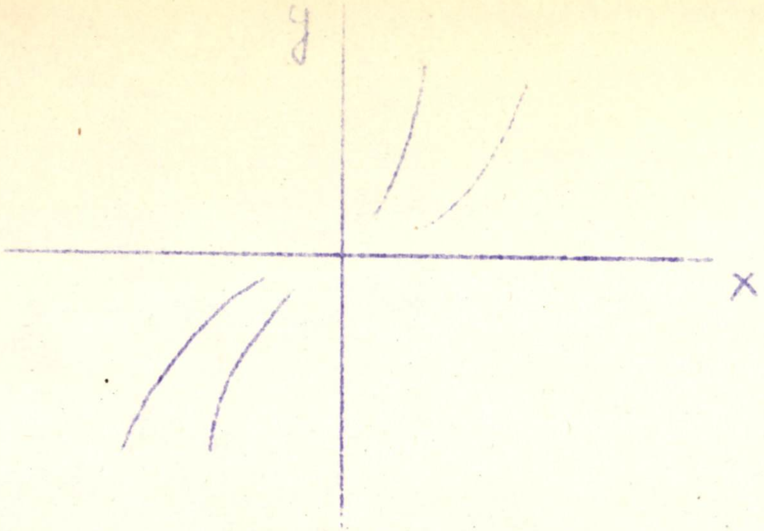


Fig. 2.7

Parabolas due to electrons on this scale figure would practically coincide with the negative x-axis.

The above method is historically important, and while it separates out particles of the same q/m, but with different initial velocities, it lacks precision and sensitivity. The first really precise method is due to Aston (about 1919) and uses a combination of electric and magnetic fields to refocus all ions of the same q/m regardless of their initial velocities.

Perhaps the most precise method now in use is due to Bainbridge, and consists of a "velocity selector" to sort out all ions except those of the particular velocity desired, and then a magnetic field is used to sort out those ions of particular q/m. Fig. 2.8 illustrates this process.

The velocity selector consists of two narrow slits of width w and separation s between which there are perpendicular electric and magnetic fields as shown. In the absence of the

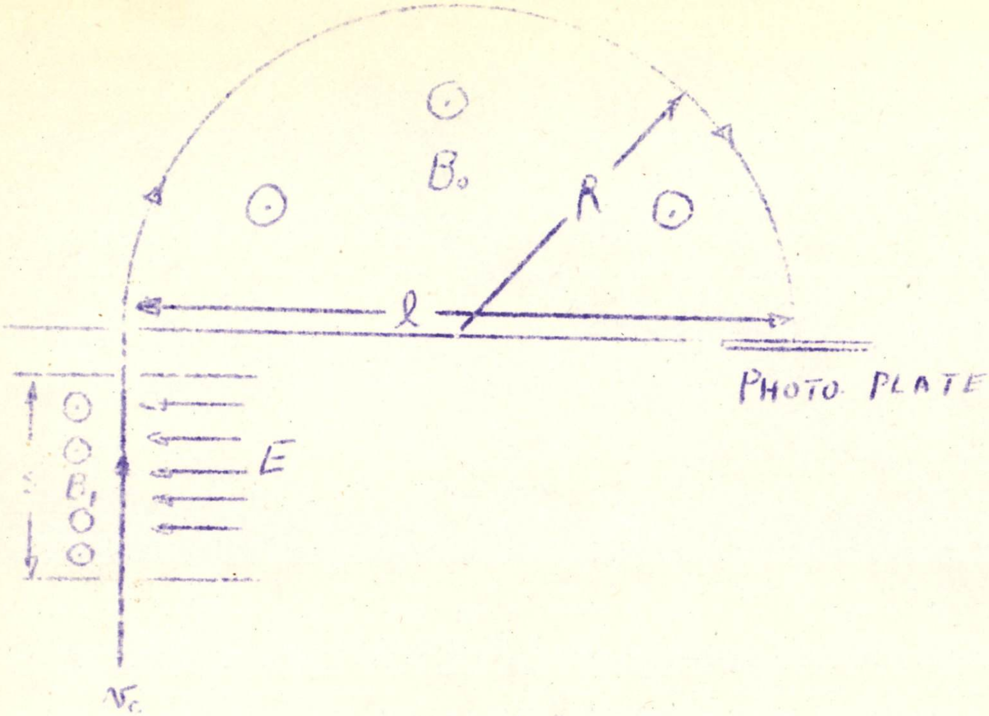


Fig. 2.8

fields, ions of any velocity could pass through the slits if their direction is correct. With the fields present only ions of velocity $v_0 = \frac{E}{B_1}$ can pass through the slits. (Refer to the equations at the top of p. 29, setting the net y-force equal to zero). These ions will then register on the photographic plate at a distance, $l = 2R = \frac{2v_0}{q/m\,B_0}$ from the exist slit. We then have

$$\frac{q}{m} = \frac{2v_0}{lB_0} = \frac{2E}{lB_1B_0}$$

Since $q = ne$, where n is an integer, we have

$$m = \frac{neB_1B_0}{2E}\,l$$

and the mass is proportional to the distance from the exist slit.

The Bainbridge mass spectrograph is not a perfect instrument although the lines on the plate are quite sharp. There are several sources of line-broadening and consequent error.

1) The line on the plate must be at least as broad as the slit.

2) Due to the finite width of the slit charges will emerge in a narrow cone of half-angle $\frac{\omega}{2}$ and this will tend to broaden the line.

3) The velocity selector is not perfect.

4) The field B_o is not exactly constant.

However, careful design can minimize all these errors, and masses can be measured to about 1 part in 10^4 or 10^5.

2.9 Measurement of the Charge on the Electron

The only careful measurement of electronic charge was made in a classical experiment by Millikan (about 1915). Millikan introduced very small spherical droplets of oil, "atomized", into an air chamber in which a uniform electric field, parallel to the earth's gravitational field, could be produced. In the process of "atomizing", the droplets are almost invariably charged by friction, and it develops in many cases, by small amounts; i.e., only a few electronic charges.

In the absence of an electric field the particles fall under the force of gravity and the viscous reaction of the air. Since they are small in size their speed rapidly attains its terminal value given by:

$$\frac{4\pi}{3} a^3 \rho g = 6\pi \eta a v_0$$

where the left hand side is the gravitational force and the right hand side is the viscous force (Stokes' Law); η is the coefficient of viscosity of air, a is the radius and ρ the density of the droplets. Millikan observed the rate of fall, v_0, of a single droplet and from the free fall measurement he determined the radius of the droplet.

If now an electric field E is produced so that the electric force is upwards the force equation for constant speed becomes

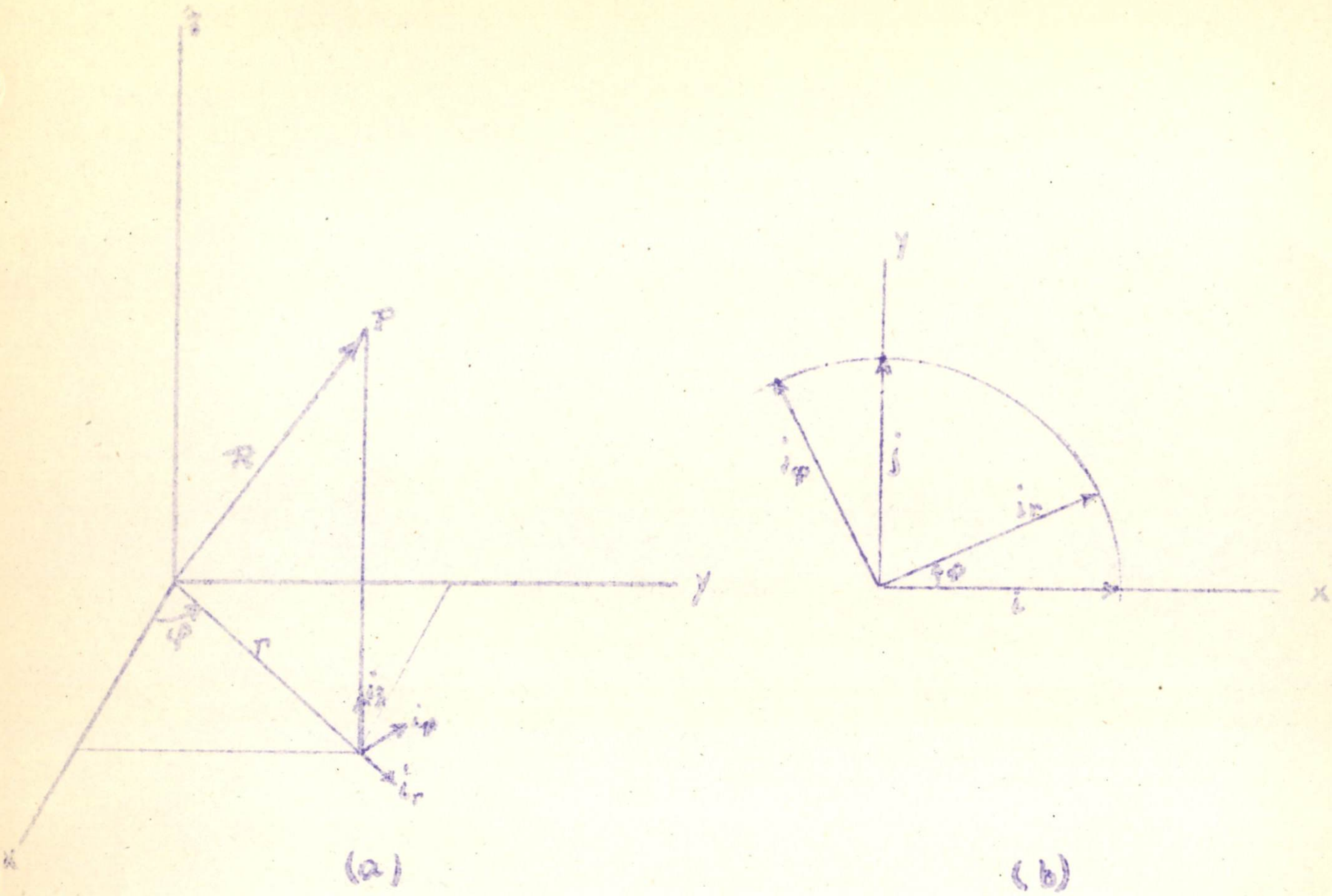
$$\frac{4}{3}\pi a^3 \rho g - neE = 6\pi \eta a v_1$$

where n is the number of electronic charges on the droplet. Millikan then observed the velocity v_1 of fall or rise of the droplet and knowing E he determined ne for a single droplet.

By then performing this experiment many times for different droplets he obtained a large number of values of ne, but all these values were the integer multiples of a single number which we now know to be the elementary unit of charge. (In Millikan's experiments he measured values of n between 1 and 200.)

2.10 Acceleration in Cylindrical Coordinates

Just as we discovered in Section 2.3, where we derived Poisson's equation in cylindrical coordinates, we must be careful in writing down the components of acceleration in any coordinate system except Cartesian. Referring to Fig. 2.9 the position P of a point may be specified by a set of cylindrical coordinates r, φ, z. In terms of these



(a) (b)

Fig. 2.9

the position vector R is given by

$$\vec{R} = i_r r + i_z z \qquad (2.10.1)$$

where i_r, i_φ, and i_z are unit vectors in the direction of r increasing, φ increasing, and z increasing, respectively. Let us specify these unit vectors in terms of the cartesian unit vectors i, j, k. Obviously,

$$i_z = k \qquad (2.10.2)$$

and from Fig. 2.9b

$$i_r = i \cos\varphi + j \sin\varphi \qquad (2.10.3)$$

$$i_\varphi = -i \sin\varphi + j \cos\varphi \qquad (2.10.4)$$

Suppose that P moves in time. The velocity of P is a vector $\vec{v}$, given by

$$\vec{v} = \frac{d\vec{R}}{dt} = i_r \frac{dr}{dt} + \frac{di_r}{dt} r + i_z \frac{dz}{dt} \qquad (2.10.5)$$

Note that i_z is a constant vector. Now

$$\frac{di_r}{dt} = (-i \sin\varphi + j \cos\varphi) \frac{d\varphi}{dt} = i_\varphi \frac{d\varphi}{dt} \qquad (2.10.6)$$

$$\frac{di_\varphi}{dt} = (-i \cos\varphi - j \sin\varphi) \frac{d\varphi}{dt} = -i_r \frac{d\varphi}{dt} \qquad (2.10.7)$$

Thus

$$\vec{v} = i_r \frac{dr}{dt} + i_\varphi r \frac{d\varphi}{dt} + i_z \frac{dz}{dt} \qquad (2.10.8)$$

where we recognize the cylindrical components of the velocity vector.

Similarly we may write for the acceleration vector, $\vec{A}$,

$$\vec{A} = \frac{d\vec{v}}{dt} = i_r \frac{d^2 r}{dt^2} + \frac{dr}{dt} \frac{di_r}{dt} + i_\varphi r \frac{d^2\varphi}{dt^2} + i_\varphi \frac{dr}{dt} \frac{d\varphi}{dt}$$

$$+ \frac{di_\varphi}{dt} r \frac{d\varphi}{dt} + i_z \frac{d^2 z}{dt^2}$$

$$= i_r \frac{d^2 r}{dt^2} + i_\varphi \frac{dr}{dt} \frac{d\varphi}{dt} + i_\varphi r \frac{d^2\varphi}{dt^2} + i_\varphi \frac{dr}{dt} \frac{d\varphi}{dt}$$

$$- i_r r \left(\frac{d\varphi}{dt}\right)^2 + i_z \frac{d^2 z}{dt^2}.$$

collecting terms

$$\vec{A} = i_r\left\{\frac{d^2r}{dt^2} - r\left(\frac{d\varphi}{dt}\right)^2\right\} + i_\varphi\left\{r\frac{d^2\varphi}{dt^2} + 2\frac{dr}{dt}\frac{d\varphi}{dt}\right\} + i_z\frac{d^2z}{dt^2}$$

and we have found the three components of acceleration in cylindrical coordinates.

2.11 The Static Magnetron

The magnetron is a very important oscillating vacuum tube in the high frequency region. A study of its dynamic characteristics is beyond the scope of these notes. However, its static properties are of interest and will be considered here. A magnetron, in its simplest sense, consists of two concentric cylindrical electrodes which are long compared to their radii and across which a static voltage V_o is applied. A uniform magnetic field B is applied parallel to the axis of the cylinders. A cross-section of such a tube is shown in Fig. 2.10.

Assuming that electrons are emitted from the inner cylinder with negligible initial velocities the equations of motion can be written as:

$$a_r = \frac{d^2r}{dt^2} - r\left(\frac{d\varphi}{dt}\right)^2 = -\frac{e}{m}E + \frac{e}{m}Bv_\varphi$$

$$a_\varphi = r\frac{d^2\varphi}{dt^2} + 2\frac{dr}{dt}\frac{d\varphi}{dt} = -\frac{e}{m}Bv_r$$

$$a_z = \frac{d^2z}{dt^2} = 0$$

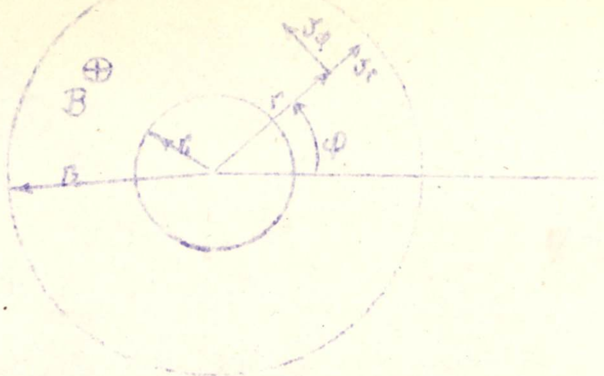


Fig. 2.10

The second of these equations can be written

$$\frac{1}{r}\frac{d}{dt}\left(r^2\frac{d\varphi}{dt}\right) = -\frac{e}{m}B\frac{dr}{dt}$$

integrating and remembering $v_r = v_\varphi = 0$, $r = r_1$

$$r^2\frac{d\varphi}{dt} = -\frac{1}{2}\frac{e}{m}B\left(r^2 - r_1^2\right)$$

or
$$\frac{d\varphi}{dt} = -\frac{1}{2}\frac{e}{m}B\left[1-\left(\frac{r_1}{r}\right)^2\right]$$

This can be substituted into the first of our differential equations and an integral can be obtained (remembering $E = E(r)$), however, we can write down the equation for the conservation of energy and accomplish the same end.

$$\frac{1}{2}m\left(\frac{dr}{dt}\right)^2 + \frac{1}{2}mr^2\left(\frac{d\varphi}{dt}\right)^2 = eV(r)$$

where we have taken $V(r_1) = 0$.

Using the expression for $\frac{d\varphi}{dt}$, we have,

$$\left(\frac{dr}{dt}\right)^2 + \frac{1}{4}\left(\frac{e}{m}\right)^2B^2r^2\left[1-\left(\frac{r_1}{r}\right)^2\right]^2 = 2\frac{e}{m}V(r)$$

Now in the passage of an electron from cathode, r_1, to anode, r_2, there will be a competition between the accelerating electric field and the magnetic field which will attempt to bend the particles back to the cathode. We can find the condition for the particle that just does or does not reach the anode, by imposing the following conditions, at $r = r_2$, $\frac{dr}{dt} = 0$, $V(r) = V_0$

$$\frac{1}{8}\frac{e}{m}B^2 r_2^2\left[1-\left(\frac{r_1}{r_2}\right)^2\right]^2 = V_0$$

This is the "cut-off" condition. If V_0 exceeds this value all the electrons will reach the anode, if V_0 is less than this value, none will reach the anode. Hence, the static magnetron has a sharp "cut-off", and its current vs. magnetic field characteristic is as shown in Fig. 2.11.

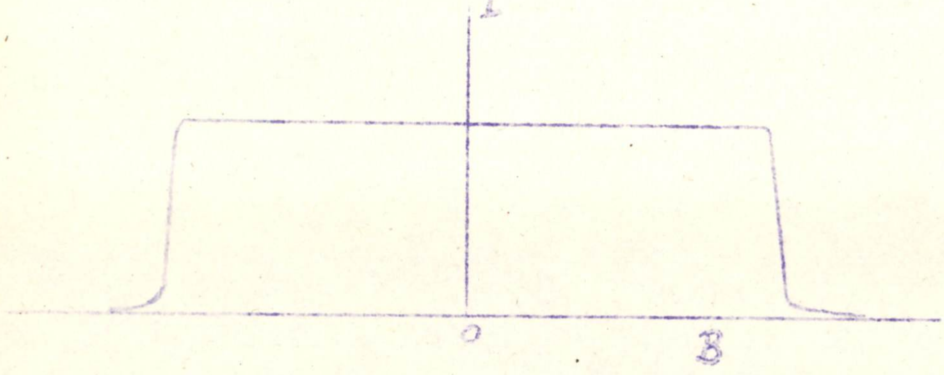


Fig. 2.11

The current reaches a flat maximum when all the available electrons reach the anode.

pg 46 – $w = c/n$

47 3 lin from quot

certainly by Fizeau's results.

• other spaces remove them

3-16 pg 50 $\cancel{\sqrt{1-\beta}}$ $\sqrt{1-\beta^{*2}}$ $* = u/c$

3-17 $\sqrt{1-\beta^{**2}}$ $\beta^{**} = w/c$