The radioactivity and gas content of minerals: with an additional part on nuclear spallation.

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THESIS

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Geoffrey Wardle, B.Sc., (Dunelm)

entitled

The Radioactivity and Gas Content of Minerals
with an additional part on nuclear spallation.

Being an account of the work carried out at the Londonderry Laboratory for Radiochemistry, Durham University, during the period 1951-1953 under the supervision of S.J.Thomson, B.Sc., Ph.D., A.R.I.C.

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SUMMARY

An apparatus has been constructed, after the pattern of that used by Paneth and Glückauf, for the measurement of micro-quantities of helium and neon. The apparatus has been used to study two problems.

1. The helium contents of several samples of coloured rocksalt (violet, yellow and blue) have been measured and a correlation between helium content and colour found. The blue variety was found to contain the relatively greater quantities of helium and the violet the least. The irradiation origin of the colours was confirmed by measurement of the absorption spectra of the samples and also by the permanency of the decolourisation effected when the samples were heated.

The helium contents found ranged from 21.5×10^{-7} ccs. He N.T.P. / gm. to 0.26×10^{-7} ccs He N.T.P./gm. These values cannot be correlated with the U-Th contents of the samples and the age attributed to the deposits from which they came. Hahn's hypothesis relating to the origin of the excess helium was accepted on the basis of the relation between helium content and colour, though an alternative source for some of this helium was suggested.

The relation between helium content and colour was satisfactorily explained assuming impurity sensitisation

of the rocksalt towards colour formation. Chemical analysis of the samples led to no specific sensitiser but the general level of impurity in each sample was in agreement with the sensitisation assumed on consideration of helium contents. Possible mechanisms for sensitisation by divalent positive and negative impurity ions were advanced.

The diffusion of helium in rocksalt was detected and the diffusion coefficient, D, measured at various temperatures T. Values of log D were shown to bear a linear relationship to 1/T in agreement with the equation for activated diffusion,

$$D = D_0 \text{ exp. } (-E/RT)$$

The value of the activation energy, E, was found to be 13.2 K cals/mole and the value for D_0 equal to 3.8 x 10^{-5} cms^2/sec. The result was compared with other values for E. The diffusion was probably "volume" diffusion.

2. The light element spallation products ^4He, ^3He and ^3H were measured in steel after bombardment with 340 Mev protons. The helium was extracted by dissolution of the steel in cupric chloride - potassium chloride reagent. After purification and measurement it was collected and examined for the isotopic ratio $^3He : {}^4He$. Values found for this ratio were from 0.0568 to 0.0322.

The tritium content was measured on different samples by a variety of methods, two different methods giving the same upper limit for the yield of tritium.

The values for the ratios $^3H/^4He$ and $^3H/^3He$ were found to be about 0.088 - 0.036 and 1.37 respectively.

Comparison with theory was made after allowanse was made for the fact that the excitation energies of the nucleii concerned in evaporation were not that of the indident protons i.e. 340 Mev. Fair agreement with these predictions was found in the experimental data though only qualitative agreement with Le Couteur's nuclear evaporation theory could be claimed.

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Introduction

The micro-determination of Helium

Since the discovery of radioactivity and the identification of α-rays as doubly charged helium ions, interest has become intensified in the micro-determination of helium, especially with respect to that which accumulates in rocks, minerals and meteorites as a result of the decay of the minute radioactive inclusions in these materials.

Taken in conjunction with the amounts of uranium and thorium present, the helium content can be applied to determine the age of a particular material, provided, of course, that the material in question retains helium quantitatively and the rates of α-decay of uranium and thorium are known. (1) This method has been extensively applied by Professor Paneth to the determination of the ages of meteorites (2) though here the scheme requires some modification since it has recently been shown that helium may be produced as a result of cosmic ray influence. (3)

Other interest in the determination of helium lies in its content in the atmosphere and the older method of purification, by removing all other gases present by adsorption on charcoal at the temperature of liquid nitrogen, requires some modification because of the presence of neon, which is not completely adsorbed in this process. (4) The newer method developed by Paneth and Gluckauf uses several charcoal units cooled to liquid nitrogen temperature, over which the mixture of gases is passed in turn. (5) By virtue of the difference in the extent to which the two gases are adsorbed on charcoal, the mixture, as it passes from unit to unit, becomes progressively richer in helium (since this is least adsorbed) and poorer in neon - a process resembling chromatographic separation.

The apparatus constructed for this research follows the pattern of that used by Paneth and Gluckauf in their work on the rare gas content of the atmosphere. (6) It is thus designed for the estimation of neon as well as helium and although occasion does not arise here for any estimation of neon, a determination of the helium content of laboratory air, in which separation from neon is essential, serves as a speedy check on the correct functioning of the apparatus.

Summary of the function of the apparatus

Briefly, the apparatus consists of a vessel wherein the gases contained in the material to be examined are liberated, in this work exclusively by solution, though fusion methods have also been used by other workers. (7)

A source of helium-free oxygen is supplied to this vessel to act as carrier gas and effect the complete removal of other gases from solution.

The gases freed in this way, along with the excess oxygen, are transferred into a closed system where they are circulated over a heated palladium wire, which serves to remove gross quantities of hydrogen as water. (8) The water so produced together with any other water which may have passed into the circulating system from the dissolving vessel, is retained in a trap cooled to the temperature of liquid nitrogen.

From the circulating system the gases are transferred to a fractionating column which consists of 15 charcoal units, each cooled in liquid nitrogen and wherein the oxygen (and most other gases) is retained quantitatively and helium and neon separated as indicated above. The fractions emerging from the column are collected in a large bulb (hereafter called the Compression Bulb) of about 1000 ccs. capacity. Since the inter-connecting dead space is reduced to a minimum, it can be stated that substantially all the helium is confined in the bulb when this is separated from the column with mercury.

After collection of the sample to be measured, it is then compressed into a volume of about 2 ccs. prior to admittance into a Pirani gauge which serves to measure the amount of helium collected. (9)

Immediately following each measurement of an unknown amount of helium, the Pirani gauge is calibrated against a known amount of spectroscopically pure helium. This pure helium is obtained from a reservoir and measured in a McLeod gauge. (10) Expansion in a system of pipettes of accurately known volume, then gives an amount of gas suitable for admittance into the Pirani gauge for calibration purposes.

The apparatus is designed to measure accurately 10^{-9} ccs. of helium at N.T.P. The quantities measured are in general of the order of 10^{-6} to 10^{-7} ccs. of helium at N.T.P. with an accuracy somewhat better than one per cent.

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Chapter 1.

The Helium content of coloured Rocksalt

A Review

Native sodium chloride or rocksalt occurs in mineral deposits in various localities widely dispersed around the world. The deposits are believed to be of marine origin, i.e. by the evaporation of sea waters which have overflowed into natural basins situated where the deposits are now located. One such basin is thought to have been centred in N. Germany and to have embraced the British Isles in its western extremity, thus giving rise to the salt beds of Britain and the more extensive deposits of N. Germany, when the enclosed waters evaporated. (11)

In the course of time, the deposits have become covered with a thousand or so feet of rock and have thus been subjected to varying changes of pressure and temperature.

Insofar as the German deposits are concerned, the rocksalt occurs in two distinct layers, an older or primary layer and a secondary younger layer, along with deposits of carnallite, gypsum, sylvine and other closely associated minerals.

The form of the Stassfurt (Germany) beds, beginning with a basal layer of anhydrite ($CaSO_4$) and gypsum ($CaSO_4.2H_2O$) is:- (12)

(1) Old rocksalt layer (primary).
(2) Polyhalite layer. 91.2% NaCl. 6.6% polyhalite. ($CaSO_4.MgSO_4. K_2SO_4. 2H_2O$) 1.5% Bischofite. ($MgCl_2.6H_2O$) and 0.7% anhydrite.
(3) Kieserite layer. 65% NaCl. 17% Kieserite. ($MgSO_4.H_2O$) 13% Carnallite ($KCl.MgCl_2. 6H_2O.$) 3% Bischofite and 2% Anhydrite.
(4) Carnallite layer. 55% Carnallite. 25% NaCl. 16% Kieserite and 4% other salts.
(5) Grey salt clay.
(6) Gypsum and anhydrite layer.
(7) Young rocksalt.
(8) Clay, soil, etc..

The composition of the rocksalt layers (13) is generally 98-99% sodium chloride (though this value may be as low as 95%) associated with the sulphates and chlorides of magnesium, calcium and potassium in varying proportions.

Sylvine, which occurs below the secondary rocksalt layers, contains about 92% potassium chloride and is similarly associated with calcium, magnesium and sodium.

The theory of the marine origin of these deposits is handsomely supported by the work of J.J. van t'Hoff, who studied the solubilities and conditions under which salts and mixtures of salts exist in equilibrium with solution (14), but the complete structure of the beds as given above indicates that a somewhat more complicated process had been in operation than the straightforward evaporation of sea water. Thus, layers, 1,2,3,4 and 5 might well have arisen by the evaporation of sea water, but continued evaporation cannot have led to layers 5 and 6. It even seems unlikely that these layers arose by a fresh influx of sea water, after the deposition of the primary layers and subsequent evaporation. In this case, one would expect to find associated with the secondary layer, layers corresponding to 2,3 and 4 in the primary layer, and this is not so.

Further, the Ca content of the deposits is far in excess of that to be expected on the basis of simple evaporation of sea water. (15)

One is thus led to the conclusion that the inland sea from which the deposits originated has been fed by fresh waters and that this water introduced the excess calcium. Further action of such fresh waters after the laying down of the primary deposit, would leech out the more soluble constituents of the primary layers, e.g. sodium chloride and potassium chloride and re-deposit them on subsequent evaporation. Thus, provided the fresh waters do, in fact, contain calcium, one can account for the secondary rocksalt layer, the sylvine layer and the additional layers of gypsum and anhydrite.

Age of the Deposits

So far, the ages of the two rocksalt layers have been referred to as old and young with no indication of the actual magnitudes involved. In this respect, geologists have set a value for the primary at 100 million years and for the secondary at 10-60 million years. (16) Whilst this value has received confirmation, at least as far as the Sylvines are concerned, by an estimation based on the potassium-argon method of age determination (17), no support is given by the helium method.

Examination of the radioactive content of the salts reveals a uranium content of about 5×10^{-10} gm. U/gm. salt on the average and a radium content of about 3×10^{-16} gm. Ra/gm. salt, i.e. roughly the equilibrium amount expected from the uranium content (18). No figures for thorium have been discovered in the literature. The amounts of thorium required to produce the quantities of helium found in the salts would be about 4×10^{-6} to 4×10^{-7} gms. Th/gm. salt in a period of about 10^{7} years.

Accepting the geological age of the deposits, i.e. roughly 2×10^{8} years for the primary deposits and $10\text{-}60 \times 10^{6}$ years for the secondary deposits and sylvines, this quantity of uranium represents, by successive α - disintegrations of itself and daughter products over the period of time stated, an accumulation in the salts of about 1.2×10^{-8} ccs. He/gm salt in the primary layer and 2.1×10^{-9} ccs/gm in the secondary layer and sylvines, provided diffusion out of the salts is negligible. The helium values actually found for the salts (19) are of the order of 10^{-8} ccs/gm. primary, 10^{-7} ccs/gm. secondary rocksalt and 10^{-6} ccs/gm for sylvines. On the basis of the helium method of age determination, this would indicate for the secondary deposits and sylvines, ages of 2×10^{9} and 2×10^{10} years respectively, which is older, on the average, than the accepted ages of the oldest known rocks (3.5×10^{9} years).(20) No correlation is to be noted in the He/U estimations carried out by Karlik and Kropf-Duschek presumably on the same samples of salt whilst their determinations on a primary rocksalt indicate an excessive age value for this sample as well.

Table 1

No	Mineral	He x 10^{8}ccs/gm	U x 10^{10}gm/gm.
1	Primary Rocksalt	18	7.3
2	Rocksalt	14	6.0
3	Blue Rocksalt	8.0 & 8.3	3.5
4	Rocksalt	8.2	2.6
5	Secondary Rocksalt	5.5	6.3
6	Old Rocksalt	6.4	8.8
7	Young Rocksalt	14 & 15	5.7
8	White (Sec)	13	3.5

From: B Karlik & F. Kropf - Duschek. Öster. Akad.d.Wiss. 13th October, 1949. p.220 - 223.

In view of the already well established age of the deposits, the helium age values must be regarded as wrong and so the salts must contain, like the Beryls, an excess of helium. (21)

Source of Helium in the Deposits

Having shown the presence in the salts, of an excess of helium, the question then arises as to the source from which this excess helium came.

Following the discovery by Käding (22) that lead crystallises isomorphously with sodium chloride and potassium chloride from solutions of these salts, Hahn has suggested that, in the natural deposits, some short-lived isotope of lead could crystallise with the rocksalts and sylvines thus giving rise to excess helium. (23) He suggests radium D as the lead isotope concerned which, by two successive β^- - decays, forms radium F or polonium. This is a short-lived α - emitter forming stable radium G.

Thus:-

$$\begin{tikzcd}
\text{RaD} \arrow[r, "\beta^-"] & \text{RaE} \arrow[r, "\beta^-"] & \text{RaF (Po)} \arrow[dll, "\alpha"'] \\
\text{RaG} & &
\end{tikzcd}$$

Taking the radium content of normal sea water as 10^{-11}gm. Ra/litre Born calculates that the radium D in equilibrium with the radium is insufficient to give rise to the quantities of helium found in the salts (24). He therefore postulates that the salts have been re-crystallised from "natural deep waters" of high radium and thus high radium D content. In support of their theory, Hahn and Born have examined "natural deep waters" from various localities in North and Mid. Germany (25) and found them to contain substantially higher amounts of radium than obtains in normal sea water. The amounts they find, from 10^{-10} to 5×10^{-9} gm. Ra/litre water, theoretically supply an adequate amount of radium D to account for the helium contents of rocksalt and sylvine.

It is interesting to note the parallel in the assumptions made by Hahn and Born (26), as to the formation of the salt layers from the point of view of possible sources of helium, and the assumptions about re-crystallisation which must be made when the structure of the beds is considered.

A further interesting parallel is to be noted too with regard to the high calcium content of the deposits compared to that obtaining in normal sea water, in that Hahn and Born find a close relationship to exist, in the waters they examined, between calcium content and radium content. They find a high radium content to be associated with a high calcium content. Allied to the excess calcium content in the deposits, this fact adds a considerable support to their argument.

A similar correlation has also been obtained between lithium and radium in natural waters. (27)

Yet another support for their theory comes from the helium contents themselves. One would expect from the theory that the primary salt layer should contain relatively less helium than the secondary layer and this is indeed the case.

Table II

No.	Mineral	Source	He x 10^6 cm^3/gm	Pb x 10^6 gm/gm	Remarks
1	Rocksalt	Krügershall	0.1		
2	Rocksalt	Salzdethfurt	< 0.01	0.17	Old series
3	Rocksalt	Salzdethfurt	< 0.01		Old series
4	Rocksalt	Hanover	0.05	0.085	Old series
5	Rocksalt	Vienenberg	0.1		Blue
6	Rocksalt	Vienenberg	0.3		Blue
7	Rocksalt	Stassfurt	0.7	< 0.01	Strong blue
8	Rocksalt	Stassfurt	0.67	< 0.01	Weaker blue
9	Sylvine	Vienenberg	0.95		
10	Sylvine	Vienenberg	1.1		
11	Sylvine	Berlepschacht	7.1		
12	Sylvine	Berlepschacht	5.0		
13	Sylvine	Berlepschacht	4.4		
14	Sylvine	Berlepschacht	6.8		
15	Sylvine	Berlepschacht	6.81	0.20	
16	Sylvine	Stassfurt	13.0		
17	Sylvine	Stassfurt	14.0		
18	Sylvine	Stassfurt	5.6		
19	Sylvine	Stassfurt	5.2		
20	Sylvine	Stassfurt	1.21	3.17	
21	Sylvine	Stassfurt	1.28	0.18	

From H.J. Born, Chemie der Erde. 9, 79, 1934.

One would also expect that the helium contents could be correlated with the ^{206}Pb contents of the salts, but this has not been looked for unfortunately. The results of Born, (Table II) seem to indicate a high helium content to be associated with a low lead content and vice-versa. (28) However, since the lowest lead content found i.e. 1.0 x 10^{-8} gm. Pb/gm. rocksalt, if all is assumed to have originated from Polonium is far in excess of that required to produce the highest helium content, this lack of correlation is not a serious objection to the theory. Even an isotopic examination of the lead present need not lead to a useful result for the greater part of the lead of radioactive origin could have been formed in the waters before the beds were laid down.

It can be seen however that the theory of Hahn and Born fits the facts extremely well, but it cannot be regarded as proven. Absolute proof of their theory would, indeed, be very difficult. It is as well then to consider other reasonable sources of helium and see if they too can be fitted to the facts if not absolutely proved.

One such possibility is that, by long exposure to the atmosphere, helium may have diffused into the rocksalts from the atmosphere. If this is the case, then it should be possible to detect a difference in helium content with depth, provided the salts did not become saturated in the process. Whilst such an effect has not yet been looked for, it is to be noted that of the salts examined in this laboratory, none has been found with a uniform distribution of helium. Rayleigh has observed the diffusion of helium (29) through a variety of substances and finds that through a crystal of rocksalt 1mm. thick helium diffuses at a rate of less than 10^{-6}ccs/cm. ^{2}/hr. at 20°C which represents the limits of detection in the apparatus he used. Whilst this value is very small, it does not invalidate the possibility of diffusion as a source of helium in the salts because of the long times involved. It will be seen later that the tendency is for helium to diffuse out of the salts, so that it is most unlikely that helium should have diffused in.

The diffusion coefficient of helium in rocksalt has now been determined in this laboratory at various temperatures and it will be shown later on the basis of these results and certain assumptions as to the size of the deposits and temperature, that appreciably no helium has diffused out of the salts in the period since their formation.

Another possibility arises through the comparatively large solubility of helium in water. (30) Although a salting out effect does occur, it is still appreciably soluble in salt solutions. (31) It is also very often the case that on crystallisation, many salts trap quantities of mother liquor within their structures, especially if the crystallisation process is carried out slowly. (32) The rocksalts examined here have been observed to contain occluded water. It could be then that this brine which has been trapped by the salt in crystallising, may contain sufficient helium to account for the high helium contents found in the deposits.

Urry has measured the He + Ne contents of several samples of sea water at various depths (33) and finds values between 12 and 20 x 10^{-5} ccs. of He + Ne/litre of sea water, whilst for sea water saturated with air at 23 and 24°C the values are 19.1 and 18.7 x 10^{-5}ccs/litre respectively.

Taking the value as 20 x 10^{-5} ccs/litre and calling it all helium, (the most favourable case), it can be seen that in order to arrive at a helium content of 10^{-7} ccs/gm, each gram of rocksalt must trap in its structure 0.5 ccs. of brine, and for a helium content of 10^{-5} ccs/gm., 5 ccs. of brine. In the case of the primary salt layer, the calculation is quite favourable and agrees with the theory that this layer crystallised from what was substantially sea water. Here the helium contents are less than 10^{-8} ccs/gm. salt which means that each gram of salt must trap less than 0.05 ccs. of brine to give the required helium content.

In an effort to examine the theory further, samples of sodium chloride were crystallised from air-saturated water as slowly as possible, i.e. over a period of about three weeks and examined for helium content. The values found were less than 5 x 10^{-9} ccs He/gm. of salt, which is not in serious disagreement with the theory. Since the two cases are not comparable, i.e. the natural and laboratory crystallisations, this result does not offer any objection to the theory.

The absence of neon in the gases obtained from the rocksalts examined in this work raises no objection either. The solubility of neon in sea water has been seen to be extremely low and since it is not of radioactive origin it can hardly have become enriched in the natural waters as is the case with helium.

It would seem however that the theory is untenable for the secondary rocksalt and sylvine, but it must be remembered that the water from which the secondary layers crystallised was probably not normal sea water but a fresh water enriched in radium and therefore possibly enriched in helium. Such enrichment of helium is quite probable, especially since the waters may have been out of contact with the atmosphere, e.g. covered with a scum of salt, thereby preventing equilibration with the helium in the atmosphere. Even in contact with the atmosphere, it may be that such equilibration is so slow as to be negligible, especially with the lower layers of water at considerable depth.

At higher partial pressures, the solubility of helium in salt solutions becomes even more favourable for such a theory. Akerlöf (34) finds that at approximately 76 cms. pressure, the solubility of helium in almost saturated sodium chloride is 0.0043 litres (N.T.P.)/litre of solution at 25°C.

It is further known that the natural gases associated with oil borings are considerably enriched in helium compared to the helium content in the atmosphere (35). This enrichment amounts to factors of about 600 to 3500 in some of the cases examined from borings in North Germany, whilst, in other cases, only a factor of two is involved. In the case of the Texas Oil Fields, an enrichment factor of 4000 has been noted and the pressure of the gases estimated at 30 atmospheres. Such enrichment at high pressure would mean considerable increase in the concentration of helium dissolved in the associated waters and lends support to an argument based on the occlusion of water in the salt as a source of their high helium content.

A parallel case exists in the potassium salts which have been examined by Gentner and Aldrich and Nier. (36) These workers have shown that not all the argon occuring in potassium minerals is radiogenic, i.e. by decay of K^{40} to A^{40}. By mass spectrometric analysis, they have shown that up to 30% of the argon present is atmospheric argon.

Thus, from Gentner's results, taking one particular case (the one with the lowest percentage of atmospheric argon).

Total A = 6.73 mm. ^{3}/100 g.K.

Radiogenic A = 5.8 mm. ^{3}/100 g.K.

So atmospheric A = 0.93 mm ^{3}/100 g.K

= 9.3×10^{-6}ccs. A/gm.K.

Now the solubility of argon in sea water, in equilibrium with the air = 0.2 to 0.4 ccs/litre. (N.T.P.)

Salting out constant for argon = 0.06 (approx).

Taking the relationship found by Akerlöf connecting the solubility of the gas in pure solvent and in salt solution:-

$$km = \log ({}^{so}/s)$$

Where;

k = salting out constant = 0.06

so = solubility of gas in pure solvent.

s = solubility of gas in solution at concentration m.

Now s1 for sea water = 0.3 (app)

Concentration of sea water w.r.t. sodium chloride = 0.1 satd. (app.) i.e. about 6.2 molar x 0.1.

Thus, $\log ({}^{so}/s) = 0.06 \times 0.62$

$= 0.0372$

$so/s = 1.089$

$so = 1.089 \times 0.3$ ccs/litre = 0.3267 ccs/l.

In a saturated solution i.e. 6.2 molar, we have then;

$\log({}^{so}/s) = 0.06 \times 6.2.$

$= 0.3720$

$so/s = 2.356$

$s = 0.3267/2.356$

$= 0.1386$ ccs/litre at 25°C.

or, the solubility of argon in a saturated solution of brine is

1.386×10^{-1} ccs/litre.

under the conditions which prevail in the atmosphere.

In order to achieve an atmospheric argon content of 9.3×10^{-6} ccs/gm. then, each gram of potassium chloride must trap in its structure:-

$$\frac{9.3 \times 10^{-6}}{1.386 \times 10^{-4}} \quad \text{ccs of brine.}$$

$$= 0.0671 \text{ ccs of brine.}$$

It is not inconceivable that this amount of brine should be trapped (37) by 1 gm. of potassium chloride on crystallisation and so the mechanism of trapping should be regarded as a distinct possibility.

A consequence of such a mechanism providing the source of excess gases in these minerals would be that the primary rocksalt layer should contain quantities of argon of the order of 10^{-5} - 10^{-6} ccs. A/gm. rocksalt. Detection of argon in the primary deposit in such quantities would lend considerable support to the theory.

The Colour of Natural Rocksalt

In nature rocksalt varies in colour from white, dirty grey, yellow, and reddish yellow to blue and purple. The colour, can in most cases, be attributed to the presence of some impurity, e.g. ferric oxide imparts a reddish colour, clay or anhydrite, grey and organic matter, brown. (38)

Here again, however, the secondary rocksalt presents an anamoly. Samples of coloured rocksalt occur in the secondary layer whose colour can be attributed to no known impurity. The colours concerned are yellow, violet and blue. The blue coloured rocksalt has attracted scientific attention for well over 100 years and is mentioned in H. Davey's letters of 1818. During this time, several theories have been advanced as to the cause of the colouration, though none are of particular interest now. (39)

It is now known that the alkali halides can be coloured by various means without introducing any elementary impurity, and in considering the natural colours, it is as well to discuss, first of all, the artificial means available for this purpose. The methods fall into two groups:-

1. Where additional sodium is introduced into the stoichiometric crystal (40) by some means or other, giving the so-called 'additive' colour, and
2. Radiation methods giving the 'radiation' colour. (41)

Additive Colouration

Excess alkali metal can be introduced into crystals of an alkali metal halide by the following means:-

a. By heating the halide concerned in an atmosphere of the vapour of the alkali metal which it is desired to be introduced. (42) The colour achieved by this means is independent of the alkali metal used, shewing that the colour is a property of the crystal. Thus, excess potassium in a crystal of sodium chloride has just the same effect as excess sodium has in a crystal of sodium chloride. (43)

b. By electrolysis, sodium ions, which move toward the cathode during the electrolysis, are discharged there, and the resulting sodium atoms constitute an excess in that part of the crystal near the cathode. (44)

c. Additive colours have been formed in potassium bromide, the excess metal being introduced initially as potassium hydride in solid solution with the potassium bromide. On irradiation, in the ultra violet, the potassium hydride is dissociated, hydrogen diffuses from the lattice leaving an excess of potassium behind. (45)

Colouration by Irradiation

Irradiation colouration is brought about, as the name implies, by exposing the crystal to a suitable source of radiant energy, e.g. X-rays, cathode rays, α- rays etc.. Here, no excess metal is introduced into the crystal, the colour is thus being produced in the pure stoichiometric crystal.

Provided that, after heating in the presence of alkali metal, the halide crystal is quenched and not allowed to cool slowly, then all the colours produced in the above ways can be attributed to the same cause. All the crystals then show an identical absorption maximum in the visible region of the spectrum, the bell-shaped absorption band being called the F-band, after Pohl.

On lowering the temperature, this bell-shaped peak can be made arbitrarily narrow, indicating that the absorbing centres responsible for the band are of a single species. These were called by Pohl, Farbzentren (F-centres or colour centres). (46)

Nature of F-centres

The properties of F-centres and other associated centres which will be referred to later, have been widely studied The pioneer work by Pohl on the photo-conductivity of crystals containing F-centres is particularly noteworthy, and it has led to a theory as to their nature.

The theory elucidated by DeBoer (47) is that an F-centre consists of an electron trapped at an anion deficient place in the lattice, and the theory has been extended by Seitz (48) to include other absorbing centres as various combinations of electrons and vacancies, or to be associated with the positive holes which remain after removal of an electron from an ion. (See table III)

Table III

Centre	Nature of Centre	Absorption Maxima(48a	
		Observed	Calculated
F	Electron + anion vacancy	4580, 4700 4650	4710
F'	2 Electrons + anion vacancy.	-	-
M	Electron + anion vacancy + anion-cation vacancy pair.	7250, 7200 7050	7010
R_1	Electron + 2 anion vacancies	5450	5470
R_2	2 Electrons + 2 anion vacancies	5960	5920
N	Higher F-centres aggregates	8300	-
V	+ ve Hole + cation vacancy	2200, 2400	-

Support for this picture of an F-centre comes from magnetic measurements in that the moment of an F-centre is found to be the same as that calculated for an s-electron (49). Both theoretical and experimental evidence are available to support Seitz's picture of other bands listed in Table III. (50).

Formation of F-centres

Since F-centres can be formed by two different methods it is of interest to note briefly the theories as to the mechanism by which they are brought about. (51)

a. By heating in alkali metal vapour it is thought that the metal atoms striking the surface of the crystal are ionised,

$$Na = Na^+ + e'$$

Cl^- at the surface, combines with Na^+ to form an addition to the lattice leaving an anion deficient place (51a) in the lattice which will attract and become occupied by the electron. More Cl^- diffuse from the body of the crystal to the surface in order to combine with further Na^+, leaving more vacancies to be occupied by the electrons.

b. By irradiation with X-rays, the primary effect is the production of photo-electrons which move through the lattice at high speed, thereby producing secondary electrons and holes. These secondary units wander through the lattice until they recombine or become trapped in the lattice. In cases where recombination with a positive hole does not occur, Seitz finds the most favourable resting place for the secondary units to be at vacancies in the lattice.

Differences between the two modes of colouration

Although the F-band is formed in all cases of colouration mentioned several differences exist between crystals coloured by irradiation and those coloured by additive means.

Firstly, since the additively coloured crystals contain an excess of alkali metal their reaction in solution is markedly alkaline. The irradiation coloured crystals, on the other hand, are stoichiometric and thus have a neutral character in solution. (52)

Another difference between the two cases lies in the absorption spectra themselves. Whereas in the additively coloured case, providing cooling has been sufficiently rapid, only the F-band appears, in the irradiation colours, other bands are found associated with the F-band (53). Thus, on the long wave-length side of the F-band appears the so-called M^- band, whilst on the U-V side appears the V-band. The latter band Seitz associates with the positive holes which remain after removal of an electron from a negative ion. Other centres may be induced in a crystal containing F-centres by irradiating the crystal with light lying in the F-band or in certain cases by thermal treatment. Thus, below certain temperatures, (25°C for sodium chloride, -75°C for potassium chloride) irradiation in the F-band produces a broad diffuse band on the long wavelength side of the F-band, called the F' -band. Above these temperatures, irradiation in the F or M bands results in areduction in the intensity of these bands and the R and N bands appear also on the long wavelength side of the F-band. Apart from the V-band all these bands are associated, by Seitz, with various combinations of electrons and vacancies, and could theoretically occur in an additively coloured crystal. In fact, where quenching has not been sufficiently rapid, the M-band may occur with the F-band in an additively coloured crystal. The R-band may also occur in crystals containing a high density of centres regardless of the rate of cooling (54). If Seitz's interpretation of the origin of the V-band is correct however, it is not possible for this band to occur at all in an additively coloured crystal.

Differences also arise in the bleaching properties of the two types of coloured crystal. On raising the temperature of an irradiation coloured crystal to about 250°C the colour can be removed completely and does not re-appear on cooling again. With the additively coloured crystal however, the colour remains even up to the melting point. (55) On cooling now, coagulation of the particles of excess metal occurs, giving rise to colloidal aggregates which still colour the crystal. This process is equivalent to slow cooling instead of quenching in the initial colouration process.

The colouration process in the natural rocksalts

Having summarised the various types and properties of artificially coloured alkali halides relevant to this discussion, it is now possible to discuss the properties of the naturally occuring coloured rocksalts to see if they lead to any conclusions as th the mode of colouration.

Firstly, with regard to their reaction in water, opinions seem to differ, though only the blue variety has

Fundort	Nr.	Lage der Absorptions-										banden in mμ						Ultramikr. Befund	Farbe	Bemerkung
		730	10	690	70	50	30	10	590	70	50	30	10	490	70	50	30			
Werragebiet	A 1									570								leer	blau	Abb. 4
„	2				674						564							schw. Kegel	blauviolett	Abb. 9
„	3				674						560							„ „	„	
„	4									576								leer	violett	
Staßfurt	B 5								598									leer	violett	Abb. 5
„	6								600									schw. Kegel	blau	
„	7				678					580								„ „	„	Abb. 10
„	8									580								leer	violett	
Hall i. Tirol	C 9														460			leer	gelb	Abb. 3
Sizilien	D 10	720								570					460			leer	violett	Abb. 6
Bad Ischl	E 11									580								leer	violett	schw. Färbung
„ „	12				670					580								schw. Kegel	blauviolett	„ „
„ „	13					650					560							„ „	„	„ „
Hallstatt	F 14								590									stuli. Kegel, orangefb.	blau	
„	15								600				510					„ „ „	„	Abb. 8
„	16				666					576					460			„ „ „	violett	
Staßfurt	G 17					645							530			440		st. Kegel	blau	Abb. 11/1
„	18				680								535			440		„ „	„	Abb. 11/2
„	19					648							330			445		„ „	„	Abb. 11/3
Mayo-Pendjab	H 20					642						525				440		st. Kegel	blau	Abb. 12/1
Ebensee	I 21						632					520				445		st. Kegel	blau	Abb. 12/2
Wieliczka	K 22				680					580								schw. Kegel	blauviolett	
add. vorf.	L 23					650												st. Kegel	blau	Na-Überschuß
a-bestr.	24	730													465			leer	braun	
„ gepr.	25	730			670										465			nicht festzustellen	braun	kurze Zeit bestr.
„ „	26	730			670					580			510		465			„ „	braun	lange „ „
„ erw.	27	730			670					580			510		465			leer	grau	
„ „	28									580								leer	violett	länger erw. als L 27
Staßfurt erw.	29									580						440		st. Kegel, gelb	violett	
„ „	30										550							st. Kegel, grün	rosa	
		730	10	690	70	50	30	10	590	70	50	30	10	490	70	50	30			

After L. Wieninger. (ref. 61).

TABLE. IV.

been investigated to any extent in this respect. Many investigators report no alkaline reaction in solution for the blue salt whilst others report that in some cases an alkaline reaction has been observed. With such conflicting results, it is difficult to arrive at any conclusion as to whether excess sodium is present or not, especially since the rocksalts are by no means pure and other factors may be involved. (56)

Siedentopf has shown on the other hand, by ultramicroscopic examination, that the blue rocksalts do contain sodium in the form of colloidal particles and that this is the basis of their colouring (57). Such colloidal colours have been achieved in the laboratory only by slow cooling after heating in alkali metal vapour or by annealing the additively coloured crystal or by heating the salt up to the m-pt. with concentrated cathode irradiation. (58).

In addition to the blue, the violet salt may also contain colloidal metal though none has been detected in the yellow.

Thus, in nature, the colours arise from centres and colloids or a combination of the two. The absorption spectra of the various salts have been exhaustively examined by Wieninger (Table IV) who arrives at the following classification:- (59)

(a) Centre Colours

Yellow - Absorption max. at 4600 Å - F-centres.
Violet - Absorption max. at 5800 - R 11 - centres
" " " " 4600 F- centres
" " " " 5700 - R 11 - centres
" " " " 7200 - M-centres

(b) Colloidal Colours

Blue - Absorption max. at 6000 Å.

(c) Centres and Colloids

1. Mainly centres

Blue-violet - Absorption max. at 5800 Å - R11-centres
6800 - Colloid

2. Mainly colloids

Blue - Absorption max. at 5200 - 5350 - R1-centres
6300 - 6800 - colloid.
4400 - 4500 - impurity.

The yellow colouration then arises from F-centres and this is regarded as the primary colouration since the R- and M-centres which occur in the blue and the violet salts are the initial products of combination of F-centres.

Since it is unlikely that the salts have had the heat treatment required to form colloids as in the laboratory, it seems unlikely that these were formed in the natural salts by further coagulation of F-centres as a result of slow cooling. Coagulation of colour centres in an irradiated crystal has been observed in the laboratory as a result of heat treatment, pressure effects and irradiation with white light or with light lying in the F or M-bands, but not to the extent of colloid formation and so Przibram has assumed that sensitisation of the salt occurs through the presence of some impurity as is the case in the silver halides containing silver sulphide (60) In the above classification of Wieningers, the only case of impurity giving rise to an absorption maximum occurs in the blue salt and Wieninger later supports this view of Przibrams attributing the formation of colloids specifically to sulphur ions. (61) The depth of colour of irradiation origin attained in the fluorites has already been related to the sulphur content of the specimen. (62)

The fact that the impurity could aid in colouration is further supported by the appearance of the colour itself. Whilst most samples appear to be uniformly coloured, close examination shows that the colour of the violet and blue is generally in the form of striations. This is the general form in which the colour occurs in impurity coloured salts, e.g. by ferric oxide.

Another suggestion for the impurity which sensitises the formation of colloids is the lead, whose content in rocksalts has already been discussed. Such a possibility has already been tested in the laboratory by Born who finds that with increasing lead content so the samples tend to become more strongly blue-coloured on irradiation. Samples with little or no lead on similar irradiation are coloured only faintly yellow, and that this primary yellow colouration becomes increasingly unstable with increasing lead content. (63) The unstable yellow is replaced by stable blue colour with increasing lead content. Similar effects were found in potassium chloride. Other investigators report an optimum concentration for sensitisation by divalent cations (64).

In view of the presence of the R and M-band maxima in the absorption spectrum of some of the coloured samples (see Table IV) it seems as though the colour is due to some radioactive influence, with an associated effect due to the presence of impurity. However, one does not know how an additively coloured salt would behave under the conditions which have been in operation in the deposits over the long period of time since they were laid down. Thus, under conditions of fairly high pressure, elevated temperature and plastic deformation due to geological changes in associated strata, it is quite possible that the F-centres in an additively coloured salt could coagulate and form R- and M-centres. Both R and M-centres, in fact can be formed in additively coloured salts under certain conditions. The presence of R and M-centres alone then cannot be taken as absolute evidence in favour of an irradiation colour.

The bleaching properties of the naturally coloured samples with increasing temperature and the permanency of the decolourisation on cooling strongly favours an irradiation source for the colours.

It may be significant that the V-band has not yet been observed in these salts, though this may be because it has not been looked for. If the V-band were observed then it would form extremely strong evidence in favour of an irradiation colour, since it is hardly possible for such a band to be formed in the additively coloured salt.

Przibram supports the belief that the colour has irradiation as basis and calculates that the energy available for this purpose from the radioactive sources present in the crystal is quite adequate provided one assumes the same end effect from a weak source acting over a considerable time as from a strong source acting over a short period of time.

The sources of energy he considers are:- (65)

1. The uranium-radium content.
2. Energy from polonium α- particles calculated from the helium content.
3. The energy from K^{40} activity.

The energy from each source is considered separately and is found to be sufficient in each case, so that the total, when all are considered as acting together is eminently sufficient. Adler et al find the K^{40} activity sufficient to colour only the yellow variety and not the blue (66)

In spite of this strong argument in favour of an irradiation colour several questions are still not answered satisfactorily. Why, for instance, are not all rocksalts coloured ?. In the secondary layer at least, the available sources of energy appear to be identical in both the coloured and uncoloured salts.

Przibram assumes some particular form of sensitisation in the coloured variety due to plastic deformation or impurity. Of the two, impurity seems the most likely since this could deposit with the salt in the earlier crystallisation and not in the later, whereas plastic deformation would probably apply to the layer as a whole. If the sensitisation is due to impurity then chemical analysis should reveal a significant difference between coloured and uncoloured samples of the salt. Such a difference has not yet been reported.

Another point to be raised is why are the sylvines, which contain a much larger source of available energy not coloured ?. It may be of course that here the difference in ease of colouration and stability of the colour produced is coming into play, (67) but again this seeme unlikely since no outstanding differance in these properties between potassium chloride and sodium chloride has been observed.

Whilst speaking of the sylvines, it is of interest to note that the coloured rocksalt invariably occurs in the close proximity of sylvine (68). It is, apparently, a maxim in the salt mines that wherever coloured rocksalt occurs sylvine is to be found near at hand. This being so, one might expect the layers of rocksalt near to sylvine to contain relatively more potassium than the rest of the layer, since here the first crystallisation of sodium chloride would overlap the last of the potassium chloride. This might provide an optimum concentration of foreign matter for sensitisation, but the effect has never been observed. Alternatively, a greater concentration of potassium would also mean a correspondingly larger source of irradiation.

The generally higher level of impurity in sylvines is also to be noted. Since an optimum concentration of divalent impurity for sensitisation towards colour centre formation has been observed, it is probable that above a certain limit of divalent impurity concentration, the tendency to form colour centres is prohibited, at least in this case where only relatively weak sources are considered. This may explain why all the salt in the secondary deposit is not coloured and also why the sylvines are not coloured. In order to explain why the primary rocksalt is not coloured, one must refer to the sources of irradiation available for the purpose. This is exemplified in the vastly different helium contents between primary and secondary, assuming that all helium is radiogenic. Indeed, the only difference between the primary and secondary deposits available at present, which might provide a clue as to why the one is coloured and the other not, is in the helium contents. No regular difference can be observed in the lead contents however.

Further, Przibram and others (69) find a correlation to exist between helium content of the coloured rocksalt and their colour and has provided samples of violet and yellow rocksalt from the Grimberg Mine in the Werra Valley for examination of helium contents in this laboratory.

It will be clear, however, from the above review, that no attempt has, as yet, been made to carry out a complete set of experiments on one and the same sample of material or even on different samples from the same locality.

It is proposed, therefore, to investigate:-

1. The helium content of the salts with a view to finding a correlation between helium content and colour, if such a correlation exists.
2. The impurities present in rocksalt with a view to detecting a sensitisor for colour formation.
3. Diffusion of helium in rocksalt - this question arose when the helium contents were examined initially.
4. The origin of helium in rocksalt,
    (a) By examination of uranium and thorium contents and
    (b) By examining the amounts of helium arising from occlusion of brine in sodium chloride when this is crystallised slowly from air-saturated water.
5. The absorption spectra of the various coloured samples.

Since the samples provided by Przibram are only sufficient for helium analyses, other samples from Wintershall have been obtained. The results of such experiments, together with a discussion of the results, appears in Chapter II.

Experimental, Results and Discussion.

Dissolving apparatus for Rocksalts

The dissolving apparatus is shown in Fig.I. It consists of two inter-connected glass vessels V_1 and V_2 of about 250 ccs. capacity which attach to the main body of the apparatus at the standard ground joint (B19) G_1. V_1 and V_2 may be pumped down to vacuum simultaneously through taps T_1, T_2 and T_3 or independently, if it is necessary to keep T_3 closed, through T_1 and T_2. V_2 may be removed at will to reject old samples and replace with new ones, through the standard ground joint (B19) G_2.

The mode of operation is as follows:-

The apparatus is attached at the ground joint G_1 and pumped down to vacuum with both V_1 and V_2 empty. The various blown joints in the glass are tested for pinholes with a Tesla coil and the whole apparatus in general tested against leaks by allowing to stand for several hours under vacuum and re-testing with the Tesla coil. The absence of appreciable discharge or the characteristic pink discharge of air is taken to indicate that the apparatus is substantially leak-proof.

Air is then admitted into the dissolving apparatus by breaking one of the two inlets B_1 and B_2. V_2 may now be removed readily, a weighed sample of rocksalt put into it, and replaced. Then with tap T_3 closed 100-150 ccs. of

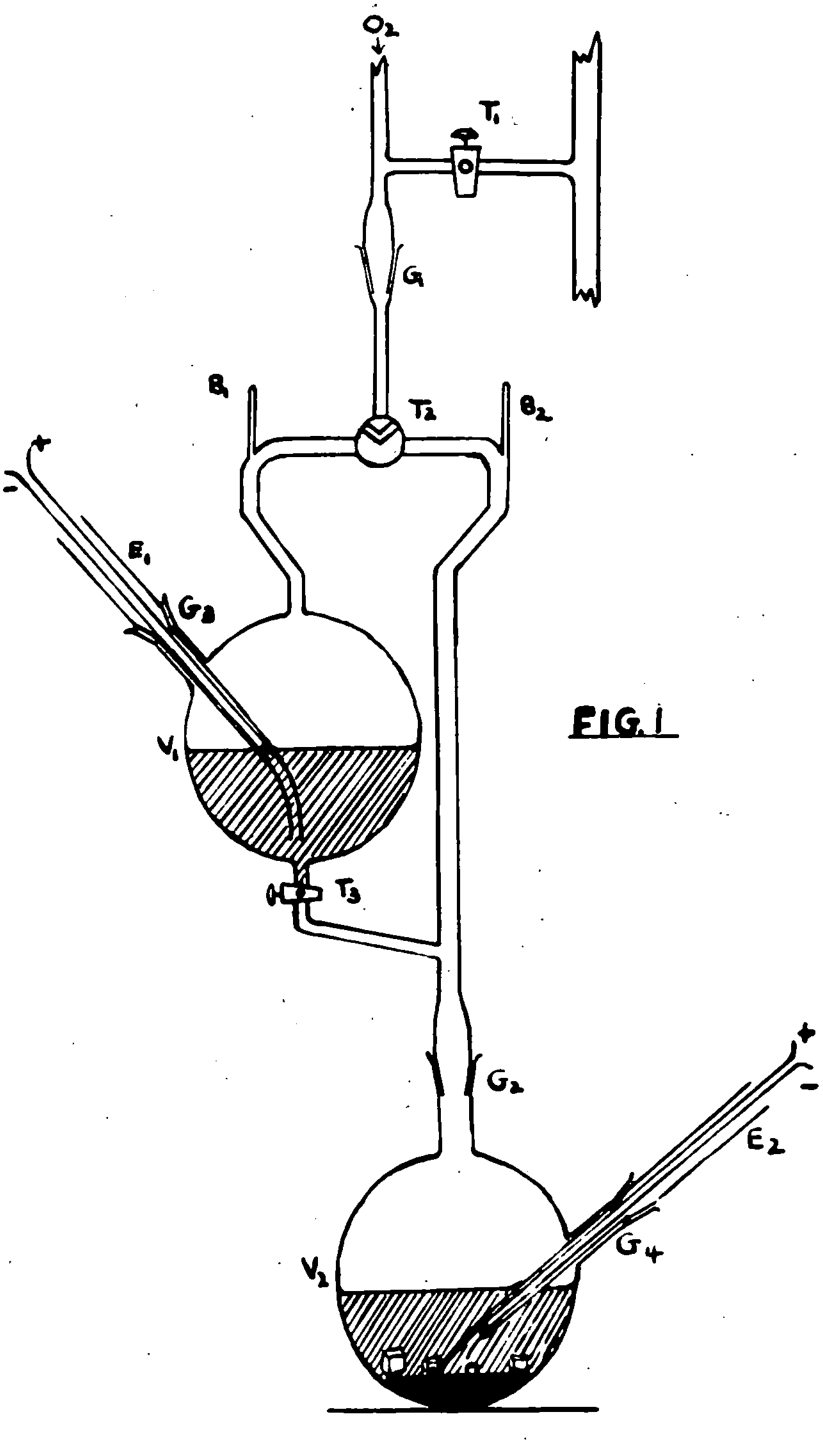

FIG. 1

distilled water containing a little sulphuric acid to facilitate electrolysis, are admitted into V_1 through B_1. B_1 and B_2 are then sealed off and V_1 and V_2 pumped down to vacuum again through the two-way tap T_2.

After the initial pumping down to vacuum of V_1 complete removal of rare gases from the water is achieved by vigorous electrolysis using the platinum electrodes E_1, which attach to V_1 through the ground joint (B14) G_3 and are connected to 24 volt, D.C. supply. Experiment showed that if the water is electrolysed for a period of one minute and the electrolytic gases pumped away, then this procedure, when repeated 6 - 7 times, is sufficient to remove substantially all the rare gases in solution with the water. A blank experiment on the water, using 2 to 3 times the amount of oxygen used in actual experiments, gave a helium value of 1×10^{-8} ccs. helium. In an actual experiment, this is less than one per cent of the total helium measured.

Having successfully removed the helium from the solvent to be used, tap T_3 may now be opened and some of the water allowed to run into V_2 which contains the rocksalt sample. Stirring to facilitate the dissolution process, is achieved by the inclusion in V_2 of a small iron nail sealed in a Pyrex glass envelope which is made to rotate by the use of an external magnetic stirrer. Sufficient water is generally accommodated in V_1 for at least three experiments.

When the solution of the rocksalt sample is complete, the gases so liberated may be freed from solution in the brine in the same way as before, i.e. by electrolysis using the platinum electrodes E_2 which enter V_2 through the ground joint G_4. Ground joints 3 and 4, being of a more permanent nature and in closer contact with the water than joints 1 and 2 and sealed with Apiezon wax W, as opposed to the Apiezon grease M used on 1 and 2.

With each successive operation of electrolysis, oxygen is added to about 1 cm. pressure to the electrolytic gases and the gases transferred onto the cooled charcoal unit in the circulating system. Here, as described later, the hydrogen produced electrolytically is removed in excess oxygen as water. (See Appendix)

Unfortunately, no account was taken in the first experiments of the chlorine, which is also produced in the electrolysis. This was found to have a profound effect on the mercury in the apparatus, a white sublimate, presumably mercurous chloride, forming in the circulating system and accumulating in the cold trap used to retain water. After cleaning out the circulating system, further trouble was avoided by using a mercury anode for the electrolysis in V_2.

As in the previous removal of rare gas from such a solution, it was found, by carrying out a test experiment on the solution remaining after a measurement had already been made on the gases liberated, that 6 - 7 operations of electrolysis and transfer to the circulating system were sufficient to release substantially all the helium from the solution, thus, in a blank experiment using more oxygen than is generally used in an experiment, 1 x 10^{-8} ccs. helium were detected.

All the measurements on rocksalts, the results of which are given below, were carried out in the manner described above.

Results and discussion.

The results of the various samples examined together with their place of origin are given in chronological order in Table V.

TABLE V

No	Place of Origin	Colour	Physical State	He.ccs/gm x 10^{7}
1	Wintershall, Herringen, Werra Valley	Yellow	Pieces	2.47.
2	"	"	"	1.85.
3	Grimberg Mine, Werra.	Violet	"	1.00
4	"	"	"	0.36.
5	"	"	"	0.26.
6	Wintershall	"	Powder	0.89
7	"	"	"	0.78
8	"	"	"	0.72
9	"	Yellow	Pieces	4.58
10	"	"	"	4.00
11	"	"	"	7.09

TABLE V (cont)

No	Place of Origin	Colour	Physical State	He.ccs/gm x 10^7
12	Wintershall	Blue	Pieces	15.0
13	"	"	"	20.4
14	"	"	"	12.4
15	Grimberg	Yellow	"	15.1
16	"	"	"	21.5

The pieces referred to in Table V under the column headed 'Physical State' are in general less than $1cm^3$ in size and are obtained by fracture of a larger single piece. It can be seen that in any series of results on any one sample, excluding result 11, the helium content of a piece of rocksalt appears to decrease with time after fracture. This may, of course, be simply a natural consequence of the previously noted inhomogeneity of the salt with respect to helium content from the results of other workers. The possibility of diffusion of helium from the salts must not be overlooked however and the reproducibility of the apparatus for these analyses was must be examined. For the latter purpose a sample of the violet salt was powdered, thoroughly mixed by quartering and examined for helium content - results 6, 7 and 8.

A loss of helium with time is still observed in the powdered sample though much smaller losses than seen in previous samples, results 1 - 5, where pieces were used in the experiments. No strict account was taken of the time between analyses on the powdered sample though this was about two to three days between each estimation.

This result rules out the possibility that diffusion from the salt is entirely responsible for the loss of helium with time in the pieces. It seems as though helium may be lost in some other way but result 11, obtained later along with results 9 and 10, indicates that the effect observed in the pieces is most likely due to the inhomogeneity of the samples. Later results 13 - 16 confirm this view. This argument does not apply to the powdered samples so the possibility of diffusion from the powder must be further examined.

With regard to the question raised by Przibram regarding helium content and colour, these results show that there is definite justification for saying that a correlation does exist between helium content and colour.

Thus the helium contents of the salts from Wintershall show a change from blue to yellow to violet, the blue having the highest helium content and the violet the least. The salts from Grimberg are similarly arrayed as far as they were examined, the yellow variety having a higher helium content than the violet, a result already anticipated by Przibram. (70)

Absorption Spectrum of salt from Wintershall

The absorption spectrum of each of the coloured varieties from Wintershall have been measured at the

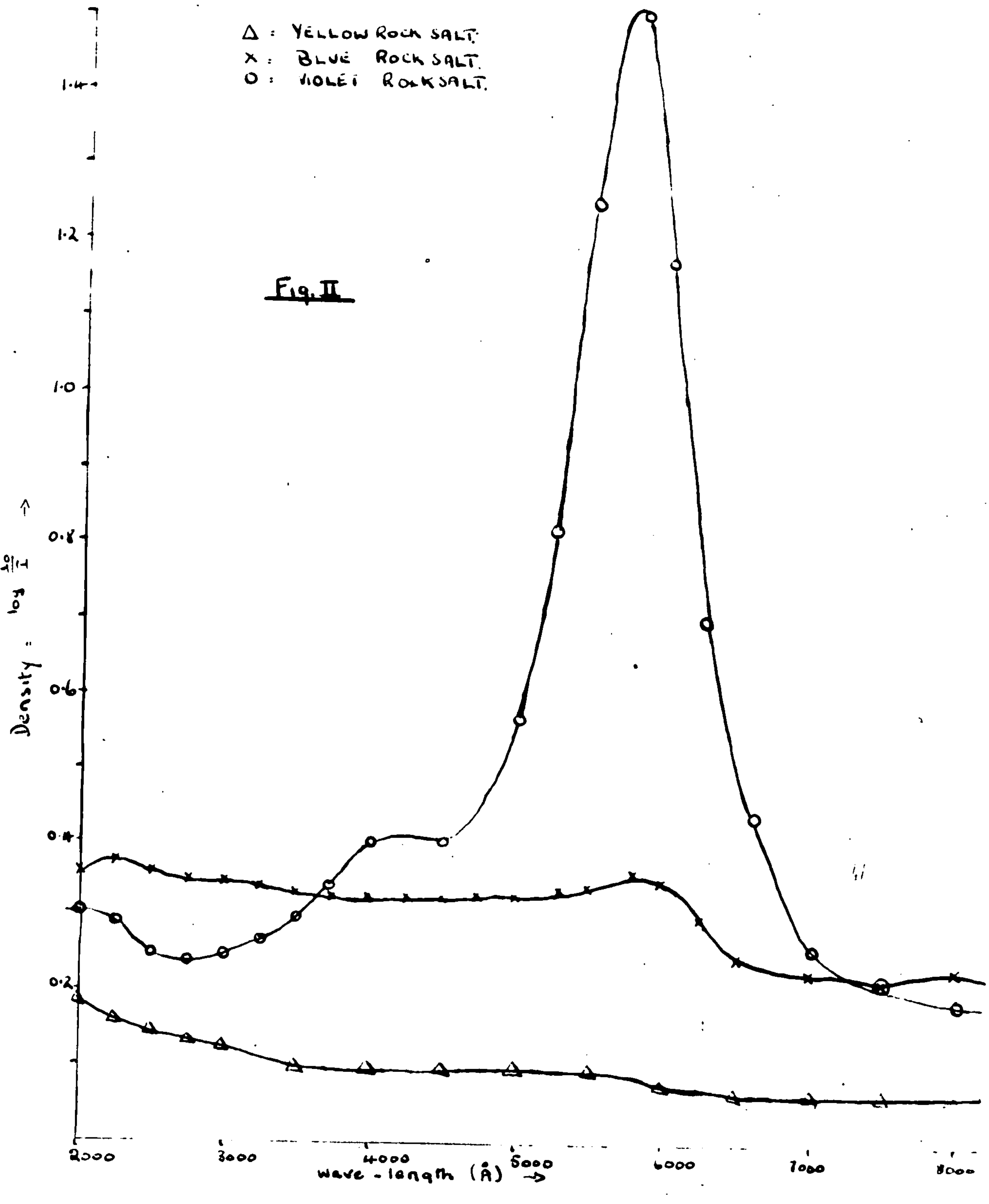

Fig. II

Δ : YELLOW ROCK SALT.
X : BLUE ROCK SALT.
O : VIOLET ROCKSALT.
Density = log I₀/I →
1·4
1·2
1·0
0·8
0·6
0·4
0·2
2000
3000
4000
5000
6000
7000
8000
wave-length (Å) →

Physics Department, Kings College, Newcastle-upon-Tyne, by Mr. R.V. Hesketh, to whom I am very much indebted. These are reproduced in Fig. II.

The violet sample shows a strong absorption maximum at 5750A which is taken to be the R.11 band, with other weaker maxima at 2000A and 4100A. The latter may be cf pink, attributed to impurity as is done by Przibram in other cases for maxima around 4400A. A maximum in this region has only been observed previously in the blue salts.

The blue sample shows maxima at 5800 - 6000A which may be the R-band again or colloids or a combination of the two, and, like the violet, at 2200A.

The yellow sample unfortunately faded before a measurement could be made, conforming to the general lability of the natural yellow varieties (71) examined by other workers. Even in the colourless samples so produced a tendency for the absorption to increase around 2000A is to be observed however, thus making the interpretation of the maxima in the violet and blue cases in this region as V-bands somewhat dubious.

Chemical content of the Wintershall Samples

In order to explain why all samples of rocksalt are not coloured, one must assume that in the cases of the ones that are coloured, some impurity or pressure effect is present, which sensitises the salt toward colour formation.

sulphide ion, for example, has been suggested by Wieninger as a sensitiser for colloid formation as is found to be the case in the silver halides. The various samples from Wintershall have therefore been subjected to spectrographic examination to see if any significant difference exists in chemical content between the three cases. The results are shown in Table VI.

TABLE VI

	Yellow %	Violet %	Blue %
Potassium	0.05	0.03	0.50 app.
Lead	* 0.0001	-	* 0.0001
Calcium	0.001	0.001	1.0 app
Copper	0.00005	0.02	0.0001
Magnesium	0.005	0.002	+0.1
Strontium	-	-	0.02
Iron	0.0005	0.0002	0.002
Silicon	trace	-	0.002
Rubidium	-	-	0.0005
Manganese	0.0002	*0.0001	-
Nickel	* 0.0001	0.0001	0.0002
Silver	* 0.001	*0.0001	-
Aluminium	trace	trace	trace

* = upper limit.

Other elements not detected in any of the samples were:- As, Au, Ba, Be, Bi, Cd, Co, Cr, Ga, Ge, Hg, In, Li, Mo, Sb, Ti, Tl, W, Zn, Zr.

The Uranium and Thorium Content

In view of the fact that natural rocksalt appears to contain excessive quantities of helium, it is surprising that no reports have been published about investigations on their thorium as well as their uranium content.

The thorium and uranium contents of a sample of rocksalt have now been determined. A large piece of blue rocksalt was broken up into smaller pieces. The smaller pieces were thoroughly mixed and quartered. Uranium and thorium analyses were then carried out by the most sensitive methods available, i.e. uranium by the fluorescence method and thorium by scintillation counting, on 200 gm. samples of the smaller pieces. I am very much indebted to Mr. J.C. Dalton for carrying out these analyses. The method of extraction of minute quantities of uranium and thorium is described later in the Appendix. The quantities measured in this way were:-

$0.17 \pm 0.02 \times 10^{-9}$ gm U/gm. salt

and less than 2×10^{-9} gm Th/gm. salt

It can be seen that the thorium value is extremely small and would not contribute very much to the amounts of helium found in the salts. The helium must certainly arise then, through some process other than uranium and thorium decay.

Bleaching Properties

Both the violet and blue samples were subjected to an increase in temperature in daylight and were found to bleach to a colourless state well below the melting point. The experiment was carried out in only a qualitative fashion to make sure that these samples conformed in behaviour to heat with samples examined by other workers.

The yellow colour was also found to fade quite rapidly on exposure to daylight and without any accompanying increase in temperature. This again agrees with the general behaviour of natural yellow irradiation coloured rocksalt observed by other workers and also with artificially irradiation coloured samples of purer sodium chloride.

Discussion of the results

The results of the helium measurements shown in Table V indicate a correlation between helium content and colour of the sample under examination. This would indicate that the colouration achieved in any sample depends at least in part on the amount of irradiation which that sample has received. This does not necessarily imply that the colourations are due exclusively to α- activity, for, accepting Hahn's hypothesis as to the source of the helium, associated with the α- activity are two β- activities which could also effect the colouration. The appearance of the colour in the blue and violet cases would favour the assumption that α- activity is the prime mover in the colouration process however. In these cases the colour is generally in the form of striations so that the individual regions of colouration are limited in extent. This could be due to the growth of radium D inthe crystallisatio process along crystal boundaries. Subsequent α- activity from the radium F arising from the radium D should produce high concentrations of F-centres in the immediate vicinity , as is usual in cases where α- activity is used in the colouration process. Such high local concentrations of F-centres would favour their aggregation into secondary units such as the R- and M- centres which occur in the violet and blue varieties, or even colloids.

Bombardment of sodium chloride (and other alkali halides) with high energy α-particles or electrons has been observed to produce initially a high concentration of F-centres. On thermal or optical bleaching a violet colour develops and the crystal now shows an absorption maximum at 5,800 A (72). This absorption band has been attributed to colloids (73) or sodium at interstitial sites (74) arising as a result of radiation damage to the crystal. No precise evidence for such designations has been put forward but it is to be noted that no colloids were detected by Wieninger in similar experiments. (See Table IV)

The similarity of this band to those which occur in the natural violet rocksalt is striking however and strongly supports the view that polonium α- particles are the prime movers in producing this colouration in nature.

That irradiation amount is not the only factor entering into the colouration process is evident from the helium values found for the yellow varieties. Thus, if irradiation were the sole effect, one would expect the blue variety, which contains the higher aggregates of centres i.e. colloids, to have the highest helium content, the violet, the next highest helium content, since this also contains secondary centres, and the yellow variety, containing only F-centres, to have the lowest helium content. The helium values actually found indicate the order of helium contents to be blue the highest, then yellow, and violet, the least. Thus one must postulate in the case of the violet variety at least, that some form of sensitisation towards centre formation and also towards aggregation of these centres, must be in evidence. This being so, it is reasonable to assume that there is also sensitisation in the other cases though not necessarily to the same degree. Thus, the yellow variety with less sensitisation than the violet, requires a greater amount of irradiation in order to achieve its colour. Similarly, the blue variety could have the same degree of sensitisation or even less than the violet variety, so that in order to achieve its colour, it must also receive a greater amount of irradiation than the violet, which may, or may not, be of the order of magnitude of that received by the yellow variety.

Thus, by considering a joint effect by irradiation and sensitisation, one can account satisfactorily for the variation in helium content amongst the various coloured specimen. Similarly, in order to explain why uncoloured samples, which contain quantities of helium of the same order of magnitude as the coloured samples, are not coloured, one must assume that these samples are not sensitised to the same degree as are the coloured varieties.

Assuming that the sensitisation occurs as the result of the inclusion of some impurity, a sample of each of the coloured varieties has been subjected to spectrochemical analysis. It can be seen from the results of these analyses (Table VI) that the samples differ widely in their content of small quantities of impurity, so much so that it is difficult to separate any single impurity as a likely sensitiser. It is, however, notable that the blue sample, in which colloids occur, is much less pure than the violet or yellow samples. It is also noteworthy that the yellow and blue samples, which on the basis of helium content have received the greater amount of irradiation, also contain the greater lead content and that they both contain as well, higher quantities of potassium than does the violet, indicating that here too in K^{40} decay they have also received the greater irradiation.

The general level of divalent impurity is greater in the violet and blue samples than in the yellow, the extremely high calcium content of the blue, and the high copper content of the violet salt being noteworthy. The copper content for the yellow and blue salts agree well with the value previously found by Biltz and Markus for a sample of blue rocksalt. (75)

The absence of lithium in any sample is also noteworthy in view of the fact that lithium has been detected in "deep natural waters" which have been taken as similar to those from which the salts crystallised. Too much significance must not be attached to this fact since the actual concentration of lithium in the waters is not recorded and may be at such a low level as to be not detectable in these analyses.

The Sensitisation of Naturally Occurring Sodium Chloride toward colour Formation

Two cases are to be considered, firstly sensitisation by divalent negative ions and secondly sensitisation by divalent positive ions. Sensitisation by plastic deformation is ignored mainly because of the appearance of the colours themselves and a lack of knowledge of the history of the deposits. Thus, if the sensitisation were by plastic deformation, one would not expect to find in the same piece of rocksalt, two patches of blue colouration separated by a colourless zone (even bearing in mind the fact that this colourless zone may have been coloured yellow originally and has now faded). Neither would one expect to find striations in the colour which are arranged orthogonally. The inference from such striations would be that they represented cracks or dislocations along which vacancies could aggregate and should therefore be arranged radially from the centre about which the deformation takes place. This assumes possibly an over-simplified picture of the deformation but the emission of this type of sensitisation is nevertheless felt to be justified.

Both types of colour formation quoted here are exemplified in the samples examined in this work.

The above difficulties do not arise in the case of impurity sensitisation since the impurity could be so distributed as to give these effects.

1. Sensitisation by Divalent Negative Ions

It has been shown in the case of the fluorites, whose colouration is attributable to some radio-active influence, that the depth of colour attained is intimately connected with the sulphur content of the sample (76). It has also been suggested that the formation of sensitivity specks in silver halides containing traces of silver sulphide, is due to the aggregation of F-centres arising from the inclusion, substitutionally, of $S^{=}$ in the halide lattice. Colloidal silver particles are thought to result from the further aggregation of F-centres (77).

On the basis of these facts, it has been suggested that sulphide ion is the sensitiser responsible for the appearance of colloidal aggregates in the naturally occuring rocksalts (78). In making this suggestion, Wienenger has assumed that since the two types of halides i.e. sodium and silver, are of similar crystalline form then what applies to the one may well apply to the other. The two cases, however, are not strictly analagous. The basis of the argument for the silver halide case is that S^{--} is incorporated in the lattice as substitutional S^{-} plus an F-centre. The presence of F-centres is then thought to aid formation of colloidal silver by aggregation. In the case of the rocksalts, this cannot be so for after bleaching by heat treatment F-centres should be re-generated and the crystal become coloured yellow. The bleaching, in fact, is quite permanent in the absence of suitable irradiation. One must assume, therefore, that the inclusion of sulphide ion in rocksalt is not by the same mechanism as that postulated for the inclusion in silver halides. This, however, does not preclude the possibility of S^{--} being a sensitiser toward centre formation under the influence of irradiation.

Since, for the above reason, it seems unlikely that S^{--} enters the sodium chloride lattice as S^{-} plus an electron, then assuming the inclusion to be substitutional, it must enter as S^{--} with an associated anion vacancy. Inclusion of S^{--} would thus increase the concentration of trapping centres for electrons released by irradiation and therefore sensitise the crystal toward F-centre formation. This should result in greater saturation values of F-centres and thus favour their aggregation. Sensitisation towards the formation of colloids should also result.

Mitchell has pointed out that the affinity for a sulphur atom to take up a second electron in forming S^{--} is much less than the affinity for a chlorine atom to take up an electron and form Cl^{-}. Without reference to lattice energies or the mode of inclusion of S^{--} in sodium chloride, it would seem probable that on irradiation of sodium chloride containing sodium sulphide an electron would be more readily given up by S^{--} than by Cl^{-}. It must be borne in mind in this respect that in the naturally occurring rocksalt, one is considering relatively weak irradiation sources acting over a long time. Such an effect would also sensitise the salt toward F-centre formation.

If indeed the electrons available, for the formation of F-centres, are derived from S^{--} then the characteristic V-band need not be present in the natural irradiation coloured rocksalt. It would be of interest to examine further the absorption spectrum of the natural salts in the U-V region to confirm whether or not the V-band is actually present. Unfortunately, the absorption spectrum measured in this region and shown in Fig. II is not sufficiently accurate to make this point certain but the indication is that the V-band is absent.

2. Sensitisation by Divalent Positive Ions

It has been seen above that sensitisation towards colour formation can be achieved by inclusion of a divalent negative ion and it may seem anamolous that divalent positive ions should produce the same effect. It must be remembered however that there are two possible fates for the secondary electrons which are released as a result of the incident irradiation. Firstly the electron may combine with an anion vacancy forming an F-centre, the chances of this process occuring being favoured by the number of anion vacancies available. Alternatively, the electrons may re-combine with the free holes from which they were originally released. Formation of F-centre will then be favoured by increasing the number of trapping centres for the free positive holes. There is good reason to believe that, in certain cases, e.g. the alkaline earth elements, that divalent positive ions enter the sodium chloride lattice substitutionally accompanied by a cation vacancy (79). Inclusion of these divalent positive ions then will increase the number of trapping centres for positive holes and should therefore sensitise the crystal towards F-centre formation.

In addition to the qualitative observation of sensitisation it has been observed that for some divalent positive ions, at least, an optimum concentration of divalent ions for sensitisation occurs. In this case one must assume that initially the two Cl^- which accompany the positive ion form fresh additions to the lattice without affecting the number of anion vacancies. At the optimum the limit to this process is reached and the Cl^- must then begin to occupy anion vacancies and thereby reduce the tendency to centre formation on irradiation.

Alternatively, it may be that at the optimum the concentration of divalent positive ions is such that clustering becomes favoured. This would tend to increase greatly the local concentration of cation vacancies in the vicinity of the clusters but reduce it generally in the rest of the crystal. Such a process could then lead to relatively less sensitisation at concentrations greater than the optimum.

If the free holes are indeed captured at cation vacancies associated with divalent positive ions, then one would expect the characteristic V-band to be modified somewhat by virtue of the presence of the divalent positive ion. Such an effect has been observed with the F-band in potassium chloride when the environment of the electron trapped at the anion vacancy has been modified by virtue of the presence of Rb^+. (80) Further investigation of V-bands associated with divalent impurity is indicated and may lead to the actual form which sensitisation takes in the naturally coloured rocksalts.

It is interesting to note in this respect that no less than six R-bands have been observed in a crystal of sodium chloride after irradiation with X-rays or electron bombardment, with maxima at 6,600, 6,300, 5,960, 5,720, 5,520 and 5,260A (61). It may be that the presence of impurity in substitutional positions in the lattice are responsible for some of these bands and suggests further investigation along these lines.

Other effects which may influence the formation of Colloids

Sensitisation of rocksalt towards colour centre formation by means of plastic deformation has already been mentioned. Once formed, there are two further effects which can aid aggregation of these centres and thus give rise to colloids. These are, increase of temperature and increase of pressure. The effect resulting from the former is due presumably to the increased mobility of the centres. In the latter there must also be a slight increase in temperature accompanied by a mechanical pushing together of the centres.

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Chapter II

The Diffusion of Helium in Rocksalt

It has already been shown that there is every reason to suspect that, on standing, a sample of powdered rocksalt which contains helium tends gradually to lose its helium by diffusion. In order to examine this further, and in a quantitative fashion, a sample of yellow rocksalt from Wintershall was carefully ground into a powder, sieved through a 100 mesh geological sieve in order to obtain a fairly uniform particle size and thoroughly mixed by quartering. The powdered sample was stored in a screw-topped jar contained in a desiccator.

Immediately following the grinding, a sample of the powder was weighed out and examined for helium content. Successive helium estimations were carried out on similar samples of the powder at intervals of 6 to 20 days over the following 90 days or so. The results of these estimations are given in Table VII and graphed in Fig. III.

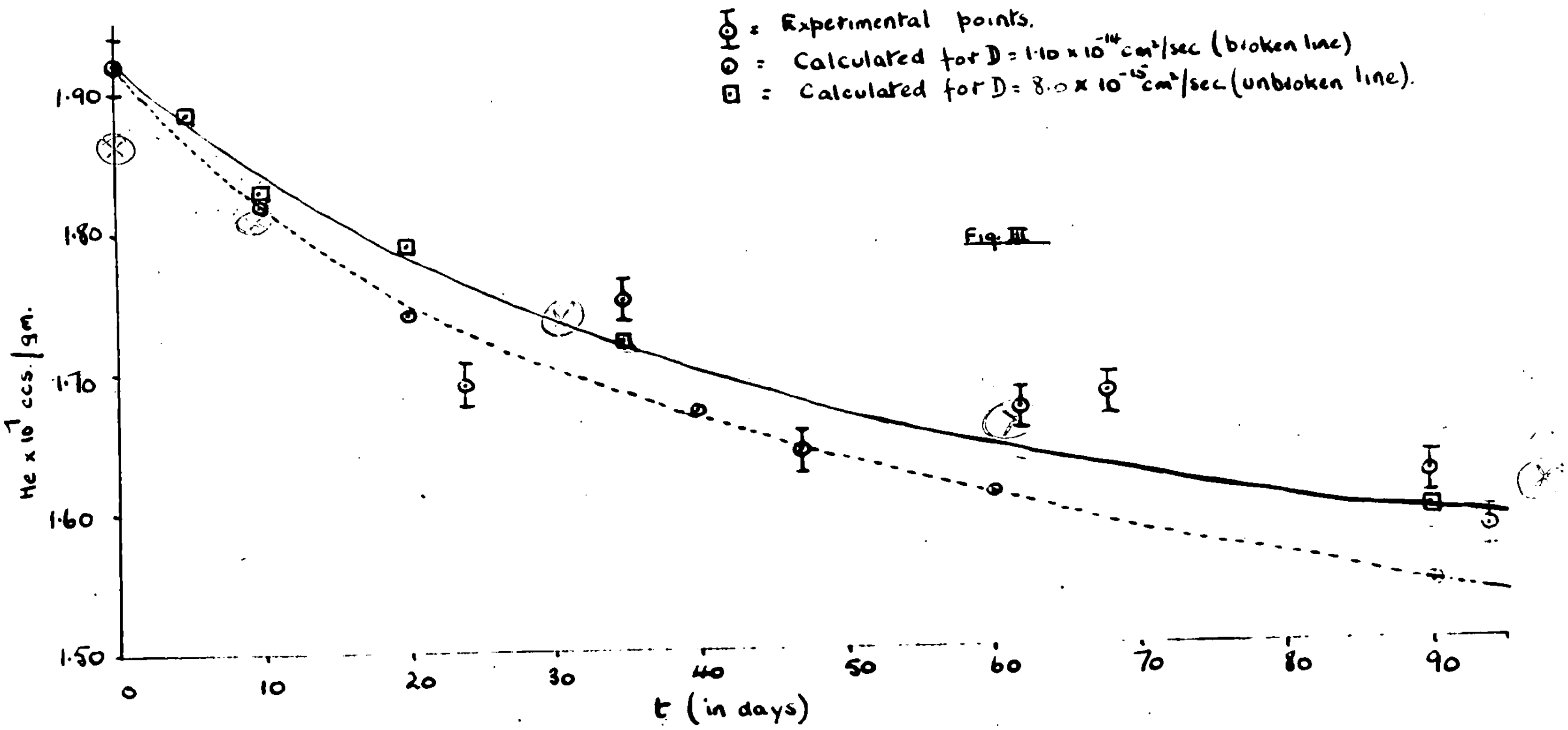

Experimental points.
Calculated for $D = 1.10 \times 10^{-14}$ cm²/sec (broken line)
Calculated for $D = 8.0 \times 10^{-15}$ cm²/sec (unbroken line).
$He \times 10^{7}$ ccs./gm.
1.90
1.80
1.70
1.60
1.50
0
10
20
30
40
50
60
70
80
90
t (in days)

Fig. III

Table VII

No	Period in days from first Estimation	Helium Content of Sample x 10^7 in ccs/gm
1	0	1.92
2	24	1.69
3	35	1.75
4	47	1.64
5	62	1.67
6	68	1.68
7	90	1.62
8	94	1.58

The results given in Table VII above show an initial rapid loss of helium with time followed by a less rapid loss.

When plotted, the graph of helium content versus time is observed to be of exponential form.

Calculation of the Diffusion Coefficient of Helium in Rocksalt at 20°C.

In the calculation of the diffusion coefficient, the particles of rocksalt are assumed to be of spherical shape. The solution of the diffusion equation;

$$\frac{\delta c}{\delta t} = D\frac{\delta^2 c}{\delta x^2} \qquad \ldots\ldots\ldots\ldots(1)$$

where $\frac{\delta c}{\delta t}$ = Change of concentration w.r.t. time.

$\frac{\delta c}{\delta x}$ = (the concentration gradient.)

D = diffusion coefficient.

for isotropic diffusion out of a sphere is given by Jost and Barrer (82) as:-

$$\frac{\bar{c} - c_f}{c_i - c_f} = \frac{6}{\pi^2} \sum_{m=1}^{m=\infty} \frac{1}{m^2} \exp \left\{ - \frac{m^2 \pi^2 Dt}{r_o^2} \right. \quad \ldots\ldots(2)$$

This formula refers to the average concentration, $\bar{c}$, in a sphere of radius r_o, whose initial uniform concentration has been c_i and its final concentration is c_f. The boundary conditions for the general case being:-

$c = c_i \neq 0$ for $0 < r < r_o$ and $t = 0$

$c = c_f \neq 0$ for $r = r_o$ and $t > 0$

Where c_i may be smaller or larger than c_f. The solution includes also the special cases:-

$c = 0$ for $0 < r < r_o$ and $t = 0$

$c = c_f \neq 0$ for $r = r_o$ and $t > 0$

$c = c_i \neq 0$ for $0 < r < r_o$ and $t = 0$

$c = c_f = 0$ for $r = r_o$ and $t > 0$

In the case under consideration here however, the particles of sodium chloride, assumed spherical in shape, are not all of uniform size.

Let there be n_1 particles of radius r_1 and mass m_1
" " " n_2 " " " r_2 " " m_2 etc.

Helium content measured after time $t = \bar{c}$ = average concentration for all particles.

$$\bar{c} = \frac{n_1 w_1 \bar{c}_1 + n_2 w_2 \bar{c}_2 + n_3 w_3 \bar{c}_3 + \cdots\cdots\cdots\cdots}{n_1 w_1 + n_2 w_2 + n_3 w_3 + \cdots\cdots\cdots\cdots} \text{ ccs/gm.}$$

$$= \frac{\text{total helium in ccs}}{\text{total weight of particles}}$$

Thus, assuming $c_f = 0$ equation (2) becomes

$$\frac{\bar{c}}{c_1} = \frac{6}{\pi^2} \left\{ \frac{n_1 w_1 \sum_{m=1}^{m=\infty} \frac{1}{m^2} e^{-\frac{tD\pi^2}{r_1^2} m^2} + n_2 w_2 \sum_{m=1}^{m=\infty} \frac{1}{m^2} e^{\frac{-tD\pi^2 m^2}{r_2^2}} + \cdots}{n_1 w_1 + n_2 w_2 + \cdots\cdots} \right. \quad \ldots(3)$$

Since all particles are considered as spheres their volumes will be

$$\frac{4}{3} \pi r_o^3$$

If the density = d

Then $w_1 = \frac{4}{3}\pi r_1^3 d$

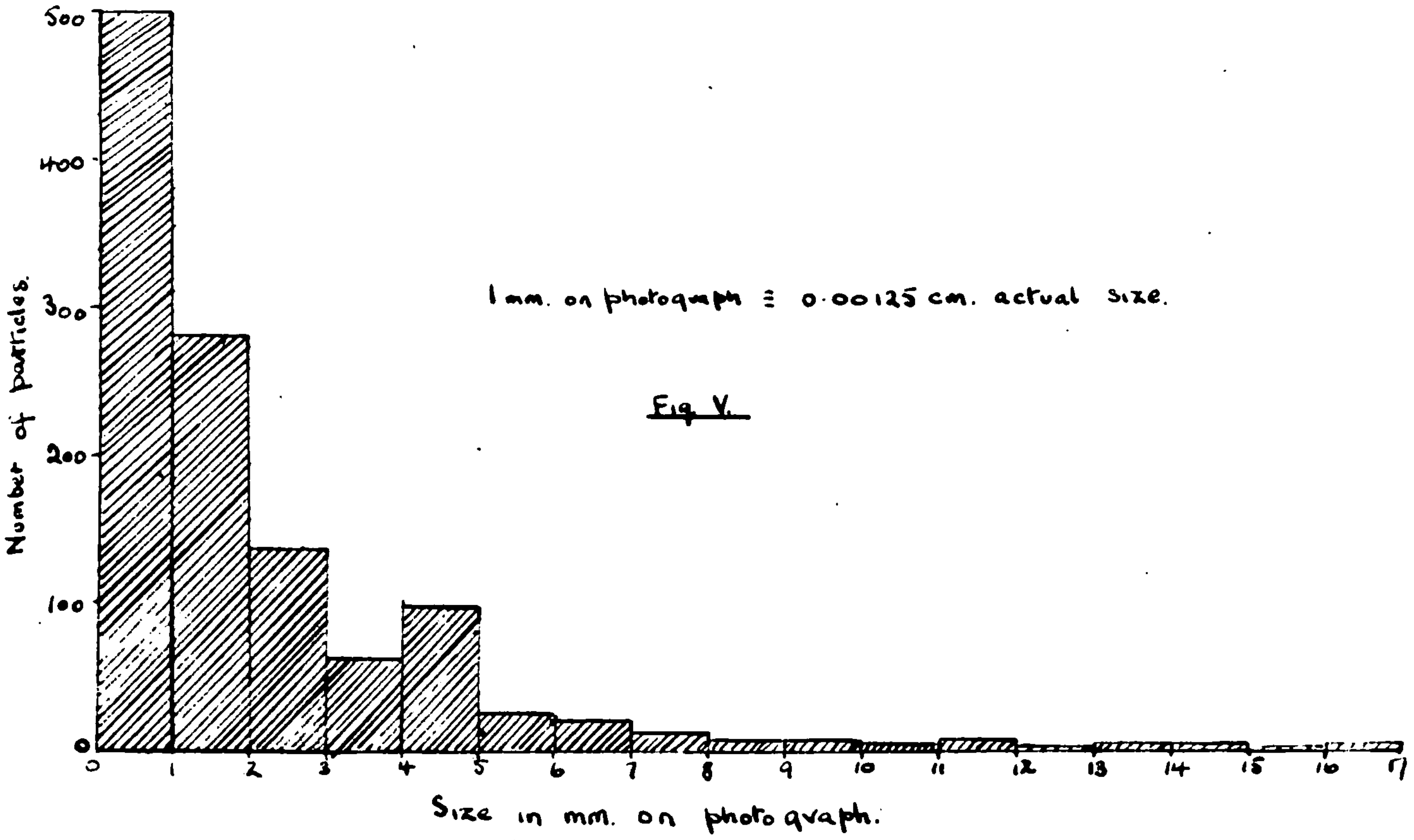
$w_2 = \frac{4}{3}\pi r_2^3 d$ and so on...

Thus (3) becomes:-

$$\bar{c} = \frac{6}{\pi^2} c_1 \left\{ \frac{n_1 \frac{4}{3}\pi r_1^3 d \sum_{m=1}^{m=\infty} \frac{1}{m^2} e^{\frac{-t\pi^2 D m^2}{r_1^2}} + \cdots\cdots}{n_1 \frac{4}{3}\pi r_1^3 d + } \right\}$$

$$\text{or } \bar{c} = \frac{6}{\pi^2} c_1 \left\{ \frac{n_1 r_1^3 \sum_{m=1}^{m=\infty} \frac{1}{m^2} e^{\frac{-t\pi^2 D m^2}{r_1^2}} + \cdots}{n_1 r_1^3 + n_2 r_2^3 + \cdots\cdots\cdots\cdots} \right\}$$

$$\text{or } \bar{c} = \frac{6}{\pi^2} c_1 \left\{ \frac{\sum_{n=1} n_o r_o^3 \sum_{m=1}^{m=\infty} \frac{1}{m^2} \exp(-t\pi^2 D m^2 / r_o^2)}{\sum_{n=1} n_o r_o^3} \right\} \ldots\ldots(4)$$



1 mm. on photograph ≡ 0·00125 cm. actual size.

Fig. V.

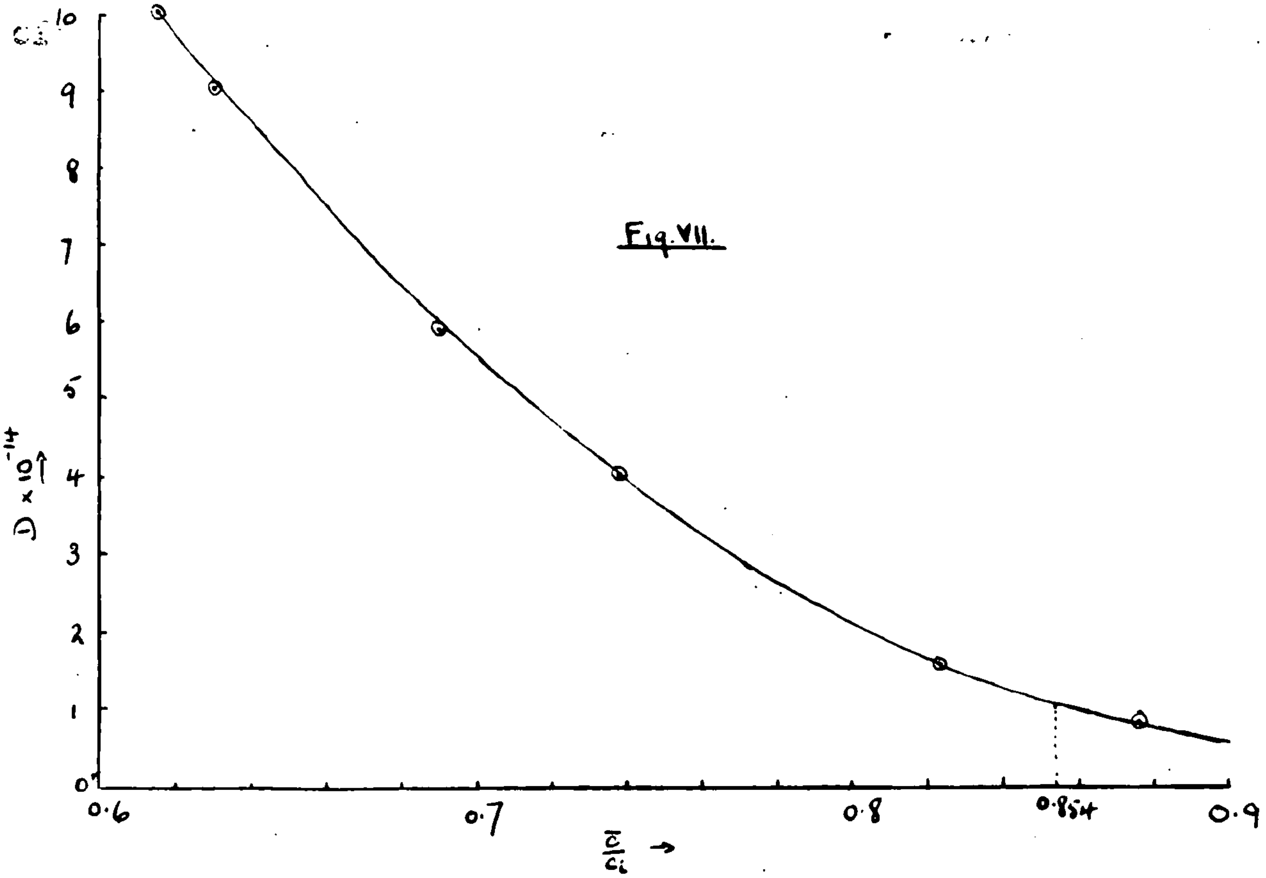


Fig. VII.

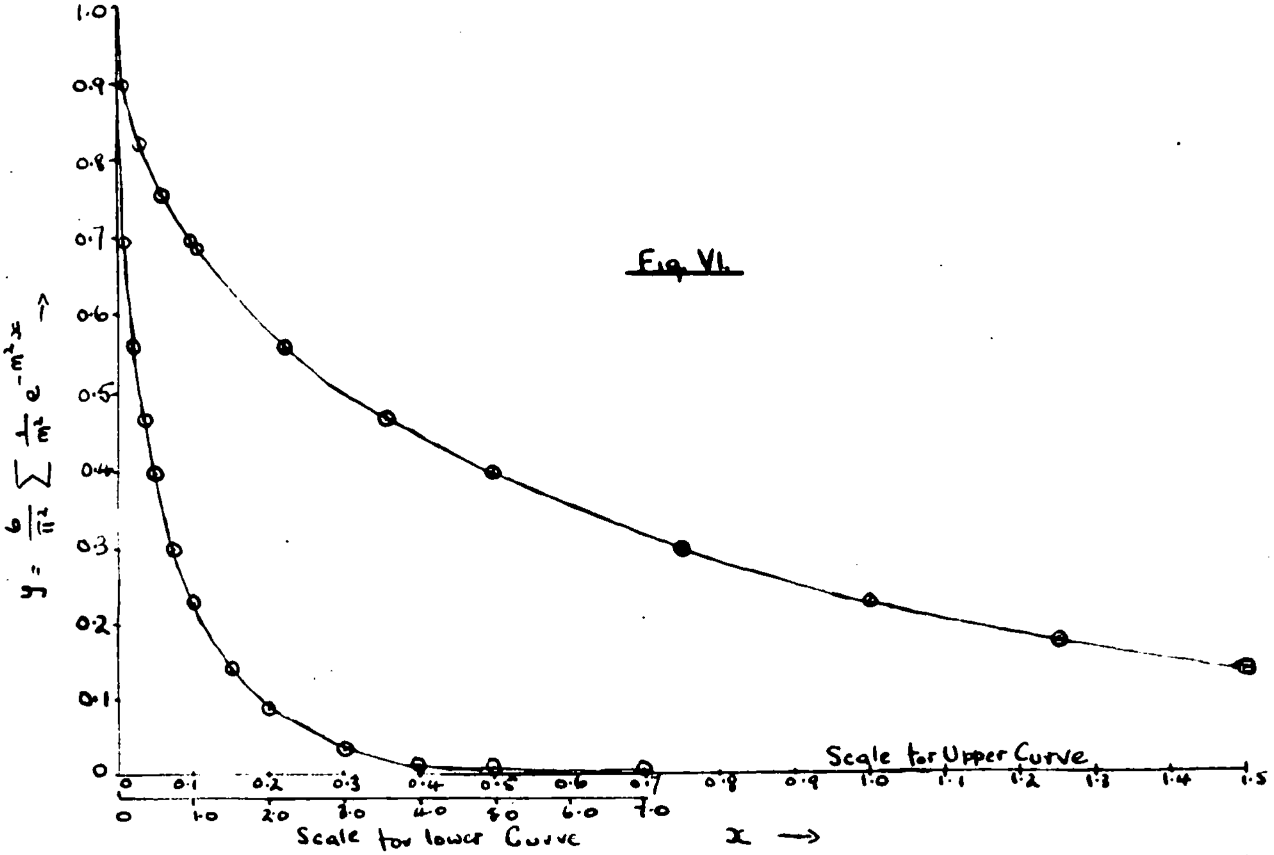


Fig. VI.

In order to obtain the values of n_0 and r_0 a sample of the powder used in the investigations was microphotographed and magnified to 80 times its normal size. The size and number of all the particles photographed was then measured and a histogram showing particle size distribution was constructed. Fig.V.

To facilitate the calculations, values of the summation of the exponential term in equation (4) are calculated. Thus,

$$\text{let } \frac{t\pi^2 D}{r^2} = x$$

$$\text{so that } \bar{s} = c_1\left\{\sum_{n=1} n_0 r_0{}^3 \frac{6}{\pi^2} \sum_{m=1}^{m=\infty} \frac{1}{m^2} \exp.(-xm^2)\right\}$$

For various values of x ranging from 0 to 10 the function

$$\frac{6}{\pi^2} \sum_{m=1}^{m=\infty} \frac{1}{m^2} \exp(-xm^2) = y \text{ (say)}$$

can now be summed over all the necessary values of m. Fig.VI.

If x is now plotted against y, then for any value of x the value of y is readily available from the graph.

Suitable values of D are now chosen so that for a given t the ratio $\frac{\bar{s}}{c_1}$ may be calculated. The various values of D are now plotted against the corresponding values of $\frac{\bar{s}}{c_1}$, Fig. VII. For an experimental value of $\frac{\bar{s}}{c_1}$ for the chosen t the value of D can now be read off this curve.

To confirm this value of D, values of $\bar{s}$ are now calculated using the experimental value for c_1, for various values of t. $\bar{c}$ is then plotted against t and this curve compared with the experimental curve.

The value for t is taken at 47 days in the initial calculation and the corresponding experimental value for $\bar{c}$ of 1.67×10^{-7} ccs/gm. c_1 is 1.92×10^{-7} ccs/gm.

It can be seen that the value of D calculated in this way (1.1×10^{-14} cm^2/sec.) does not give satisfactory comparison with the experimental values.

This simply means that the value of 1.67×10^{-7} ccs/gm. at 47 days is not quite accurate.

Similar calculation using $D = 8.0 \times 10^{-15}$ cm^2/sec. gives a more satisfactory comparison.

Using this value for D (8.0×10^{-15} cm^2/sec.) one can calculate the loss of helium to be expected from any size of sphere of rocksalt during the geological age of the deposits, assuming the temperature of the deposits to be 20°C.

Thus for a sphere of radius 100 cms $t = 10^8$ years and $D = 8 \times 10^{-15}$ cm^2/sec.

$$\frac{\bar{c}}{c_1} = \frac{6}{\pi^2} \sum_{m=1}^{m=\infty} \frac{1}{m^2} e^{\frac{-\pi^2 Dt}{r^2}} = \frac{6}{\pi^2} \sum_{m=1} \frac{1}{m^2} e^{-m^2 x}$$

$$x = \frac{{}^2 \times 8 \times 10^{-15} \times 10^8 \times 365 \times 24 \times 60 \times 60}{10^4} = 2.5 \times 10^{-2}$$

$$\frac{\bar{c}}{c_1} = 0.84.$$

i.e. the loss during geological time = 16% of initial concentration.

For the secondary layer now $t = 2 \times 10^7$ years

to that $x = .005$

and $\frac{\bar{c}}{c_1} = 0.95$

i.e. loss from the secondary layer for particles of this size = 5%.

Similarly for $r = 200$ cms.

$t = 10^8$ years and $D = 8 \times 10^{-15}$ cm^2/sec.

$x = .006$

and $\frac{\bar{c}}{c_1} = 0.95.$

i.e. the loss of helium = 5%

For $r = 200$ cms.

$t = 2 \times 10^7$ years and $D = 8 \times 10^{-15}$ cm^2/sec.

$x = .001$

and $\frac{\bar{c}}{c_1} = 1.0$

i.e. loss is negligible.

Thus for spheres of radius 200 cms. losses of helium during geological time in the primary layers are quite low whilst for the secondary layer they are negligible.

Loss from a sphere of radius .5mm. = 0.05 cms.

With $t = 24$ hours and $D = 8 \times 10^{-15}$ cm^2/sec.

$$\text{then } x = \frac{2 \times 8 \times 10^{-15} \times 24 \times 60 \times 60}{.0025}$$

$$= 3.0 \times 10^{-12}$$

$$\frac{\bar{c}}{c_1} = 1.0$$

This last value calculated for $\frac{\bar{e}}{e_1}$ is in agreement with the fact that Rayleigh was unable to detect the passage of helium through rocksalt, within the limits of detection of the apparatus he used.

The Diffusion at Elevated Temperatures

It is intended to treat the diffusion as an activated process so that a relation of the type :-

$$D = D_0 \exp \left(- \frac{E}{RT} \right)$$

should be followed. By measuring the values of D at various temperatures it should then be possible to calculate E, the activation energy for the process. This value for E may then be compared with other values of the activation energy for other diffusion processes in sodium chloride.

A fresh sample of yellow rocksalt (about 400 gms) is broken down in the manner described previously. Large well-formed crystals of about ½ to 1 inch side and apparently without defect are chosen for the purpose. Subsequent X-ray analysis of a particle of the ground sample indicated it to be a single crystal with a little strain (83).

40 gm portions of the ground sample, each containing not less than 90% of the initial helium content of the original sample, are then heated under vacuum in a silica glass tube at known temperatures. 10 gm. quantities are removed after certain noted time intervals and examined for helium content. In order to prevent caking of the sample, which will arise on the expulsion of occluded water at the higher temperature, each sample is dried in a

desiccator before being subjected to the heat treatment. Temperatures are measured with a mercury thermometer, placed in close contact with the silica glass vessel in which the salts are heated.

Results

The results of these experiments are presented in Table VIII.

TABLE VIII

Temp°C	Time of heating in hours	He content x 10^7ccs/gm.
96	0	2.00
	23	1.78
	46	1.70
	70½	1.57
123	0	2.00
	16½	1.46
	40½	1.26
	64½	1.13
147	0	2.00
	16½	1.16
	22½	0.97
	40½	0.84
308	23	0.14
312	5	0.16
20	0	2.04
20	About 14 x 24	1.99

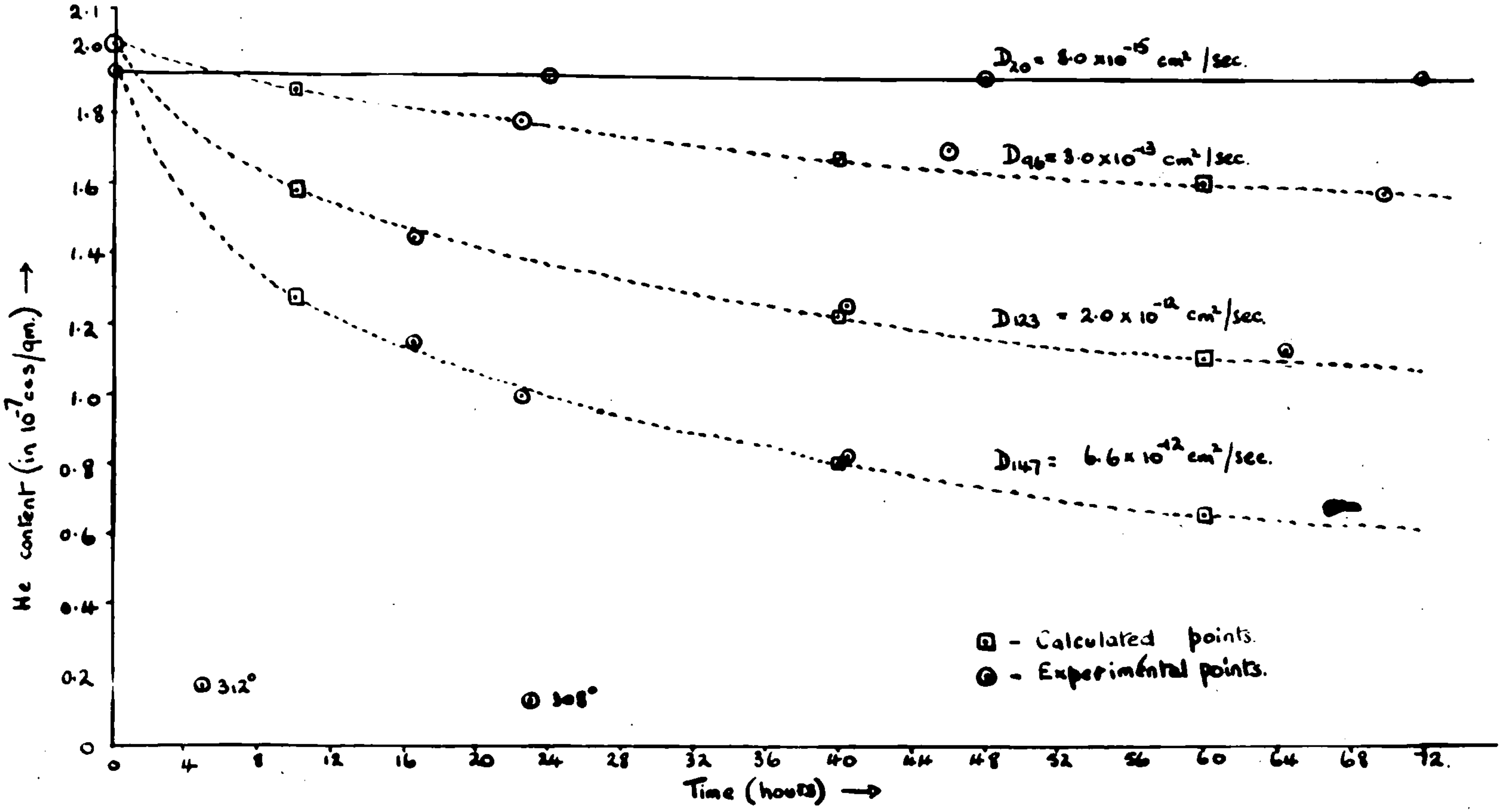

2.1
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
He content (in 10⁻⁷ ccs/gm.) →
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
Time (hours) →
D₂₀ = 8.0 x 10⁻¹⁵ cm²/sec.
D₄₆ = 3.0 x 10⁻¹³ cm²/sec.
D₁₂₃ = 2.0 x 10⁻¹² cm²/sec.
D₁₄₇ = 6.6 x 10⁻¹² cm²/sec.
⊡ - Calculated points.
⊙ - Experimental points.
⊙ 312°
⊙ 308°

Fig. VIII

The comparatively rapid loss of helium at 308°C and 312°C is to be noted. Such rapid losses do not lend themselves to quantitative estimation in these experiments, though the diffusion in this temperature region could be studied using particles of a larger size.

The initial concentration of helium is measured both before and after the experiments. It can be seen that the loss of helium during the time taken in the experiments is comparatively small. A common value for the initial concentration in the particles is taken, this being chosen as 2.00×10^{-7} ccs He / gm salt for convenience in the subsequent calculations.

The values of the diffusion coefficient D are calculated in exactly the same manner as described previously. Fig VIII shows the theoretical curves for the loss of helium at various temperatures on the basis of these values of D. Experimental values are included in figure VIII and these can be seen to fit the theoretical curves extremely well. The curve for the diffusion at 20°C is also included in Fig. VIII for the purpose of comparison.

Assuming a relation of the type :-

$$D = D_0 \exp\left(-\frac{E}{RT}\right) \quad ....(1)$$

to hold, it should now be possible to calculate the activation energy E for the diffusion process.

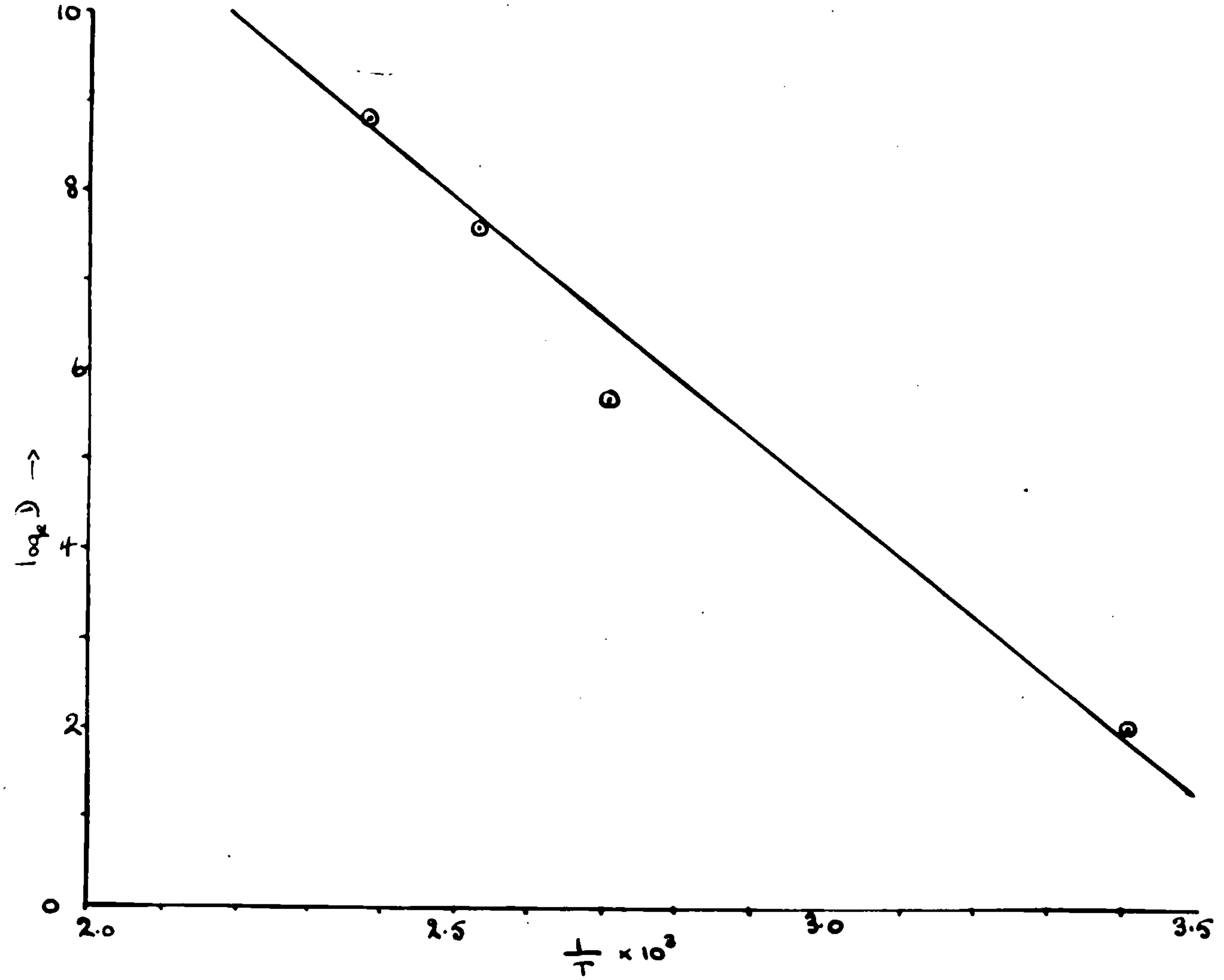


Fig. IX

From equation (1) above :-

$$\log D - \log D_0 = \frac{-E}{RT}$$

thus the plot of log D against $\frac{1}{T}$ should be a straight line whose slope is $-\frac{E}{R}$.

Experimental values of $\log_e D$ are plotted against $\frac{1}{T}$ in Fig. IX. It can be seen that the plot is in fact a straight line. The slope of this line when measured is found to be -6.60×10^3. Taking R = 2.0 cals/mole then, the activation energy for the diffusion of helium in natural yellow rocksalt is calculated as 13.2 K cals/mole.

The value of D_0 is calculated to be 3.8×10^{-5} cm^2/sec.

Table IX shows values of activation energies and D_0 for various other species in sodium chloride.

TABLE IX

Substance	Activation Energy in K cals/mole	D_0 $cm^2/sec.$
NH_3	~ 6.3	
Na	41.4	3.13 $T > 550°C$
	17.7	1.6×10^{-5} $T < 550°C$.
Cu	12.6	0.50
Ni	12.7	0.20

The activation energy for ammonia is determined by sorption measurements (84) on a polycrystalline mass of sodium chloride and is hence assumed to represent grain boundary diffusion. Since the activation energy found for the diffusion of helium in rocksalt is so much higher and in view of the difference in size of the molecules concerned, it is reasonable to assume that the diffusion of helium in rocksalt is a volume diffusion process.

Such a conclusion is in agreement with the effect [illegible] expected on consideration of the results of the X-ray analysis mentioned previously. It would be expected also that breakdown of a larger piece into many smaller pieces would tend to reduce the number of defects per particle, thus favouring volume diffusion.

An alternative method has been used to study the diffusion of argon in naturally occuring potassium chloride by Smits and Gentner (85). These workers have observed a variation in argon content of samples of potassium chloride which seems to bear a relation to the size of the sample taken. The larger pieces in the samples examined having the higher argon content. Smits and Gentner account for the difference in argon contents between large and small pieces as being due to volume diffusion of argon out of the pieces during the course of geological time. The smaller the piece, the greater the relative loss of argon.

They then correlate the argon content and size of the pieces with various assumed values of the diffusion coefficient D using different values for the age of the deposit. Good agreement between calculated and experimental values is obtained but there are limitations in the method from the point of view of diffusion.

Thus the diffusion coefficient can only be estimated at one average temperature. No value for the activation energy of the process or for D_0 can be calculated. It would be of interest therefore if the method used in this work could be applied to the argon in potassium chloride case (and also helium in potassium chloride) in order to determine the values of E and D_0 for this process and also to compare the results of the two methods.

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Chapter III

Spallation Products in Irradiated Steel

Introduction

It has been recently pointed out by Bauer (86) and Huntley (87) that the geological ages of meteorites as computed from helium - uranium - thorium contents are in error because the helium contents are probably not solely effected by the decay of uranium and thorium.

Observing that, in general, small meteorites contain relatively higher amounts of helium than large meteorites and the consequent indication of a relation between helium content and pre-atmospheric mass, Bauer postulates that the extra helium in small meteorites is produced by cosmic radiation.

Thus the larger bodies would be protected from cosmic rays to a greater extent than the smaller bodies and furthermore would lose relatively more mass in passing through the earth's atmosphere, at the same time therefore losing the outer layers having the higher helium contents.

Bauer's more precise predictions on the effect to be expected were invalidated by the absence of a radial variation in helium content in the meteorites examined by Paneth et al (88). The problem was pursued further however and samples of meteoritic helium were subjected to mass spectrometer examination. It was found in the samples examined that the ratio $He^3 : He^4$ varied from 0.178 to 0.315 (89), indicating that a substantial amount of the helium present was of cosmic ray origin since radiogenic helium is known to be all of mass four.

Later experiments on the meteorite 'Carbo' have shown that there is a variation in helium content with depth from the surface (90) and the extent of this variation agrees well with the calculations of Martin (91).

In order to investigate the effect further, it would seem profitable to examine the 'light element' spallation products in a sample of terrestrial steel which has been bombarded with protons of as high an energy as is attainable (92).

Le Couteur has treated such interactions on the basis of a theory of nuclear evaporation (93) and arrived at conclusions regarding the relative yields of neutrons, protons, deuterons, tritons ^3He and α- particles and the energy distributions of the evaporated particles. In certain respects the evaporation theory is well substantiated by experimental work on evaporation stars produced in photographic emulsions (94), but no direct evidence is available at present on the exact ratios of He^3, He^4 and H^3 produced in such reactions.

Two blocks of steel have been bombarded with 340 Mev protons in the Berkeley (California) Synchrocyclotron and are examined in this work for helium content and tritium content.

In addition, the helium, after purification and measurement, is collected and examined for the ratio of ^{3}He to ^{4}He.

Experimental

Bombardment Data

The steel target consists of two blocks of steel (3.8 cms x 3.6cms x 1.3cms) separated by a thin aluminium block (3.8 cms x 3.6 cms x 0.3 cms), all three being securely bolted together. Bombardment of the blocks was thought to take place along one edge of the blocks and only in a fairly thin section of about 1 mm. thickness.

The protons were of 340 Mev energy and bombardment took place intermittently over a period of about six months. Total bombardment in fact lasted 26 hours at 0.5 μa giving a total dose of 13 μa hours.

In order to check on this bombardment data and locate the active parts of the blocks, radioautographs were taken of each block i.e. two steel and one aluminium. This was done by laying each block in noted position on an unexposed X-ray film (Ilford Industrial G X-ray film) and developing the film after a suitable time interval. When developed the films showed the active portions of each block to be localised along the edges remote from the two boltholes where the three blocks had been bolted together.

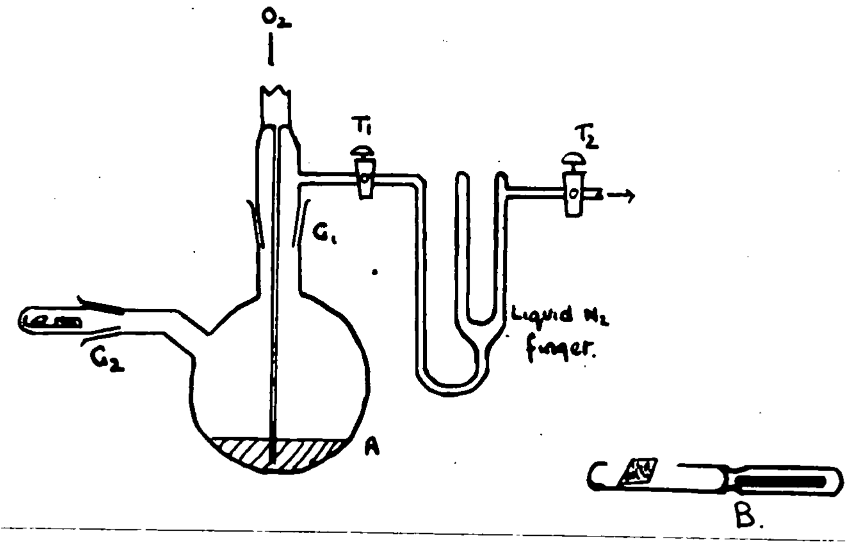


Fig. X.

Determination of the helium content of the active steel.

Choice of Reagents

A review of the methods available for the extraction of gases from terrestrial irons and steels has been published by Nash (95) who recommends either mercuric chloride or cupric chloride-potassium chloride double salt solutions as solvents. Both these reagents were examined in a qualitative fashion using pieces of steel from the inactive end of the irradiated blocks and contrary to Nash's findings it was found that the cupric chloride-potassium chloride double salt reagent was by far the most effective. Sulphuric acid was also tried but it was found to be even less effective than mercuric chloride.

Cupric chloride-potassium chloride double salt was therefore used to dissolve the steel in all the helium estimations, the composition of the solution being:-

400 gms. double salt.
30 ccs. concentrated hydrochloric acid.
850 ccs. water.

The solution is of the same composition as that used in the investigation of the gases in meteorites.

Dissolving Vessel for Steel Samples

The dissolving apparatus is shown in Fig X . It consists of a flask A of about 300 ccs. capacity which is attached to a source of helium-free oxygen at the ground joint G_1. In addition flask A has a side-arm containing a standard joint G_2 and is connected to the body of the apparatus through taps T_1 and T_2.

Between taps T_1 and T_2 is a trap, cooled in liquid nitrogen, the purpose of which is to prevent transfer of water from the reagent in flask A to the rest of the apparatus. The need for this arrangement will be discussed later when the determination of Tritium is considered.

In a typical estimation a piece of steel about 1 mm. thick is sawn from the active edge of one of the blocks. This is then weighed and placed in a boat of the type shown in Fig. X B. This boat is made of pyrex glass and is attached to a small iron nail sealed in a pyrex glass envelope. Such an arrangement affords ready movement of the boat inside by the use of a magnet outside the apparatus.

About 75 ccs of reagent are then admitted into A, together with a stirrer, and A then re-attached at G. With A in position the boat containing the steel sample is placed inside the sealed male component of joint G_2, which is then attached to the flask A.

Flask A is then evacuated through taps T_1 and T_2 and complete removal of rare-gases from the solution effected by flushing through with helium-free oxygen. In practice, six to eight flushingswith oxygen, each sufficient to produce a pressure of about 1 cm. of mercury in the flask, were found to remove substantially all the helium from the solution.

When the reagent is satisfactorily de-gassed, taps to the pumps are closed and the steel brought into the reagent by pulling the boat along with a magnet outside the flask. The steel sample invariably drops free into the solvent and the boat may be removed, if so desired, into the side-arm whence it came.

The dissolution of the steel is then assisted by use of a magnetic stirrer. Generally, about two hours stirring are required, the sample allowed to stand overnight, followed by another one hour stirring, to ensure complete dissolution.

The gases so released from the steel are then transferred, using oxygen carrier, into the circulating system, and the determination and collection of the helium carried out in the manner described in Appendix I.

Efforts were made in all these experiments to isolate the tritium released in a suitable form for estimation. Such methods as were used will be discussed later.

Blank estimations were carried out on the oxygen supply, reagent, and the inactive end of the steel blocks and found to be satisfactory e.g. the helium obtained from 0.4 gms. steel from the inactive end was found by this method to contain 5 x 10^{-8} as He at N.T.P. This would yield in the amounts of steel from the active ends used less than one percent of the total helium. Where this amount becomes significant e.g. samples (1) and (2) in Table X , a suitable correction is applied.

The validity of the procedure was tested by carrying out an estimation on the meteorite 'Carbo'. The helium value found for 'Carbo' was 16.9 x 10^{-6} cs He/gm. meteorite which is identical with the figure found by Reasbeck on a different apparatus using a part of the same sample of meteorite (96).

Results of the analyses

The results of the various helium analyses are shown in Table X together with the approximate distance from one edge of the block from which the sample was taken.

TABLE X

	Steel taken in gms	Distance from edge of block.	Total He x 10^5 ccs	He content in 10^{-5} ccs/gm.	Counts on Solution	$\left(\frac{\text{Cnts on Sol}}{\text{total He}} \times 10^{-8}\right)$	$\frac{He^3}{He^4}$
1	.0186	0-1mm		1.37	-	-	
2	.0471	0-1mm		1.30	-	-	
3	0.5240	1-9mm	1.35(calc)	2.58(calc)	1630, 1615	-	0.0568
4	0.270	9-15mm	1.314	4.87	1600	1.218	0.0564
5	0.1346	15-21mm	0.721	5.356	868	1.204	0.032
6	0.0992	15.21mm	0.538	5.43	654	1.216	0.0322

Helium samples 3 to 6 in Table X were collected and have been examined for ^{3}He : ^{4}He ratio by Mr. K.I.Mayne at the Clarendon Laboratory, Oxford. The results of these analyses are shown in the last column of Table X.

The helium value for sample 3 is a calculated value, the method of calculation will be discussed later.

Monitoring.

A considerable difference in helium content is to be noted amongst the samples of steel examined. This underlines the need for adequate monitoring in order to determine the amount of bombardment which each sample has received.

Data is available on the spallation products in iron including the yields of various isotopes and their half-lives (97). Difficulty in absolute monitoring arises here since the material bombarded is not pure iron and other components in steel will produce spallation products which will add to the yield of any particular isotope considered.

Of the various isotopes produced in iron, ^{47}V seems to be the one which has the most favourable yield and half-life but here again difficulty could arise in the extraction of small quantities of vanadium from the gross quantities of copper present in solution.

Since monitoring of a relative nature only is possible and in view of the above consideration it would be a considerable help if it were possible to monitor the solutions as such without extracting any particular isotope. Each solution contains approximately the same volume of reagent i.e. 75 ccs. so that if all are made up to the same total volume they should all be about the same density.

All the solutions containing steel are therefore made up to a volume of 250 ccs. The plateau for the liquid counter used is obtained using an external ^{60}Co source and a background count taken with distilled water in the counter. 10 ml. of each solution are pipetted into the counter in turn and a count taken on each. The counter is washed out with distilled water and acetone before admitting a fresh sample of solution, the acetone being removed in a current of air.

The counts obtained for the various solutions are noted in Table X , together with the ratios of total helium to total counts on solution for each of steel samples 3 to 6.

It can be seen that for the three samples for which reliable helium values have been obtained (4, 5 and 6) the ratio is constant. The helium value for sample 3 was uncertain because the galvanometer deflection (see Appendix I) obtained when this sample was measured was too large for accurate estimation.

It is on the basis of the constancy of the ratio of total helium to total counts on solution that the helium value for steel sample No. 3 shown in Table X has been calculated.

The solutions of samples 1 and 2 were discarded long before monitoring took place but again because of the above constant ratio, confidence in the helium values is felt to be justified.

Estimation of Tritium in the Active Steel Samples

In all the helium analyses discussed above, attempts were made to extract the tritium in a suitable form for analysis. The method used originally was to attempt to catalyse the reaction between tritium and oxygen as the tritium was released from solution. This involved the inclusion in the dissolving vessel (Fig. X) of an additional side-arm which carried leads to a spiral of platinum wire within the dissolving vessel. The platinum wire was heated electrically to dull redness (98) in an atmosphere of oxygen during the dissolution and transfer of the gases released from the steel on solution. The water was confined to the dissolving apparatus during transfer by passing the gases over a liquid nitrogen finger (see FigX). At the end of an experiment the water condensed on this finger would be re-condensed into the dissolving vessel by cooling the vessel in an ice salt freezing mixture and allowing the liquid nitrogen finger to warm up to room temperature.

Provided the catalyses is efficient, the tritium should now be confined in the bulk solution as oxide. By taking aliquots of this solution it should now be possible to convert the tritium oxide into a suitable form for counting.

It was proposed initially to count the tritium as tritiobutane after the method of Glascock (99), the

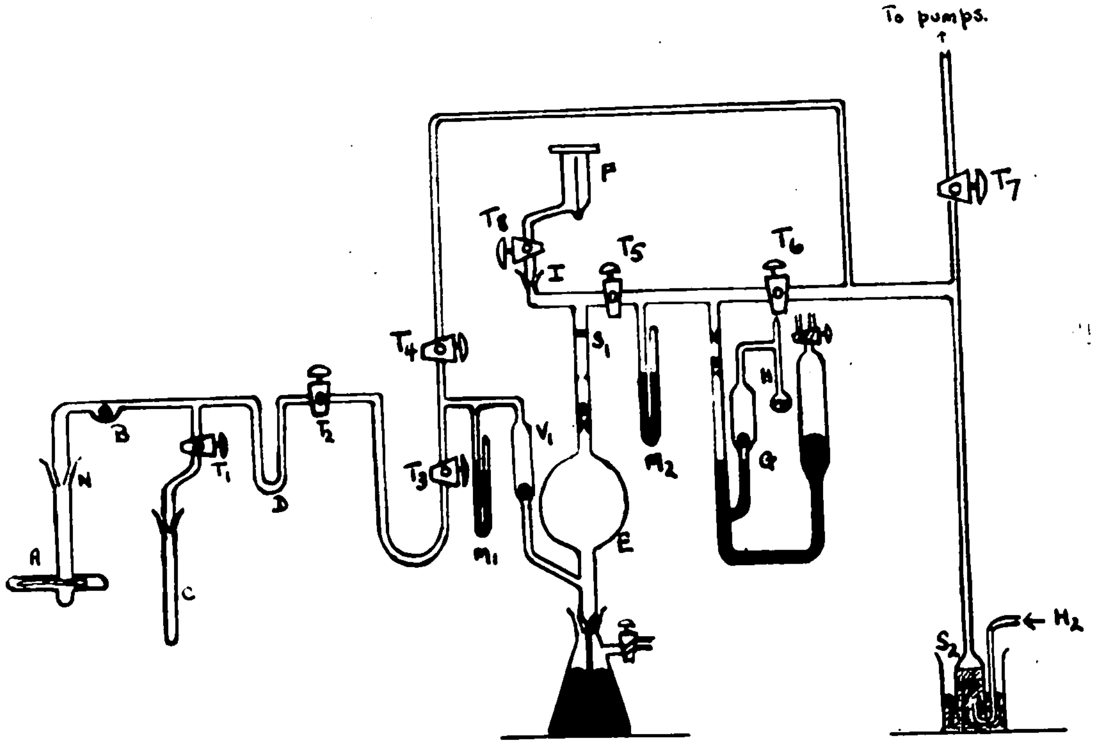


Fig. XI

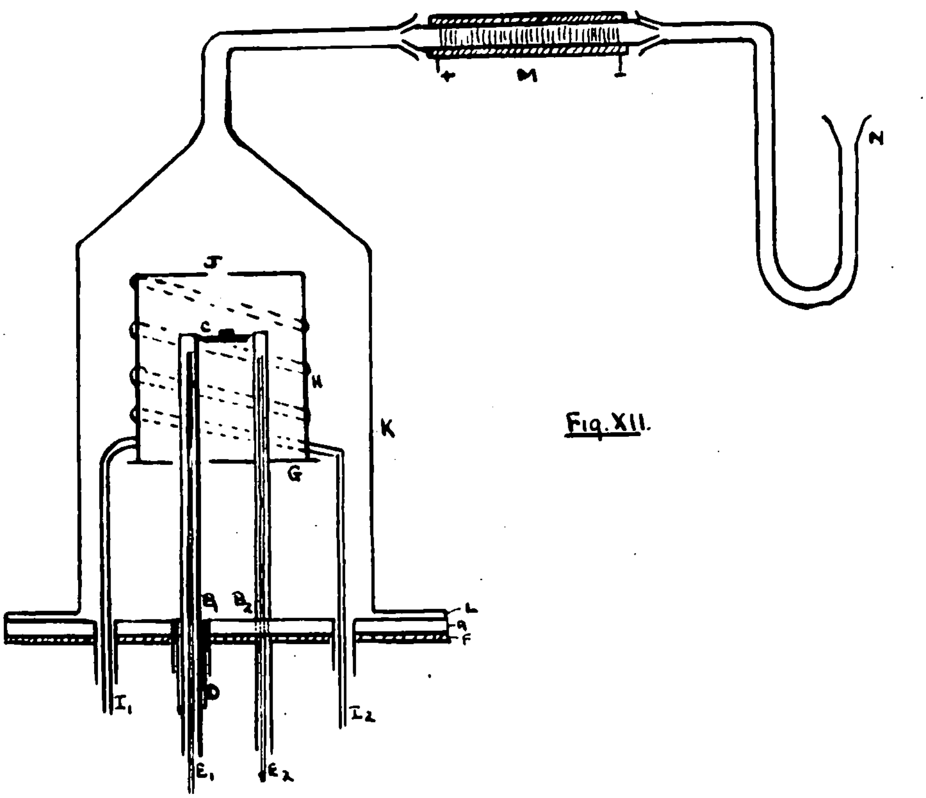


Fig. XII.

conversion to tritiobutane being carried out by reaction of the aqueous solution with n-butylmagnesium bromide. The method was found unsatisfactory however since no counter plateau could be obtained.

It was therefore decided to count the tritium as such i.e. convert the oxides into tritium and hydrogen and use alcohol as quenching agent (100).

Weighed quantities of the solution (about .05 gm) are sealed into thin walled glass phials. One such phial is placed horizontally in the container A Fig. XI. The whole apparatus in Fig. XI is maintained under vacuum.

After evacuating container A, the steel ball B is allowed to fall freely on to the phial containing the solution, breaking it and thus allowing the oxides to condense into vessel C which is cooled in liquid nitrogen.

Vessel C contains metallic sodium which has already been de-gassed under vacuum and vaporised on to the walls of the container.

When all the liquid has condensed in C, tap T is closed and the liquid nitrogen removed. This allows the vessel to warm up and reaction between sodium and water takes place, 20 to 30 minutes being allowed for completion of the reaction.

The mercury in the Toepler pump E is then fully raised to the limits defined by the ventil V_1 and the sinter S_1

and the mercury in the system G lowered. When the mercury in G has reached a sufficiently low level, alcohol vapour is able to escape from bulb H into the apparatus. With tap T_6 closed and T_5 and T_8 open, alcohol vapour to a pressure of 2 cms. is admitted into the counting tube F, the pressure being measured on the manometer M_2. The mercury in G is then fully raised.

When the reaction in vessel C is complete, U-tube D is immersed in liquid nitrogen, tap T_4 is closed and taps T, T_2 and T_3 opened. The hydrogen and tritium resulting from the reaction may now be transferred into the counting tube F by the action of the Toepler pump E. The total pressure in the counting tube indicated on manometer M_2 is usually about 10 cms.

Cylinder hydrogen may be admitted into the system through the sinter-mercury seal S_2 for those cases where insufficient hydrogen and tritium is released to achieve a total pressure of 10 cms, for the purpose of background calibration or for flushing out the counting tube to remove adsorbed tritium from the glass walls of the tube.

Once filled with the mixture of gases which is to be counted the gases are thoroughly mixed by lowering the mercury in the Toepler pump E to about half way down the bulb, allowing the gases to expand through the sinter S_1 and then fully raising the mercury again. This process is repeated twice or thrice so that good mixing is ensured. Tap T_8 may now be closed and the counting tube carefully removed from the apparatus. The tube is then re-assembled inside a lead castle as a normal Geiger counting tube and counting commenced.

The validity of the use of such a gas mixture for counting was verified when a plateau was obtained using inactive Hydrogen in the counter and an external ^{60}Co source. Backgrounds with inactive hydrogen were around 20 counts per mm.

When samples of the solution were examined in the manner described no counts above background were obtained. This indicates that either the quantities of tritium oxide are so diluted in the bulk solution as to be beyond detection or that the method of catalysis is inefficient.

Accepting the latter as the most probable reason for the low recovery of tritium another method of assaying was tried. In this the gases freed by solution of the steel are transferred into the Circulating System using electrolytic gas together with excess oxygen as carrier. Transfer of water into the Circulating System is prevented as described previously and the conversion of hydrogen in excess oxygen to water achieved using a heated palladium catalyst (see Appendix I). A blank experiment using gross quantities of electrolytic gas showed that this reaction was complete after 20 minutes circulation of the gases over the heated catalyst.

A storage vessel of the type shown in Fig (see Appendix I) is included in the Circulating System. This vessel contains the sodium which is previously de-gassed and throughout circulation is cooled in liquid nitrogen to prevent premature mixing of the sodium and water.

When circulation is completed the helium to be estimated, together with any excess oxygen remaining is removed from the Circulating System by Toepler action (see Appendix I), the water trap in the circulating system is allowed to warm up so that all the water condenses in the storage vessel containing sodium.

When condensation is complete, at least one hour being allowed for this process, the vessel may be removed from the apparatus by drawing off the constriction. The storage vessel may now be allowed to warm up and the reaction between water and sodium takes place. The vessel may now be connected to the apparatus shown in Fig Xl , taking the place of the container A. Breaking the septum of the storage vessel now by allowing the steel ball B (Fig. Xl) to fall freely on it releases the hydrogen and tritium into the apparatus so that it can be transferred into the counting tube under the action of the Toepler pump E.

Previous measurement of the amperage and time during the production of electrolytic gas for the transfer operations described above affords a means of calculating the total quantity of hydrogen available from the water produced. Measurement of the pressure of the hydrogen in the counter and a knowledge of the volume then leads to the fraction of the total gas taken in the counter. Thus the total tritium released from solution may then be calculated from the count obtained on any one sample.

The results found in this way gave values of tritium corresponding to values 4, 5 and 6 in Table X of

1.81×10^{-10} ccs ^{3}H. N.T.P.

1.80×10^{-9} ccs ^{3}H. N.T.P.

9.95×10^{-10} ccs ^{3}H. N.T.P.

Whence $\frac{He}{^{3}H}$ ratios are :- 7.26×10^{4} 3.98×10^{3} 5.42×10^{3}

It can be seen that these results show very poor agreement with each other. They also show a wide divergence from the predicted value (101) for this ratio which is about 3 : 1.

The quantities of tritium found then are considerably smaller than the amounts predicted by theory and a further search for tritium must be made.

It seems unlikely that an approach along the same or similar lines to those already described i.e. determining helium amd ^{3}H in one and the same sample will prove very useful. It was decided therefore to extract the tritium by fusion of a separate steel sample.

In this a furnace was constructed similar in design to that described by Alberman. The form of the furnace is shown in Fig. Xll.

It consists of a turned brass base-plate through which pass two copper tubes B_1,B_2, sealed at one end, which serve to carry the current to the heating element C. One of these tubes is insulated from the base-plate by using a pyrex glass sleeve (D) which seals to both the tube and the base-plate with Apiezon wax W.

The two electrodes B_1, B_2 are cooled by passing water through the two inner tubes of copper E_1, E_2. The base-plate itself is water-cooled through the copper tube F which is soldered to its under surface.

Situated about half-way down the two electrodes is a copper disc G which is soldered to one electrode and out of contact with the other. This serves as a radiation shield and prevents excessive transfer of heat to the base-plate.

The brass cylinder H rests on the copper disc G and is water cooled through the copper tubes I_1, I_2 which pass through the base-plate and are soldered to the outer surface of H in the form of a spiral. Cylinder H serves as a radiation shield also and prevents the outer envelope K of pyrex glass from becoming overheated. With the exception of the small observation hole J at the top, the radiation shield H plus the copper disc G on which it rests, completely surrounds the heating element C.

The outer casing K is of pyrex glass and is attached to the base-plate at the flanged joint L with Apiezon wax W.

The furnace is in immediate contact with a tube containing copper oxide which can be heated to red heat electrically. The whole unit then can be attached to the apparatus shown in FigXl at the standard ground joint N, taking the place of vessel A.

Several elements were used in the furnace in different experiments. In all the cases where tritium values are quoted the steel was observed to have melted or reacted with the element which should mean complete expulsion of any occluded gases including tritium.

In an actual experiment the furnace is thoroughly evacuated and observed to be leak-proof. Cylinder hydrogen is then admitted through S_2 to a known pressure (about 4 cms. of mercury) into the volume defined by S_1, T_6, and the counting tube F. Surplus hydrogen is pumped away and the known amount allowed to expand into the volume defined by T_7,T_5, V_1 and S_1. Tap T_4 is then closed and the small fraction of hydrogen enclosed between T_4, T_5 and V_1, is allowed to expand into the furnace by opening taps T_3 and T_2. Tap T_2 is then closed and the hydrogen remaining outside the initial volume transferred back into this volume by the action of the Toepler pump E.

The hydrogen so transferred into the furnace acts as a carrier for the tritium on its release from the steel.

With the water cooling circuits functioning correctly the current is applied to the element containing the steel sample. At the same time the copper oxide is heated to dull redness, whilst the U-tube D is cooled in liquid nitrogen so that the water will condense in D as it is formed.

On completion of the fusion, any uncondensable gases are pumped away and the copper oxide allowed to cool down. The remaining hydrogen enclosed in the counting tube is then allowed to expand over the copper oxide, which is then reheated. By circulating the hydrogen in and out over the copper oxide by the action of the Toepler pump E all the hydrogen is converted into water and condensed in D.

Tap T_2 is then closed and the reconversion of water and transfer of the resulting hydrogen to the counting tube F carried out in the manner described previously.

Since a known amount of hydrogen is taken initially, measurement of the final pressure of hydrogen regenerated should lead to the recovery yield of hydrogen in the experiment. In all cases where significant counts were obtained from the steel samples the recovery of hydrogen was more than 100%. In one other case where the steel did not fuse the recovery of hydrogen was 44%.

In this way three estimations of tritium in the steel were carried out. Since no simultaneous helium analyses are possible on the steel samples used, the amounts of tritium are related to the weight of steel taken, for comparison with previous helium values. For this purpose the helium content of the neighbouring piece of steel is taken (5.4×10^{-5} ccs. He/gm steel) as that of the steel used in the tritium estimations.

The ratios of helium to tritium found in this way were 75 : 1, 40 : 1, and 75 : 1, respectively.

In yet another method of estimation of the tritium a portion of the active steel (0.054 gms) was heated in the presence of chlorine gas until all had reacted. On completion of the heating the resulting tritium chloride and ferric chloride were dissolved in 2ml. of water saturated with sulphur dioxide. Aliquot portions of this solution are then sealed in thin glass phials as described previously. In this method, however, the regeneration of tritium is achieved by passing the oxide vapour from the solution repeatedly over zinc heated to about 400°C (103).

The counting procedure was then carried out as described previously. Since the total gas available from 2 ml. of water is known, the total tritium yielded by the steel could be calculated. In this experiment 8.35 cms. pressure of hydrogen plus tritium in the counter gave a count of 218 ± 5 per. min. This value gives a ratio of helium to tritium of about 44 : 1.

This method of recovery of tritium was repeated on another sample of steel taken from deeper in the block, situated approximately beneath samples 3 and 4 used for helium analyses. This time 1 ml. of sulphur dioxide - water was used to take up the chlorides formed. 0.0413 gms of steel were taken initially and no magnetic fragments were detected in the residue. Counting of the tritium regenerated from this solution gave a total count of 250 per min. on a sample of the gas contained in 23 ccs at a pressure of 7.8 cms of mercury. Calculations of the tritium content of the steel and comparison with the helium contents from samples 3 and 4 gave ratios of 23 : 1 and 43 : 1 respectively for the ratio of helium to tritium.

Interpretation of the Results

An examination of the activity of the aluminium block, which was also irradiated with the steel, shows that the activity varies with the distance from the surface. The above comparisons then of helium and tritium values related to unit weight of steel are of doubtful validity.

The ideal case would be to compare ^3H, ^3He and ^4He values in relation to the number of spallation events which have taken place in each piece of steel, producing radioactive vanadium etc. For this purpose the γ-activities of the solutions of steel are counted under standard conditions, and the values for ^3H and He related to the number of counts obtained from the solution. Figure XIII shows diagramatically

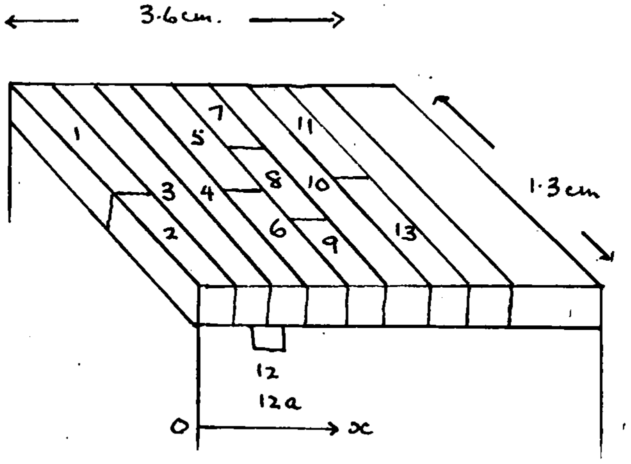


Fig. XIII. Sampling of Steel Block.

the relative positions from which each sample is taken (no account being taken of the width of the saw-cut). The numbering of the samples in Fig. XIII coincides with the numbering given in Table XI which shows the results of the various analyses.

TABLE XI

No	Gms. Steel	He×10^6 ccs.	He×10^5 ccs/gm	$\frac{^3He}{^4He}$%	Cts. on Soln.	^3H×10^6 ccs/gm	^3H meth.	p(gas)	e.p.m.	ox (mm)
1	0.0186		1.37							0-1
2	0.0471		1.30							0-1
3	0.524	1.35	2.58	5.68	40,500					2-10
4	0.270	1.314	4.87	5.64	40,000					11-17
5	0.1346	0.721	5.36	3.2	21,700					18-24
6	0.0992	0.538	5.43	3.22	13,850					18-24
7	0.0326					0.653	fus.			25-27
8	0.0523					0.333	"			25-27
9	0.0325					0.333	"			25-27
10	-					-	Br$_2$ fld			28-30
11	0.054					0.705	Cl$_2$	8.35	218	31-33
12	0.041					0.560	Cl$_2$	7.8	250	
12a	0.045				2,320					31-33
13	0.067				8,568					

For the purposes of comparison ^3H and ^3He values are now related to the counts from the respective solutions in the following manner:-

1. For sample 13.

Counts on solution/gm. of steel = 127,700.

For sample 11.

Tritium in ccs/gm. of steel = 0.705×10^{-6}

Comparison of samples 11 and 13 (see Fig. XIII) is considered valid in view of the correspondence of helium contents in ccs/gm of samples 5 and 6 which are similarly oriented . Thus,

$$\text{ccs. tritium/count on solution} = \frac{0.705 \times 10^{-6}}{127{,}700}$$

Now compare this with the ^3He in sample 5.

Thus, total He in sample 5 = 0.721×10^{-5} ccs

$$\frac{^3He}{^4He} = 3.2\%$$

$$\text{Therefore } ^3He \text{ from sample } 5 = \frac{3.2 \times 0.721 \times 10^{-5}}{103.2}$$

Total counts from this steel solution = 21,700.

$$\text{Therefore ccs } ^3He\text{/count on solution} = \frac{3.2 \times 0.721 \times 10^{-5}}{103.2 \times 21{,}700.}$$

$$\text{Thus, } \frac{^3H\text{ccs}}{^3He\text{ ccs}} = \frac{0.705 \times 10^{-6} \times 103.2 \times 21{,}700}{127{,}700 \times 3.2 \times 0.721 \times 10^{-5}}$$

$$= 0.53.$$

$$\text{Or, } \frac{^3H \text{ atoms}}{^3He \text{ atoms}} = \frac{1.06}{1}$$

Similarly, comparison with the ^3He content of sample 6 gives a ratio $\frac{^3H \text{ atoms}}{^3He \text{ atoms}} = 0.915.$

2. In the same manner, values for the tritium from sample 12 and the counts from the solution of sample 12a are compared with the respective helium values and counts on solutions for samples 3 and 4. The ratios given are, respectively:-

$$\frac{{}^{3}\text{H atoms}}{{}^{3}\text{He atoms}} = 1.18 \text{ (for sample 3)}$$

$$= 1.23 \text{ (for sample 4).}$$

Comparison with the Predictions of Le Couteur on the Number of Particles Produced in Spallation

Direct comparison of the results obtained above with the predictions of the evaporation theory is somewhat obscured by the fact that the excitation energies of the various nucleii which undergo spallation is not known. Although the energy of the incident protons is quoted as 340 Mev, this is probably not the same as the excitation energy of the nucleii.

It is possible, for example, that on collision with a nucleus the proton may leave only a fraction of its energy for evaporation of the nucleus. In addition mesons may be created, a process which requires energies of the order of 200 Mev, so that the energy available for evaporation is much less than 340 Mev.

A further basis for comparison is thus required. This is at hand in that the yields of the heavier spallation products in iron are known for interaction with 340 Mev protons. (104).

TABLE XII

	Product		σ m-barns	ΔA	U.Mev	^{3}He/star	^{3}H/star	α/star
I.	^{57}Co		20					
	^{55}Fe		41	2	26			
	^{53}Mn		43	4	55			.13
	^{51}Cr		41	6	83			.35
	^{49}V		31	8	110	.04	.09	.54
	^{47}Ti		21	10	136	.06	.16	.70
	^{45}Sc		15	12	164	.08	.24	.84
	^{43}Ca		9	14	188	.11	.29	.96
	^{41}K		3	16	216	.15	.40	1.10
II.	^{56}Co	^{56}Fe	0.24	1	13			
	^{54}Fe	^{54}Mn	12	3	41			
	^{52}Mn	^{52}Cr	12.9	5	68			.25
	^{50}Cr	^{50}V	13	7	96	.02	.04	.42
	^{48}V	^{48}Ti	10.3	9	123	.05	.13	.62
	^{46}Ti	^{46}Sc	6	11	150	.07	.20	.76
	^{44}Sc	^{44}Ca	2.6	13	175	.10	.27	.90
	^{42}Ca	^{42}K	0.7	15	203	.13	.36	1.04
	^{40}K	^{40}A	0.3	17	230	.16	.44	1.17

Thus, from Le Couteur's relationships for relative yields at various excitation energies one can calculate the number of units of mass lost in spallation at any required energy (105). From the known isotopes produced in spallation of iron one can calculate for each one, the number of mass units lost for its particular spallation (see Table XII) and hence from Fig. XIV the excitation energy. Having found the excitation energy for each process one then arrives at the predicted ratios of the ^{4}He, ^{3}He and ^{3}H atoms produced, again from Fig XIV. The various values for the yields are then weighted according to the cross section for the particular processes by which they arise.

Summation of these weighted yields of ^{4}He, ^{3}He and ^{3}H for all the spallation reactions up to a mass loss of 16 mass units (A) is carried out (Table XIII). This should then form a basis on which to compare the present experimental results with Le Couteur's predictions.

The predicted ratios together with experimental values are shown in Table XIV.

TABLE XIV

Predicted Ratio		Experimental Ratio
$\frac{^3\text{He}}{^4\text{He}}$	0.068	0.0568, 0.0564, 0.032, 0.0322.
$\frac{^3\text{H}}{^4\text{He}}$	0.178	0.085, 0.088, 0.042, 0.036.
$\frac{^3\text{H}}{^3\text{He}}$	2.62	1.49, 1.56, 1.32, 1.12.

predicted and experimental values which are compared above, little can be said as to the validity of the evaporation theory of Le Couteur. The various values however may be said to conform qualitatively with Le Couteur's predictions and in that sense support the validity of the evaporation theory.

No further light is thrown on the question of helium production in meteorites by cosmic ray interaction with the constituents of the meteorites except in so far as Le Couteur's theory of nuclear evaporation is qualitatively confirmed at low excitation energies.

Exact agreement with Le Couteur's predictions could not be expected for his calculations have been made for heavier nucleii viz. silver and bromine. In the iron case the products will be different for the Coulomb barrier for ^{3}H, ^{3}He, and ^{4}He will have altered. Furthermore, Le Couteur's calculations and predictions are based on processes of higher energy producing 7 to 14 "prongs" per "star" and it is doubtful if his yield curves can be extrapolated to lower energies.

- - 0 - -

APPENDIX I

The Apparatus

The Preparation of Helium-free Oxygen

Helium-free oxygen is prepared (108) and stored in a suitable reservoir. Fig. XV.

A source of impure oxygen from a cylinder is attached to the reservoir and so adjusted so that oxygen bubbles past the mercury in manometer M_1 with tap T_2 closed. This flushes any air out of the dead space up to tap T_2.

Then, the reservoir having been previously evacuated through tap T_1 and the charcoal C_2 heated to about 250°C for at least 1 hour, tap T_2 is opened so that oxygen can now enter the reservoir and bubble past the mercury in manometer M_2 for a short while. Tap T_2 is then closed and the oxygen supply removed.

Then, with tap T_3 open, bulb C_1 is immersed in liquid nitrogen. Oxygen then liquifies in C_1 to a residual pressure of about 15-16 cms. mercury whilst the rare gases present will still be in the gaseous state. Tap T_3 is then closed and the remaining oxygen taken up on the charcoal in C_2 by immersion in liquid nitrogen. When the residual pressure reaches a value of about 3-4 mm. mercury tap T_1 is opened and the remaining gases pumped away. Pumping is continued for about 10 minutes, the oxygen

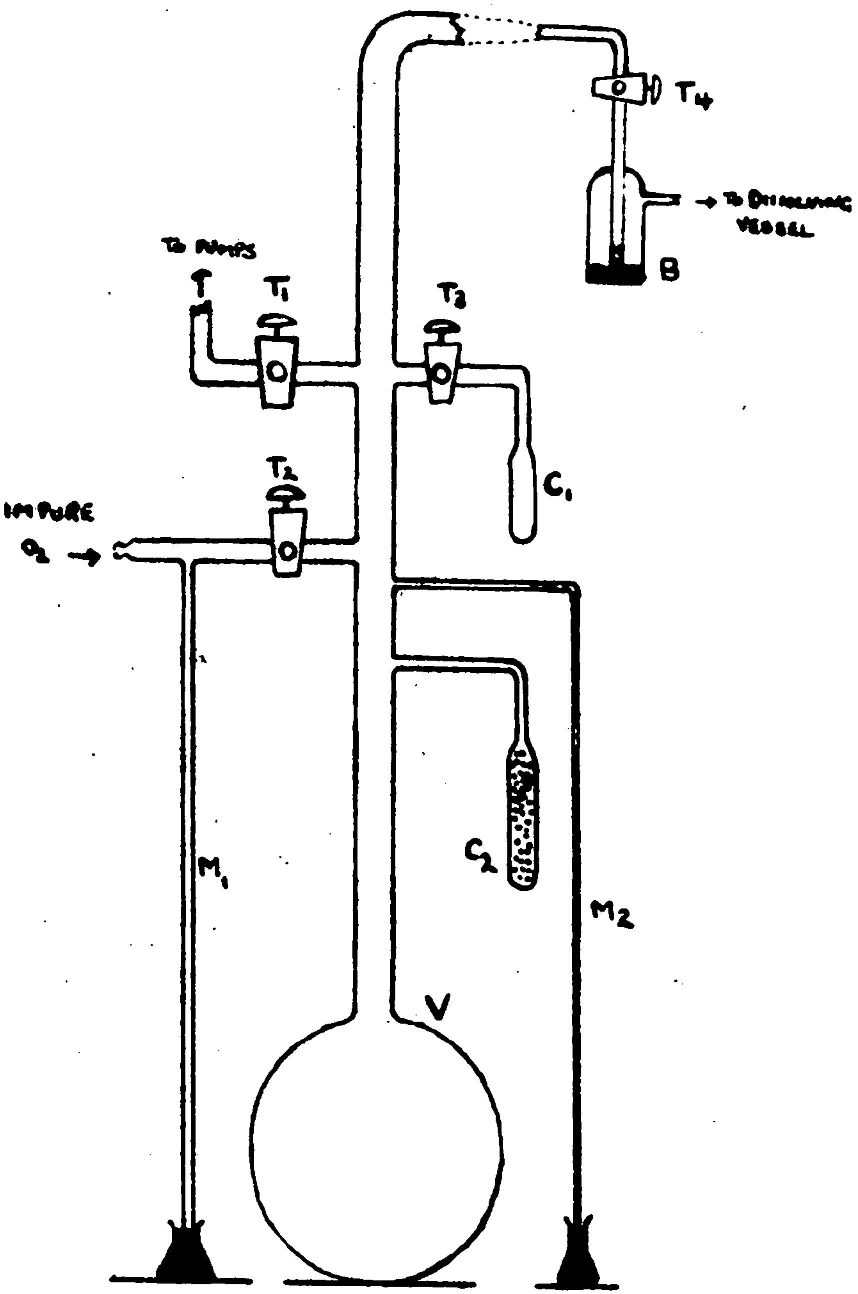

TO PUMPS
T
T1
T3
T2
IMPURE O2 →
C1
C2
M1
M2
V
T4
B
→ TO DISSOLVING VESSEL

FIG. XVI

remaining quantitatively on the charcoal C_2 and the rare gases, being much less strongly adsorbed, are removed.

Tap T_1 is then closed and the liquid N_2 removed from C_2 so that the oxygen is desorbed and expands into the reservoir. Tap T_3 may now be opened and the liquid nitrogen removed from C_1 so that all the oxygen returns to the gaseous state.

The above process is carried out six times in all and a blank determination carried out on the oxygen using an amount somewhat in excess of that used in a normal experiment on an unknown, to test its purity with respect to helium. If necessary the process is repeated until satisfactory blanks are obtained.

Dissolving Vessel

Since each particular case requires its own method of approach with regard to the liberation of the gases to be examined, it would be as well to leave discussion of the dissolving vessels used as the particular cases arise.

The Circulating System

The gases released in the dissolving vessel are transferred into the Circulating System (FigXVI) in the following way.

The Circulating System is first thoroughly evacuated through taps T_1 and T_2 with the mercury in ventils V_1 and V_2 lowered and the charcoal in C heated to 250-300°C under vacuum. Ventil V_2 is then fully raised and both taps

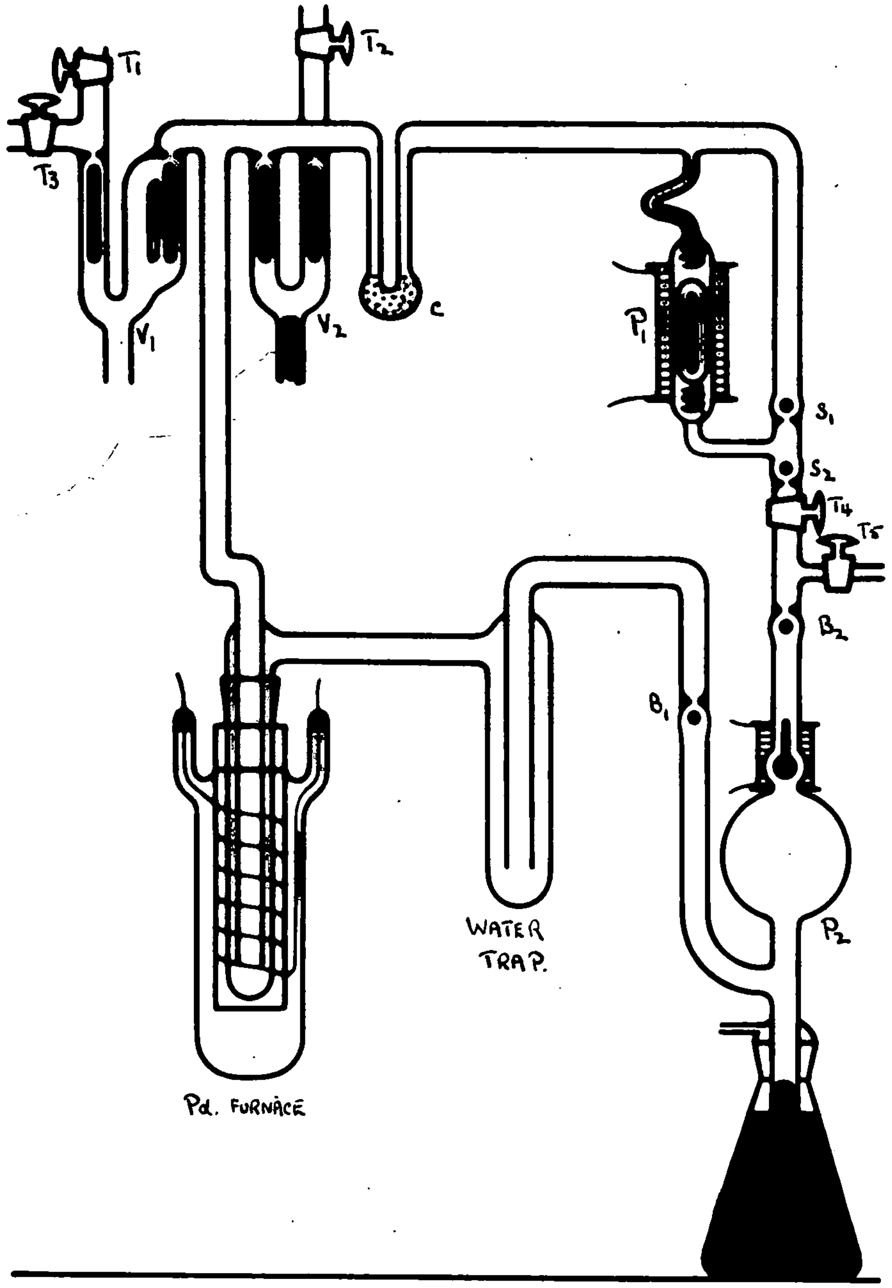


Fig XVI.

b.

to vacuum closed. Charcoal C may now be immersed in liquid nitrogen and about five minutes allowed for temperature equilibration. Meanwhile the mercury in ventil V_1 is raised to a convenient level such that with a small pressure of oxygen on the one side, the gas may bubble past the mercury on to the cooled charcoal and seal off when the bubbling ceases.

Oxygen is then admitted into the dissolving vessel to a pressure of approximately 1 cm. of mercury. The dissolving vessel connects to the circulating system through tap T_3. If this tap T_3 is now quickly opened, oxygen will bubble past the mercury in ventil V_1 to be immediately taken up on the cooled charcoal in C. Thus the pressure in the circulating system is always substantially zero, and the process may be repeated several times if necessary.

When the bubbling ceases or, if the dissolving medium has an appreciable vapour pressure, after the initial rush of gas has ceased, tap T_3 is closed and a further similar amount of oxygen from the reservoir admitted to the dissolving vessel. The process is then repeated.

It has been shown with an identical system that 100% transfer is achieved in six such operations (107) and confirmed in this work. In order to completely eliminate uncertainty, the above process is usually repeated eight times for each transfer.

On completion of a transfer the mercury in ventil V1 is fully raised and the liquid nitrogen removed from around charcoal C so that the oxygen is released into the circulating system. The pressure of oxygen present in the circulating system at this stage is generally from 2 to 4 cms of mercury. Larger pressures of oxygen than 4 cms become fairly difficult to handle in transference of the gas from the circulating system to the next stage of the analysis, i.e. the fractionating column.

Before transferring the gases into the fractionating column, it is essential to remove traces of hydrogen which are often generated in the dissolution process if not actually present in the gases contained in the material under examination. Since hydrogen follows helium and neon in order of adsorbability on charcoal (108), it is possible that traces may affect the neon value obtained if not the helium value. (It is always advisable to look for neon even in a helium estimation in order to ensure that there has been no leakage of air into the vacuum system during the course of the estimation).

The removal of hydrogen is effected by circulation of the gases over a heated palladium wire which catalyses the formation of water by reaction of the hydrogen with the excess oxygen present. The palladium furnace is shown diagrammatically in Fig.XVI . It consists of an inner tube around which the palladium wire is coiled, enclosed in an outer casing containing a standard ground glass joint. This standard joint provides means of attachment to a further outer casing of pyrex glass which contains the heating element of the furnace. The heating element consists of 'nichrome' tape wound on a former which constitutes the outer casing to the system already described. It is vacuum jacketed to minimise heat transfer to internal seals in the glass and thus reduce the risks of fracture. As a further precaution, the whole furnace is immersed in a water bath.

The heating element is fed from the 24 volts D.C. supply with a current of 1 - 2 amps and in operation is run at a dull red heat. Under these conditions it is found that with adequate circulation the hydrogen is completely removed in about 20 minutes.

Circulation is achieved by the use of the simple pump P_1 (Fig.XVI). This consists of a solenoid, sealed in a glass envelope, which moves up and down under the influence of an interrupted magnetic field i.e. with current flowing through the coil the solenoid is lifted, falls again when the circuit is broken and is raised once more when the circuit is remade. The glass envelope containing the solenoid is made as good a fit as possible to the tube in which it moves in order that circulation shall be as efficient as possible. Two small wire springs are fitted in this tube at the limits of travel of the solenoid to protect it from undue shock and thereby reduce the risk of a fracture.

Thus, as water is formed in the palladium furnace it tends to move towards the trap, immersed in liquid nitrogen, situated between the furnace and the Toepler pump P_2 and is retained there.

On completion of the circulation, the gases are transferred into the next section of the apparatus, the fractionating column, by means of the Toepler pump, P_2. In this, tap T_4 is closed and the mercury in the pump raised so that the bulb of the pump, full of gas, is cut off from the rest of the circulating system. Tap T_5, which provides communication between the circulating system and the column, may now be opened. It is as well in these initial strokes of the Toepler pump to exercise caution and not transfer the gases too quickly. Although the main constituent of the gases is oxygen and they are being transferred on to charcoal cooled in liquid nitrogen, it may be that if the transfer is carried out too quickly a pressure may build up in this section of the column sufficient to force down the mercury which separates the first charcoal unit from the second. Apart from a grave risk of damaging the column, escape of a fraction of the gas on to the second charcoal unit at this stage would make it difficult to assess a neon estimation since here charcoal unit No. 2 is allowed to warm up to room temperature to expediate transfer of the gas.

Having partially raised the mercury in the Toepler pump and opened Tap T_5, the mercury may now be raised further, until it lifts the weighted ground glass seal situated just above the bulb of the pump. On lowering the mercury quickly, the glass seal, being weighted, becomes seated before all the mercury has flowed past it. Mercury is thus trapped here and hence forms a useful non-return valve. When the mercury is fully lowered, gas from the rest of the circulating system expands into the vacuum thus created in the bulb and the process may be repeated.

It often happens that on the subsequent upward strokes a small bubble of gas may become trapped in the mercury at the seal, so that on lowering the mercury it escapes back into the circulating system and leads to inefficient transfer. However, once the mercury has been partially raised and the rest of the system separated from the bulb, the glass seal may be raised so that the mercury trapped there flows into the body of the mercury below and the risk of trapping a bubble there is eliminated. Raising of the glass seal is achieved by making the weight contained within it of iron and using a magnet to lift this.

In practice it is found that 10 strokes of the Toepler pump are required to effect complete transfer from the circulating system to the column, but here again the operations are carried to excess in order to eliminate uncertainty. In fact 20 strokes are generally made.

Having completed the required number of strokes and effected the transfer, the mercury in the Toepler pump is fully raised to the limit allowed by the two steel ball valves B_1, B_2. Thus the dead space over charcoal No.1. is constant and fixed by the steel ball valve B_2 supported by mercury and the tap T_4. It is essential that this dead space remain constant otherwise, as will be seen later, the characteristics of the column with regard to separation of helium and neon will change. It is also advantageous to make this dead space as small as possible.

The Fractionating Column

The fractionating column (Fig. XVII consists essentially of 15 charcoal units containing 0.8 to 0.9 gms. of steam activated coconut charcoal in each. Each unit is connected to a bulb of about 20-25 ccs. capacity, the bulbs being connected to a common mercury reservoir.

Each unit is connected to the next unit in the series via another bulb of similar dimensions to the first and these bulbs too connect to a common mercury reservoir. Thus, the level of the mercury in the two series of bulbs can be raised or lowered independently.

The whole column may be evacuated through Tap T_2 (Fig. XVII) and before each estimation the charcoal units are thoroughly outgassed by heating to 250-300°C for about a half an hour, under the action of the pumps.

Operation of the Column.

Whilst circulation of the gases in the circulating system is in progress tap T_1 connecting the two sections

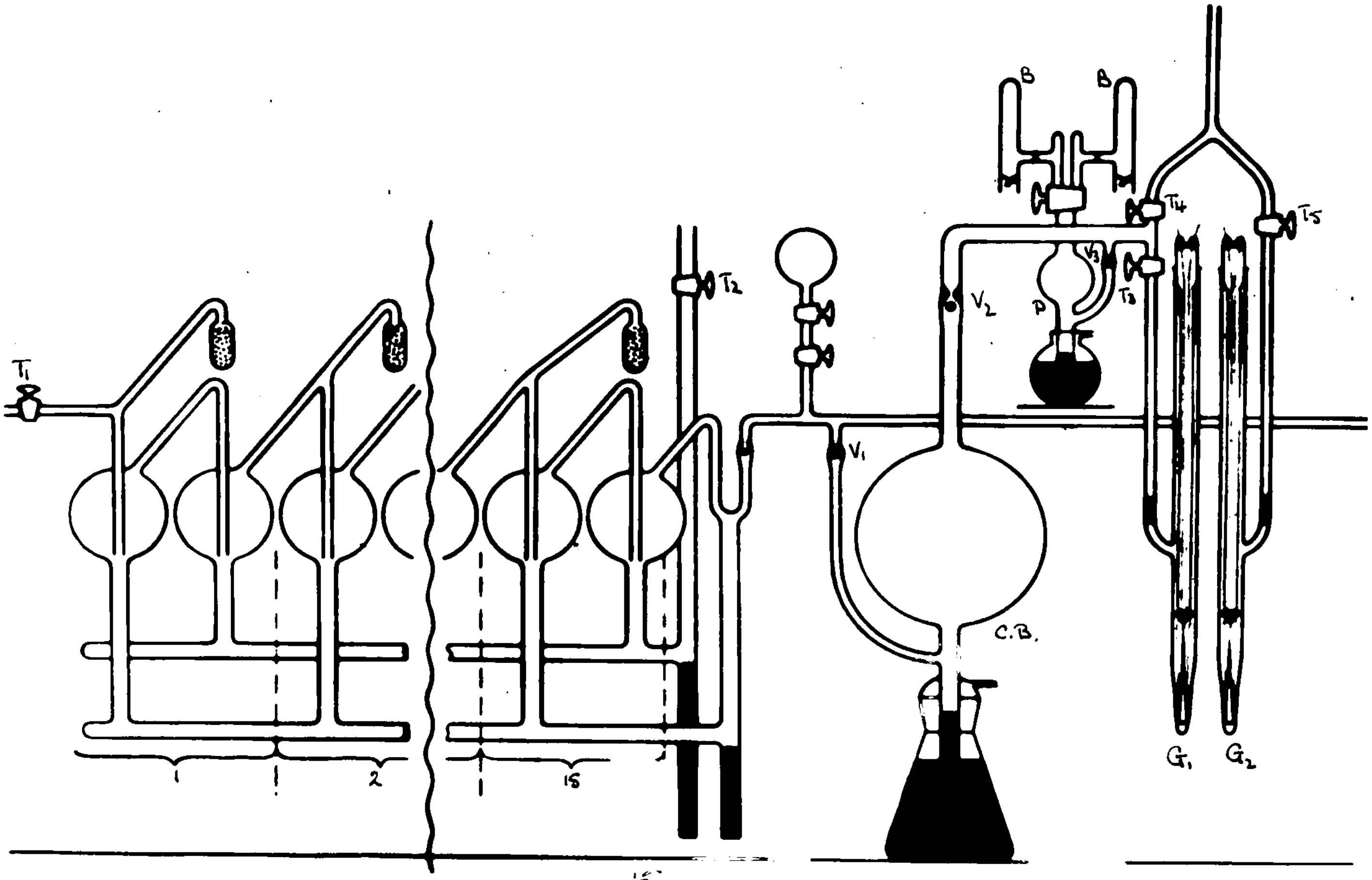


Fig. XVII

of the apparatus in question is closed. Before transference of the gases to the column commences the mercury levels in both series of bulbs are raised so that all bulbs are filled with mercury and about 5 mm. of the vertical connecting tubes. Thus each unit is separated from the next. The height to which the mercury is raised in the bulbs at this stage is made during construction of the apparatus, the maximum height to which the mercury can reach. This avoids the possibility of mercury being pushed from one bulb into the next during operation of the column and the chance of an inter-connecting tube being thereby blocked.

Having separated the units in this way, each unit is now cooled in liquid nitrogen, the units being so arranged that three or four may be accommodated in one Dewer flask. Five or ten minutes are usually allowed for temperature equilibration. Tap T_1 may now be opened and transfer of the gases to the column, as described in the preceding section, commenced. Examination of Fig. XVII. will show that the gases transferred under the conditions described will all be accommodated on charcoal unit No.1. Oxygen, which is the main constituent of the gases, will be retained throughout the subsequent operations on charcoal unit No.1., provided this is at all times immersed in liquid nitrogen. Since the pressure of oxygen in the circulating system is approximately 2 - 4 cms. usually, it can be seen that this amount of gas confined in the small dead space over charcoal unit No.1 would generate a pressure sufficient to allow it to escape violently from unit No.1. This could cause serious damage to the column and so unit No.1 is never allowed to warm up at all until the mercury has been lowered in both series of bulbs and the column connected to the pumping system.

Since the inter-connecting tubes between the bulbs are of quite narrow bore, it can also be seen why it is essential to retain water vapour in the circulating system. Any appreciable quantity of water would freeze in the tube above charcoal No.1., blocking it and thereby preventing further transfer of the gases from unit to unit.

On completion of the transfer procedure as previously described, five minutes are allowed for equilibration of the oxygen on the cooled charcoal before starting the fractionation of the gases, which is the next stage of the process. Fractionation of the gases involves transfer of the gases from the dead space in one unit into the next unit and the collection of the fractions at the end of the operation.

Transfer of the gases from unit to unit is carried out in the following way:-

The mercury in the first series of bulbs i.e. those in direct contact with the charcoals is lowered to a level about 1 cm. below the bottom of each bulb so that the gas in the dead spaces expands into the respective bulbs.

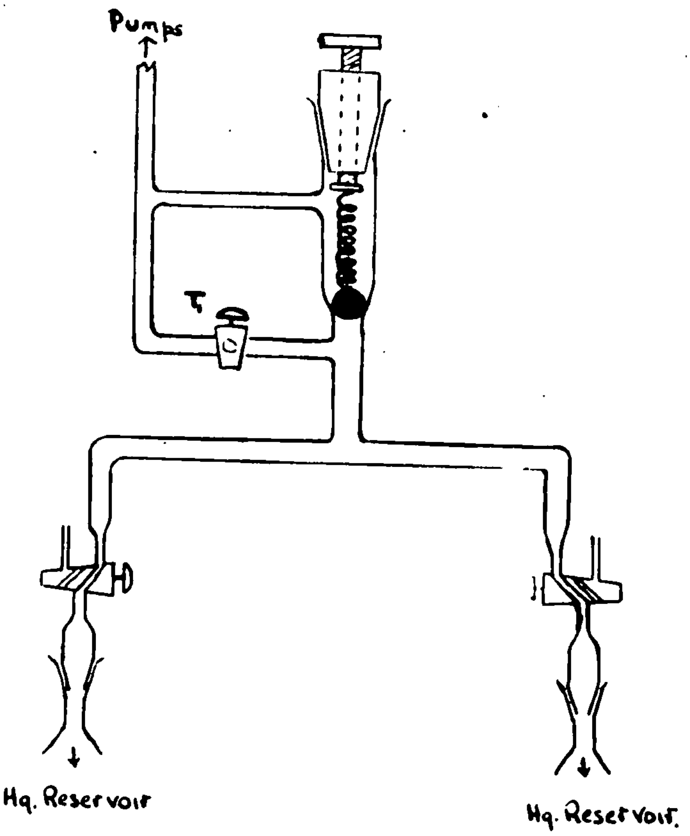


Fig. XVIII

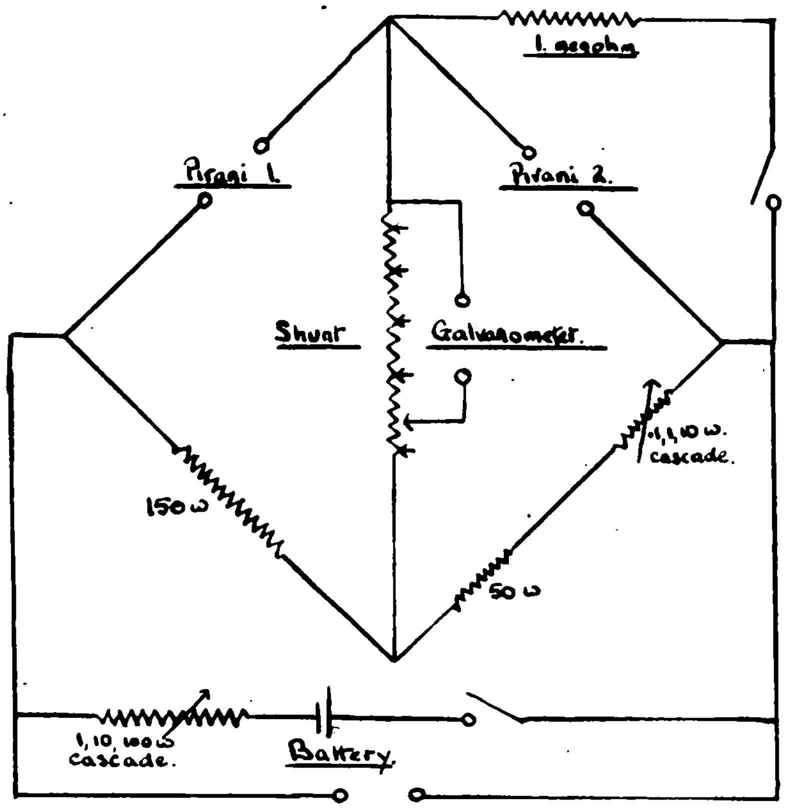


Fig. XXIIIa

The level to which the mercury falls is limited by an adjustable spring-loaded ball valve (Fig.XVIII). The mercury may be fully lowered when required by connecting the reservoirs directly to the secondary vacuum system through tap T_1 (Fig.XVIII).

On raising the mercury again to its previous height the gas in each bulb is compressed into the side arm which connects it to its opposite number in the second series of bulbs. Repetition of these operations with the mercury in the second series of bulbs then transfers the gas into the next charcoal unit. Transfer from one unit to the next unit is called one operation and it can be seen that in any one operation transfer from unit No.1 to unit No.2 occurs simultaneously with transfer from unit No.2 to unit No. 3 or unit No.14 to unit No.15. Since all the gas fractionated starts on unit No.1 it can be seen that 14 operations are required before the first fraction reaches the last charcoal unit, No.15. The 15th operation transfers the first fraction into the dead space which precedes the collecting vessel, the so-called 'Compression Bulb' and the 16th operation transfers it into the compression bulb. Thus operations 1 to 15 should yield no gas provided the column has been adequately evacuated before the experiment and no leakage has occurred into the compression bulb. Measurement of the gas collected during operations 1 to 15 therefore serves as a check for such irregularities.

Considering the relative adsorbabilities of gases least adsorbed on charcoal at the temperature of liquid nitrogen, helium should predominate in the earlier fractions, closely followed by neon and then much later by hydrogen and nitrogen. In order to use such a system to separate and measure quantities of helium and neon, one needs to know at which stage in the fractionation procedure corresponds to the most efficient separation of helium and neon or alternatively which stage corresponds to 100% helium in the absence of neon. This is found by calibration of the column using a sample of laboratory air. Since only relative values are required at this stage, the exact amount of air used for this calibration is not very important. Air to a pressure of about 1 cm. mercury is admitted into the circulating system and the mercury in the Toepler pump raised to transfer part of it on to charcoal unit No.1., this being cooled in liquid nitrogen. This provides an amount of air adequate for the calibration.

Operations 1 to 15 are now carried out, the gas yield measured and the experiment continued if satisfactory. Each subsequent operation is now carried out separately and the gas yield measured. The results are recorded graphically as a plot of gas yield (or galvanometer deflection) versus operation number.

It has been shown by other workers using a similar system and also by calculation (109), that the amounts of helium collected on successive operations should be initially small rising to a fairly sharp maximum and then falling again to a minimum. The minimum attained is dependent in this case on the stage in the procedure at which neon begins to contaminate the helium fractions.

Consider any single gas in a mixture of gases in contact with the charcoal units at the temperature of liquid nitrogen. Let a fraction 'a' of this gas be adsorbed on the solid phase at each stage of the fractionation so that a fraction (1-a) remains in the volume phase. Constant fractions are assumed to be adsorbed at each stage. Since in each case the volume dead space in each unit, with the exception of unit No.1, the amount of charcoal in each unit, and the temperature are the same for all units, this is not an unreasonable assumption.

Thus, with each operation a fraction (1-a) of the gas will be transferred from one unit to the next and there redistribute itself between a solid phase and a volume phase. The gas remaining in the solid phase after such a transfer will also come to a new equilibrium between solid and volume phases.

Starting with unit amount of gas then on the first charcoal unit, a fraction 'a' is adsorbed on the solid phase and (1-a) remains in the volume phase. In the first operation 1-a passes into unit No.2, where a(1-a) will be taken up in the adsorbed phase and $(1-a)^2$ remains in the volume phase. Of the fraction 'a' left in unit No.1, a x a (i.e. a^2) will form the new adsorbed phase whilst a(1-a) will remain in the volume phase to be passed on to unit No.2 in the next operation. Thus after two operations the fraction of the original gas in unit No.2 will be 2a(1-a) i.e. a(1-a) remaining adsorbed on the charcoal plus a(1-a) being passed on from unit No.1. The whole process up to the first 6 or 7 operations is shown in Table XV .

Operation Number	UNIT No. 1		2		3		4	
	Solid	Volume	Solid	Volume	Solid	Volume	Solid	Volume
1	a	(1-a)						
2	a^2	a(1-a)	a(1-a)	$(1-a)^2$				
3	a^3	$a^2(1-a)$	$2a^2(1-a)$	$2a(1-a)^2$	$a(1-a)^2$	$(1-a)^3$		
4	a^4	$a^3(1-a)$	$3a^3(1-a)$	$3a^2(1-a)^2$	$3a^2(1-a)^2$	$3a(1-a)^3$	$a(1-a)^3$	$(1-a)^4$
5	a^5	$a^4(1-a)$	$4a^4(1-a)$	$4a^3(1-a)^2$	$6a^3(1-a)^2$	$6a^2(1-a)^3$	$4a^2(1-a)^3$	$4a(1-a)^4$
6						$10a^3(1-a)^3$	$10a^3(1-a)^3$	$10a^2(1-a)^4$
7								$20a^3(1-a)^4$

Taking unit No.4 as a typical case the total gas reaching the volume phase is:-

$$(1-a)^4 + 4a(1-a)^4 + 10a^2(1-a)^4 + 20a^3(1-a)^4 + \ldots\ldots$$

This can be represented in series form thus,

$$(1-a)^4 + {}^4_1Ca(1-a)^4 + {}^5_2Ca^2(1-a)^4 + {}^6_3Ca^3(1-a)^4 + \ldots\ldots$$

Where ${}^n_rC = \frac{n!}{r!\,(n-r)!}$

Thus for the Nth unit the amount of gas passing through the volume phase will be:-

$$(1-a)^N + {}^{N}_{1}Ca(1-a)^N + {}^{N+1}_{2}Ca^2(1-a)^N + \ldots\ldots\ldots\ldots \text{etc}$$

Where $(1-a)^N$ represents the gas resulting from operation No.1.

${}^{N}_{1}Ca\ (1-a)^N$ represents the gas resulting from operation No.2.

and so on.....

The total gas which has passed through the Nth unit then after m operations will be:-

$$(1-a)^N + {}^{N}_{1}Ca(1-a)^N + {}^{N+1}_{2}Ca^2(1-a)^N + \ldots + {}^{N+m-2}_{m-1}Ca^{m-1}(1-a)^N$$

and the amount of gas corresponding to the mth operation will be,

$${}^{N+m-2}_{m-1}C\ a^{m-1}\ (1-a)^N$$

Thus the ratio of the amounts of gas resulting from two successive operations m and m+1 will be:-

$$\frac{\Delta m+1}{\Delta m} = \frac{{}^{N+m-1}_{m}C\ a^m\ (1-a)^N}{{}^{N+m-2}_{m-1}Ca^{m-1}\ (1-a)^N}$$

$$= \frac{a(N+m-1)!\ (m-1)!(N-1)!}{m!(N-1)!\ (N+m-2)!}$$

$$= \frac{a(N+m-1)}{m}$$

$$a = \frac{\Delta m+1}{\Delta\ m} \qquad \frac{m}{(N+m-1)}$$

In this system, as already pointed out the first fraction of helium collected is from operation No.16 i.e. m=1 corresponds to operation 16, and N = 15.

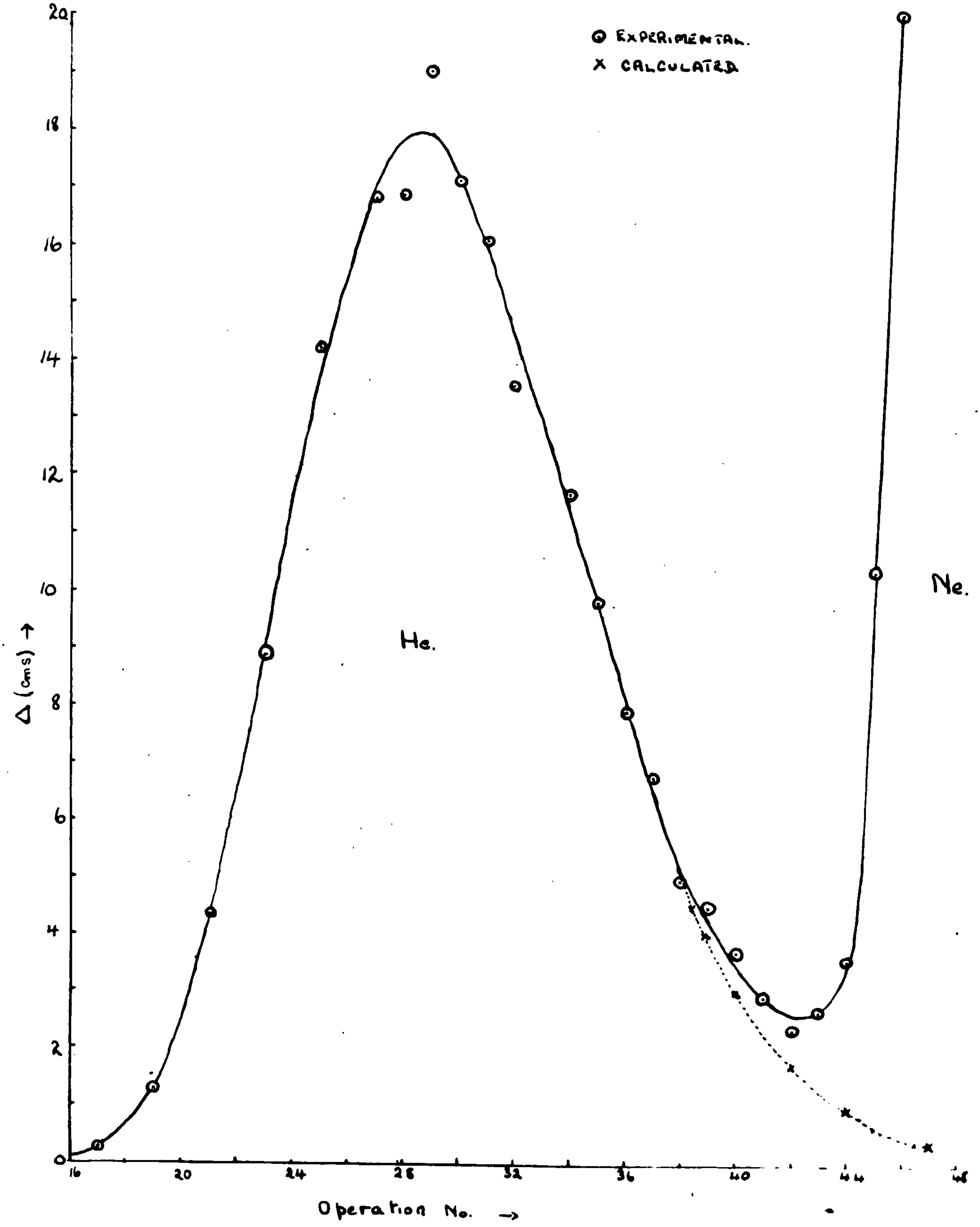
Thus $$a = \frac{\Delta 17}{\Delta 16} \times \frac{1}{15}$$

$$a = \frac{\Delta 18}{\Delta 17} \times \frac{2}{16}$$ and so on...

Since in the form of measurement of the gas used here the amount of gas is directly proportional to the galvanometer deflection, the latter may be used directly to reach a value for 'a'.

It should be pointed out that since the dead space connected with charcoal No.1 is not approximately the same as in the rest of the units, the first few values are not used in calculating 'a'. Other values are used however up to a point well in advance of the stage where neon begins to fractionate and an average value for 'a' calculated.

Using the value of 'a' thus found it is now possible to calculate the theoretical amounts of helium being fractionated in the later stages where neon also comes through and by difference of this amount from the amonnt indicated by measurement, the corresponding amount of neon. It is then a simple matter to calculate at what stage the amount of neon coming through exactly balances the deficiency of helium which is yet to come.



O EXPERIMENTAL.
X CALCULATED
He.
Ne.
Δ (cms) →
Operation No. →
0
2
4
6
8
10
12
14
16
18
20
16
20
24
28
32
36
40
44
48

Fig. XIX.

The experimental curve obtained in this calibration is shown in Fig. XIX and the results give a value for 'a' of 0.48. The theoretical curve calculated on the basis of this value for 'a' is shown as a broken line in Fig. XIX. For an air sample where neon is present, it is calculated that the total deflection obtained up to operation No.42 will give a helium value 0.7% low and the corresponding figure up to operation No.43 will be 0.5% high. Further, for cases where neon is absent, it is shown that 99.5% of the total helium is obtained if operations are taken up to No.44.

It is also to be noted that in the first instance the theoretically ideal amount of charcoal was used in each unit calculated from the value for 'a' quoted by Glückauf. This however did not give a satisfactory separation. The helium yield per operation increased to a maximum as anticipated but thereafter decreased extremely slowly. This indicated that either the separation of helium and neon was inefficient due to inactive or insufficient charcoal or there was a constant leak occurring into unit No.1. The latter was ruled out by rough calculation of the total deflection expected and comparison with that actually obtained.

Since the past history of the charcoal used was not known and also because the appearance of a white sublimate on the glass tube above each charcoal unit was observed, it was decided to attempt to reactivate the charcoal. This was to be done by allowing the charcoals to take up air at the

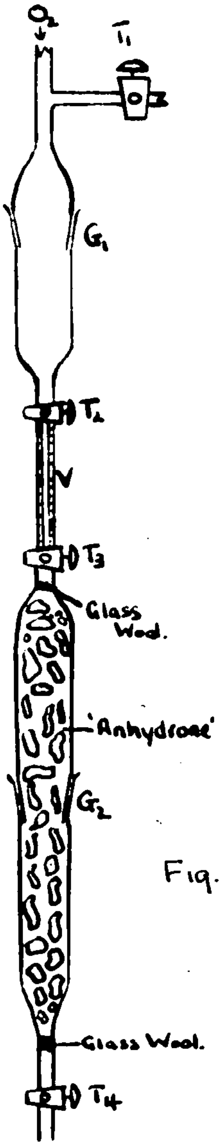


Fig. XX.

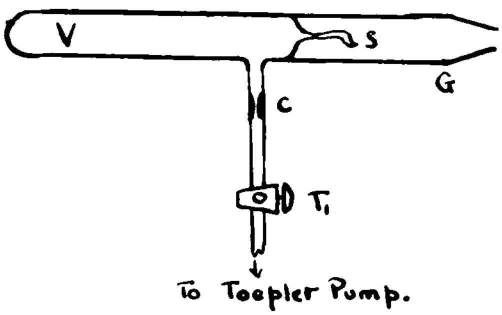


Fig. XXI.

temperature of liquid nitrogen and purging under vacuum at 250 - 300°C. However on carrying out this procedure six times, no improvement in the behaviour of the charcoals was evident. It was decided, therefore, to change the charcoals in the units and this time to use rather more than was used previously, i.e. about 0.9gms/unit. An unspoiled sample of Hopkins & Williams steam activated coconut charcoal was used exclusively.

It can be seen from Fig.XIX that this gives quite a satisfactory separation of helium and neon though not as sharp a separation as obtained by other workers. This is thought to be a consequence of using an excess of charcoal in each unit but this is not a serious drawback.

Having now determined at which stage theoretically 100% helium is delivered by the column, it is necessary to test the system absolutely and also to test its reproducibility. The quickest method of checking the apparatus and one which is used frequently between measurements on unknowns is to measure the helium content of a sample of dry air. This value has been accurately estimated by Glückauf and others and forms a useful standard to work by.

Helium content of air at ground level

The air pipette used in obtaining air samples is shown in Fig.XX . It can be attached to the apparatus at the standard ground joint G_1 and is in contact with the supply of helium-free oxygen.

The pipette is evacuated through taps T_1 and T_2, tap T_3 remaining closed. On completion of the evacuation tap T_2 is closed and tap T_4 opened, admitting air into the volume contained between taps T_3 and T_4, which contains a quantity of fresh anhydrone. Thus, on opening tap T_3 a sample of dry air at atmospheric pressure is admitted into the accurately known volume V (0.494 ccs.) contained between taps T_2, T_3. Barometric pressure and the laboratory temperature are noted to convert this volume to standard temperature and pressure.

The sample is now ready for transfer to the fractionating system by way of the circulating system as described previously.

Results of air analyses

The first result have a helium content for ground level air of $4.67 \times 10^{-4}\%$ which is much lower than the recognised value of $5.24 \times 10^{-4}\%$.(110). In this experiment the above system of sampling the air was not used. Instead a pipette of about 48ccs. capacity was used which necessitated reducing the pressure of the air to about 1cm in order to obtain a convenient amount. Further, no precautions were taken to dry the air before the experiment. Difficulties inherent in this method of sampling were eliminated by using the method outlined above.

The next result using the improved method of sampling indicated a value of 4.67 x 10^{-4}% again but this result is obscured by an unsatisfactory calibration of the measuring gauge.

With increasing familiarity with the technique, the next two results show much better agreement, being 4.59 and 4.55 x 10^{-4}% respectively. Whilst these results agree in themselves to better than 1% there is still a large difference between them and the recognised value (about 13% too low).

The possibility of incomplete transfer of the sample from pipette to fractionating system has already been examined in the analyses carried out so far since two methods of transfer were tried, i.e. by direct Toepler transfer and transfer using Oxygen carrier. Both methods of transfer gave the same low result. Neither did increasing the number of strokes with the Toepler pump produce any difference.

It would seem then that either there is a real retention of helium at some stage in the process, most likely in the column, or the apparatus used for calibration of the measuring gauges is inaccurate. To test the latter possibility samples of helium were measured out in the calibration system and transferred into a storage vessel of the type shown in Fig. XXI . by means of a small Toepler pump. The storage vessel consists of a closed tube of about 10 to 20 ccs. capacity, being sealed at one end with a thin walled septum, S, and attached at the same end by means of an internal seal to a standard ground joint G. A side arm, containing a constriction C, connects the vessel through tap T_1, which serves the purpose of a one-way valve, to the Toepler pump. Having transferred the sample of helium into the vessel by Toepler action, the vessel may now be sealed off at the constriction C and removed from the apparatus. It is rejoined to the apparatus by means of the standard joint G and takes the place of the air pipette, Fig. XX . After pumping down the outer space above the septum, this may now be fractured by means of a steel ball raised by a magnet and allowed to fall freely on to the septum. The sample of helium may now be transferred to the fractionating system in the usual way.

Measurement of such samples should show no discrepancy between initial and final values if there is a consistent error in the calibration apparatus but should show a difference if there is retention or loss of helium at some stage in the fractionation process.

Results of helium loss experiments

The first sample of helium measured in this way was of an amount approximately the same as that expected to be delivered by the air pipette in a routine air analysis. After the fractionation procedure, the amount measured was 13.3% lower than the amount measured in the calibration system.

This compares well with the value of about 13% low for air analyses and indicates that the technique of transfer and fractionation is not quantitative.

The efficiency of the transfer procedure has already been examined, two different methods giving comparable answers. The only common operation in the two methods is that of the Toepler action so this can be the only source of inaccuracy in the transfer. Increasing the number of operations of the pump from 10 to 20 has also been shown to have no effect so it is difficult to arrive at any conclusion as to what the source of the trouble, if any, might be. It may be that the operations have been carried out too quickly so that back diffusion of helium into the system has occurred, but this seems extremely unlikely.

Similarly, it could be that in the column, operations have been carried out too quickly to allow equilibration of the helium between solid and volume phases, which would result in retention of helium there. Reasbeck and Chackett ([111]) have already examined a similar system for such an effect and have concluded that equilibration is substantially instantaneous. Nevertheless another sample of helium of about the same amount as the first was made up and measured as before. In this experiment, Toepler operations were carried out at a much slower rate and the time allowed for desorption and equilibration of the gas in column operations increased from about 2 to 5 seconds to 10 seconds. In addition the total helium fractionated up to operation No.40 was measured first and then the helium delivered for each successive lot of five operations until the amounts became too small for measurement. In this way it was hoped to be able to compare the behaviour of the pure helium sample with that predicted from the calibration using an air sample.

Thus the helium delivered in operations 51 - 55 was about 0.5% of the amount delivered up to operation No.40. The total helium to operation No.55 was found to be 10.5% lower than the amount initially measured in the calibration apparatus and the total helium to operation No.45, 12% low. This agrees fairly well with the above figure on a similar quantity of helium, 13.3%, considering that one more operation was carried out in this case and small amounts of helium are still being fractionated.

Taking the total helium to be that obtained up to operation No.55, the helium delivered up to operation No.45 represents 98.2% of this amount; this again compares favourably with the amount predicted from the air calibration of 99.5% up to operation No.44.

It can be seen that the speed with which the various components are operated appears to have little effect on the final result. The only conclusion which one can arrive at now is that helium must be retained in the column presumably by some process of irreversible adsorption. If such is the case then in order to use the system to measure helium one must ascertain whether the amount of helium retained is constant or depends on the amount of helium initially taken, i.e. whether or not this adsorption is pressure dependent. To this end then samples of helium were prepared of amounts varying from 1 x 10^{-7} ccs. N.T.P. to 5 x 10^{-6} ccs. N.T.P. and measured in the above way. The results of these experiments are shown in Table XVI and it can be seen that in all cases a loss of helium in fractionation has taken place, both the fraction lost and the absolute amount lost depending on the amount of helium taken.

TABLE XVI

No.	V(N.T.P.) He x 10^6 ccs	% low	Amount low x 10^7 ccs.	log %	Gas in gas phase x 10^6 ccs.
1.	2.38	12.4	2.95	1.0934	2.09
2	2.40	13.5	3.24	1.1303	2.08
3	3.11	13.3	4.14	1.1239	2.70
4	2.40	12.0	2.88	1.0792	2.12
5	0.41	19.6	0.80	1.2927	0.33
6	9.45	5.8	5.48	0.7653	8.90
7	5.24	9.9	5.19	0.9956	4.72
8	1.75	14.75	2.58	1.1685	1.47

It should be noted that in result 8 in Table the lost helium was sought by allowing the last seven charcoal units to warm up to room temperature and carrying out three lots of eight operations, each lot being measured separately. The total galvanometer deflection obtained from these operations

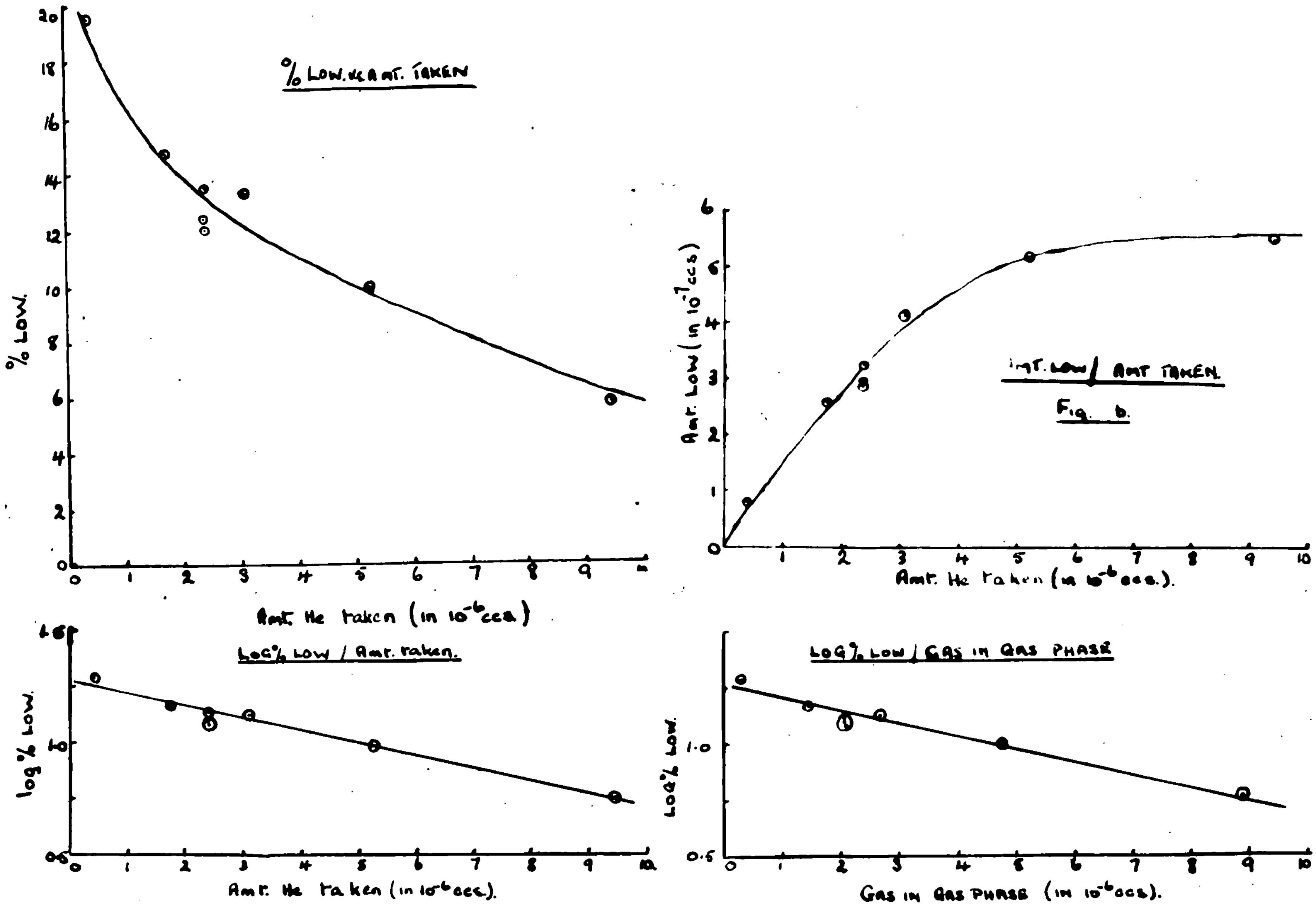

% LOW. vs AMT. TAKEN
% LOW.
20
18
16
14
12
10
8
6
4
2
0
0
1
2
3
4
5
6
7
8
9
10
Amt. He taken (in 10^{-6} ccs.)
AMT. LOW / AMT TAKEN.
Fig. b.
Amt. LOW (in 10^{-7} ccs)
6
4
3
2
1
0
Amt. He taken (in 10^{-6} ccs.).
LOG % LOW / Amt. taken.
log % LOW.
1.5
1.0
0.5
Amt. He taken (in 10^{-6} ccs.).
LOG % LOW / GAS IN GAS PHASE
LOG % LOW.
1.0
0.5
GAS IN GAS PHASE (IN 10^{-6} ccs).

Fig. XXII.

indicated a quantity of helium about 15% of that initially taken. It can be seen from the table that the amount low in the actual experiment was 14.75%, a strong indication that helium is in fact being retained in the column.

Results 1 and 2 in Table XVI correspond to the two air analyses already discussed. The gas in the gas phase shown in the last column of Table XVI corresponds to the amount of helium taken minus that lost in fractionation.

The results are represented graphically in various forms in Fig. XXII. These curves show that the relative amount of helium lost increases as the pressure (i.e. the amount taken) decreases but that the absolute amount lost increases with increasing pressure and seems to approach a limiting value.

The curves also reveal a linear relationship between the logarithm of the percentage lost and the pressure (whether this is expressed as amount of gas taken or as the amount of gas in the gas phase, or not).

Let the amount of helium lost = x in arbitrary units.

Assuming that the amount of helium taken is proportional to the pressure 'p' then x/p will be proportional to the percentage lost.

Therefore from the curve

$$\log. x/p = A - Bp.$$

where A and B are constants.

Expressing this in another form then,

$$x/p = e^{(A-Bp)} = e^{A}.e^{-Bp}$$

$$\text{or} \quad x/p = A'e^{-Bp}$$

If the loss of helium during fractionation is due to irreversible adsorption then this expression is the adsorption isotherm for this process and as might be expected deviates from ideal 'Langmuir' behaviour.

An isotherm of similar form to this one has already been published for the adsorption of helium on charcoal at 6 - 20°K.

$$\log. x/p = A + Bx. \qquad (112)$$

When x/p is plotted here against corresponding values of x, it is found that with one exception the points lie on a straight line which could otherwise be represented by an equation of the form,

$$\log. x/p = A - Bx.$$

Other deviations from ideal behaviour have been noted in many cases notably in the case of the adsorption of neon on charcoal (113). The cases however are by no means comparable unfortunately since the pressure at which the adsorption of helium is observed here is so much lower than the pressure of neon.

The main point, since one is to attempt the determination of small quantities of helium, is that the amount of helium lost is pressure dependent and the extent of this dependence has now been determined. Using the values obtained above then an unknown amount of helium may now be fractionated and the value obtained corrected for loss of helium during fractionation. The validity of such a procedure is demonstrated by the reproducibility of the air analyses carried out between experiments on unknowns. Still further support is given later in the determination of the helium content of a sample of the meteorite 'Carbo'. The value obtained using this system together with correction for helium lost was identical with that obtained on a different apparatus by Reasbeck.

Collection and measurement of helium fractions

The various fractions emerging from the column are collected in a bulb of about 1000 ccs capacity, the so-called Compression Bulb. The compression bulb is supplied with a reservoir of mercury so that on completion of fractionation the mercury level may be raised and the gas collected confined into the volume of the bulb and the limits of the connecting tubes defined by the taps T_3 and T_4 (Fig XVII) and the ventil V_3 of the small Toepler pump P. Since the volume of the bulb is so large in comparison with the interconnecting tube, substantially all the gas fractionated is thus confined.

On raising the mercury further, i.e. to the limits defined by the two ventils V_1 and V_2, the gas is compressed into the small volume (of about 2 ccs capacity) between taps T_3, T_4 and ventils V_2, V_3.

The gas may now be admitted at will into the Pirani Gauge G_1 for measurement by way of tap T_3 and subsequently removed through tap T_4 which connects to the vacuum system.

In cases where the helium which has been measured in

Fig xxiii

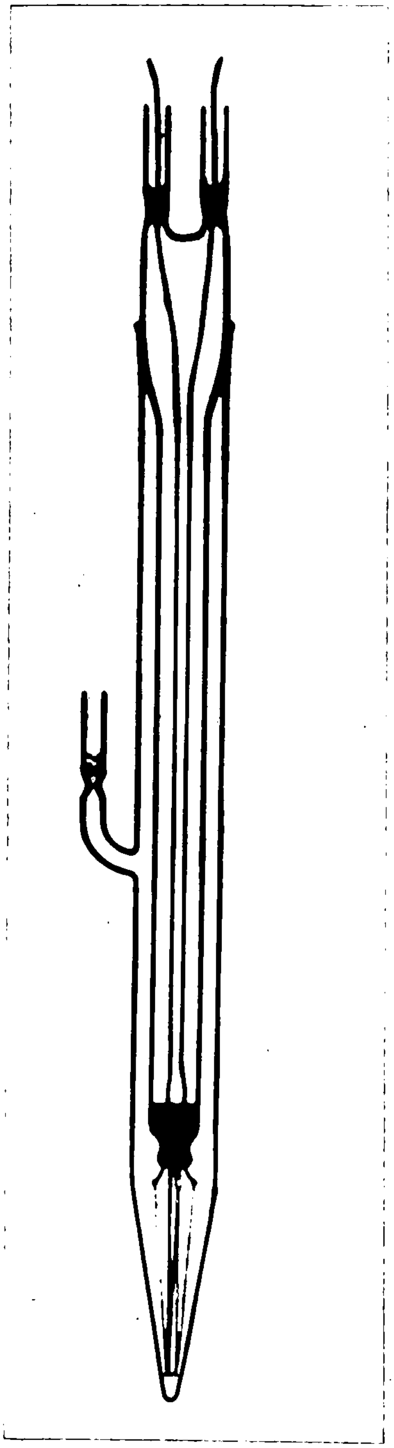


Fig. XXIII.

this way is required for further examination, the gas is collected in small storage vessels B in Fig.XXI by means of the Toepler pump P as has already been described.

In addition to being in direct connection with the column, the compression bulb is also connected to the apparatus used to measure samples of helium for calibration of the Pirani Gauge. The transfer of calibration samples to the gauge is thus carried out in the same way as described above. Similarly, in the investigation of the loss of helium in fractionation, the samples of helium used there were transferred from the calibration apparatus, through the compression bulb and Toepler pump P into the storage vessels. No initial measurement in the Pirani Gauge was necessary in this case.

The Pirani Gauges used for measurement are shown in Fig. XVII, G_1 and G_2 and in more detail in Fig.^{XXII}. They consist of an inner casing of Pyrex glass, evacuated and sealed off, which supports leads to a length of thin nickel tape (0.5 mm.). This nickel tape forms the element of the gauge. It is about 30 cms in length and is soldered to the leads from the inner case (Copper coated tungsten wire) with soft solder. It is maintained in the shape of a W by passing it alternatively over a glass former, a loop attached to a tungsten wire spring and then over the former again. Both former and spring are attached to the inner casing, the purpose of the spring being to keep the wire taut and eliminate unsteadiness due to vibration of the element.

The inner casing which supports the element is attached to an outer casing of soda glass through a standard joint. The outer casing being connected to the pumping system through a side arm, which contains a small quantity of charcoal. The purpose of the charcoal is to take up oxygen which is soluble in the tap grease and this was found by Glückauf to lead to unsteadiness of the gauges.

In this arrangement two gauges are used, one connecting to the compression bulb and/or the pumping system through taps T_3 and T_4 and the other connecting directly to the pumping system through tap T_5, Fig. XVII . In use the former is the one which performs the actual measurement whilst the latter acts as a nearly equal balance. The two gauges form two arms of a balanced Wheatstone Network Fig. XXIIIa

In use the two Pirani gauges are thoroughly évacuated and the charcoal outgassed by heating them with a soft flame under the action of the pumps. They are built as close together as practicable so as to be able to immerse them in a common bath of liquid nitrogen thereby ensuring approximately equal conditions in each. Immersion in liquid nitrogen not only ensures approximately constant temperature conditions around the outer casing of the gauges but also provides as large a temperature gradient between the nickel elements and the outer casings as possible thereby giving greater sensitivity.

With the Wheatstone net balanced a sample of gas is admitted into the measuring gauge through tap T_3, Fig. XVII . As a consequence of the increased pressure in this case thermal conductivity between the element and cooled outer case is increased and the element thereby cooled. Its resistance is thus altered and the disturbance of the balance of the Wheatstone net reflected in a deflection in the galvanometer. The extent of the deflection is measured and the galvanometer takes up a new position of equilibrium. If now the gauge is connected to the pumping system and evacuated a deflection is observed in the galvanometer in the opposite sense to that previously noted. Provided no changes have taken place in the pumping system to alter the final pressure reached in the gauge on evacuation, the two deflections should be of equal magnitude if the gauge is functioning correctly. Differences greater than one percent are suspect and the average of the two deflections is taken.

Immediately following the measurement of an unknown sample the deflection due to a known sample of helium is measured. This calibration then leads to the quantity of helium in the unknown.

The galvanometer used in the network is of the suspended mirror moving coil type. The deflections are thus manifested as the movement of a spot of light over a 50 cm. scale supported at a distance of some 60-70 cms from the galvanometer. Since the scale forms a chord to the arc in which the spot of light moves unequal effects are given dependent upon the position on the scale at which the measurements are made. It is therefore necessary to calibrate the scale for non-linearity. For this purpose, a megohm resistance is connected through a switch across one of the gauges so that when contact is made the resistence in this arm of the net is changed and a deflection in the galvanometer results. Using this device deflections can be obtained at various points on the scale for the same change in the network. The deflections obtained are then corrected to a standard value and a scale drawn up showing the value of the true scale readings from the observed ones.

Since both the Pirani gauges and the galvanometer are extremely sensitive to external vibration, the bench upon which the apparatus is constructed stands on a block of concrete separated from the rest of the laboratory floor. Thus no vibration can reach the Pirani gauges as a result of movement across the floor, slamming of doors, etc.. Similarly the galvanemeter stands on its own separate concrete and brick support.

E.M.F. is supplied to the network from the 2 volt battery B, Fig. XXIIIa., and the resistance R so arranged that the P.D. across the network is exactly 1 volt. The galvanometer is shunted so that the sensitivity may be changed to suit the amount of gas handled. The general range is

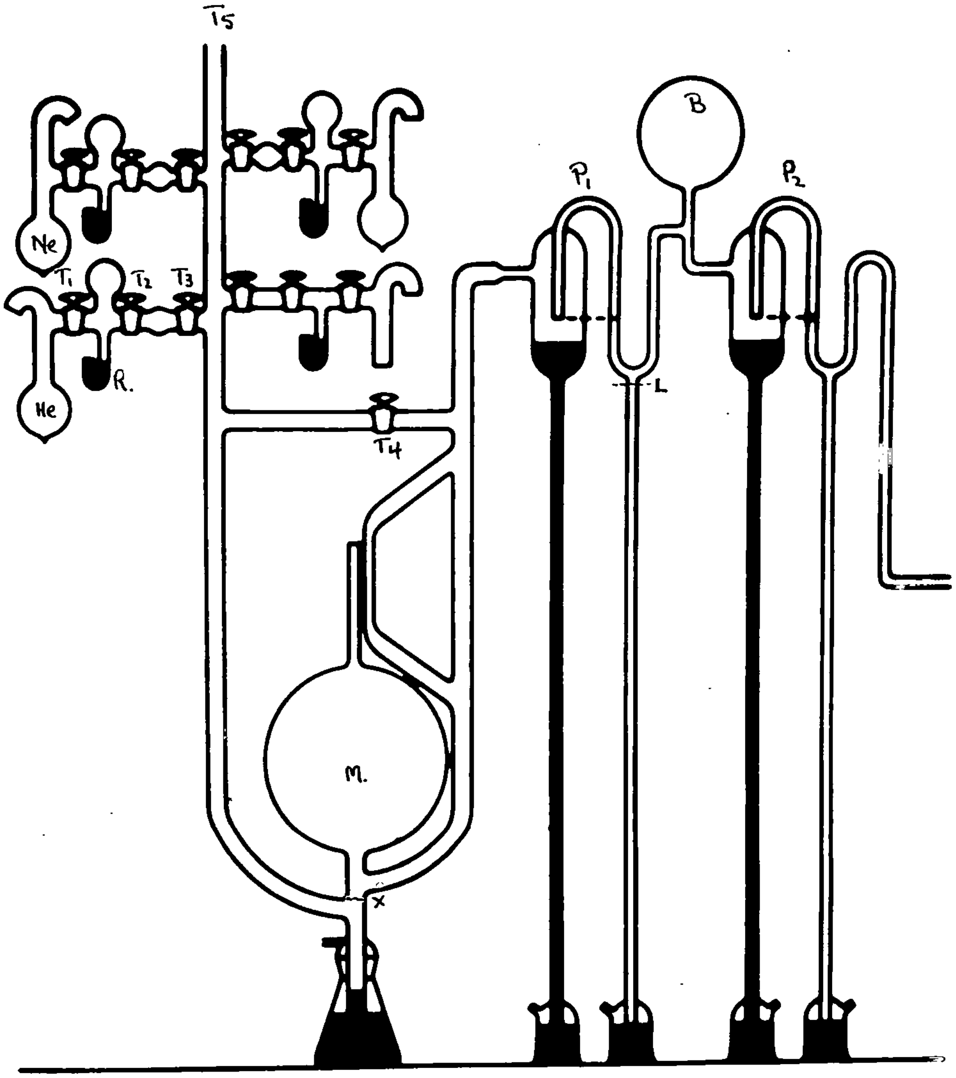


Fig. XXIV.

10^{-6} to 10^{-7} ccs of helium at N.T.P.

Calibration Apparatus - The Pipetting System

The apparatus used for the measurement of quantities of helium suitable for admittance into the Pirani gauge for calibration purposes is shown in Fig. XXIV.

It consists of a reservoir R connected through a tap T_1 to a source of spectrally pure helium (B.O.Co.). This arrangement allows a means of suitably reducing the pressure of the helium from the source to a level convenient for the purpose in hand. The reservoir is also connected to a smaller volume, between taps T_2 and T_3, into which the sample of helium is admitted before passing on to the McLeod gauge M for measurement. This again serves the purpose of supplying a suitable amount of helium ready for direct measurement and avoids the need for partial evacuation necessary if too large a sample is taken.

The McLeod gauge is evacuated through tap T_5 and is connected to a system of pipettes P_1, P_2 and Expansion bulb, B. The closed limb of the McLeod gauge is calibrated along its length before construction. Graduation marks are made at about 1 cm distances from the closed end by etching with hydrogen fluoride. The volume contained up to each mark is then measured by filling the tube with mercury up to the mark concerned and weighing. Since, in operation, the tube is inverted, the volume obtained in this way needs correction for the volume occupied by two mercury menisci. In addition to this calibration, the distance from each graduation mark to the upper limit of the closed tube is measured and the results plotted against the respective volumes. Thus, if necessary, volumes may be used intermediate to those represented by the graduation marks.

The pipettes P_1 and P_2 are calibrated in a similar way between the limits indicated by the broken lines in Fig. The expansion volume B is calibrated by a gas expansion method.

The various volumes are:-

P_1 = 4.6315 ccs.

P_2 = 4.1289 ccs.

$B + P_1 + P_2$ = 161.8 ccs.

In order to carry out the gas expansion calibration mentioned above and also for measurement of calibration samples it is essential to know the total volume of the McLeod gauge and side arms. The gauge is first built in position and then cut off as close to pipette P_1 as practicable. In this way the gauge may be rebuilt into the apparatus with the minimum change in volume as possible after the calibration of its volume. Then with this open end of the side arm securely corked and tap T_4 closed, the gauge is inverted and filled with water to a fixed mark X, Fig.XXIV . Delivery of the water from a previously calibrated burette leads to the volume of the vessel filled. The remaining volume between the place where the side arm was cut off and the open end of pipette P_1 is estimated by measurement and calculation. This volume represents only about 0.3% of the total volume so any errors in measurement cannot be very serious.

Volume of gauge + side arms obtained thus = 890.6 ccs.

The method of measurement of a sample of helium for calibration purposes is as follows:-

A suitable amount of helium is admitted into the gauge, previously evacuated through tap T_3, tap T_5 leading to the pumping system being closed. The mercury in the gauge is then raised so that gas is cut off in the bulb. Tap T_5 is then opened and the excess helium in the side arms etc pumped away. The mercury in the gauge is then raised to the level of one of the graduation marks in the closed limb and the pressure of the gas enclosed measured with a cathetometer. Thus a known volume of gas is taken at known pressure, the temperature being taken from a thermometer suspended near the gauge.

Having measured the pressure of the gas, tap T_4 is now closed and the mercury in the gauge lowered to the fixed level X. By suitably arranging the mercury levels in pipette P_1 the gas is allowed to expand into P_1. Thus a volume of gas P_1 at a much reduced pressure may now be allowed to expand into the expansion bulb and pipette P_2. By isolating P_2 now a known amount of gas is obtained suitable for the Pirani gauge calibration.

P_2 connects directly to the compression bulb and the calibration sample is transferred to the Pirani gauge in the manner previously described.

Simple calculation shows that, using the volumes obtained above for the various components of the calibration apparatus, the volume of gas delivered to the Pirani gauge will be:-

$$\frac{pv \times 4.6315 \times 4.1289 \times 273}{76 \times (T^{o}C + 273) \times 895.23 \times 161.8} \text{ ccs.N.T.P.}$$

$$= \quad pv \times \frac{.03611}{76 \times (T^{o}C + 273)} \text{ ccs.}$$

Where v = volume of gas to graduation mark in the McLeod.

p = pressure of this volume v of gas.

Since thermal conductivity of gases at low pressure is dependent upon the nature of the gas as well as on the pressure the response of the Pirani gauge is not the same for neon as for helium (114). In order to measure neon then separate calibrations need to be carried out. This simply involves the inclusion of a reservoir of neon like that for helium in the apparatus. Several such reservoirs are in fact shown in Fig. XXIV.

The whole apparatus is maintained under vacuum by the use of two mercury diffusion fore pumps with a "Highvac" oil backing pump. A secondary vacuum system using only a "Highvac" oil pump is included for the manipulation of mercury levels.

With the exception of the mercury diffusion pumps, the inner casing of the Pirani gauges and the casing of the palladium furnace (Pyrex) the entire apparatus is constructed of soda glass, this being substantially impermeable to helium. (115)

"Apiezon" grease L is used on all tap-keys and "Apiezon" grease M on most ground joints. Where "Apiezon" grease M is not used the joint is sealed with "Apiezon" wax W or Everett's "very low vapour pressure" vacuum wax, these being the joints of a more permanent nature.

With the exception of two-way taps in the secondary vacuum system, all taps used are hollow bore and are carefully ground with fine 'Cera' powder and tested before building into the apparatus.

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APPENDIX 2

The Separation of micro-quantities of Uranium and Thorium from Rocksalt (116)

1. Uranium

200 gms. of rocksalt are dissolved in about 1¼ litres of distilled water and hydrochloric acid added to make the solution approximately 1 N with respect to acid. 60 mg of aluminium are added as chloride to this solution and carbonate-free ammonia gas passed into the solution till precipitation occurs.

The precipitate of aluminium hydroxide is dissolved in nitric acid and re-precipitated with ammonia gas so as to free it from chloride. This precipitate is now dissolved in 20 ml. of concentrated nitric acid and 10 to 20 gms of solid ammonium nitrate added to the solution.

The solution is then shaken with four separate lots of ether (20 ml. each time) to extract the uranium. All the ether is removed from this extract by heating on a water bath in the presence of 100 ml. of water, and the volume of water then reduced cautiously with a burner to less than 10 ml.

The resulting solution is made up to 10 ml. with water and 1 ml. portions evaporated to dryness in platinum fluorimeter trays. 0.94 gms of sodium fluoride are added, the solids fused and the resulting phosphors examined in the fluorimeter.

Blank sodium flouride phosphors are prepared so that the difference in fluorimeter readings represents the uranium present.

2. Thorium

200 gms. of rocksalt are dissolved in about 1½ litres of distilled water and hydrochloric acid added to make the solution approximately 1 N with respect to acid. 100 mg. of iron are added as chloride.

The precipitate obtained on passing carbonate-free ammonia gas into this solution is dissolved in 50 ccs. of concentrated hydrochloric acid, producing a solution which is 6.5 N with respect to acid. This solution is then shaken four times with 50 ml. portions of ether equilibrated with 6.5 N hydrochloric acid till the solution is almost free from iron. 5 mg. of iron are then added as chloride and the ether in the aqueous phase evaporated on a water bath. The total volume of solution is reduced to 20 ml. and then diluted with 20 ml. water to give a solution which is now approximately 2 N with respect to hydrochloric acid.

Carbonate-free ammonia gas is passed into this solution. The small precipitate of ferric hydroxide is collected and re-dissolved in 25 ml. of 0.2 N hydrochloric acid. This solution is stored for one month.

2 mg. of lead are then added as acetate. Hydrogen sulphide is passed into the solution and the resulting precipitate of lead sulphide collected and re-dissolved in the minimum amount of warm concentrated hydrochloric acid.

This solution is evaporated to dryness on a polystyrene scintillation counter disc and counting started 45 minutes after precipitation.

The ThC α-particles (in equilibrium with parent ThB - half-life 10.6 hours) are counted over a period of 16 hours. Subtraction of the 16 hour background count then gives the thorium present. This is compared with a standard source.

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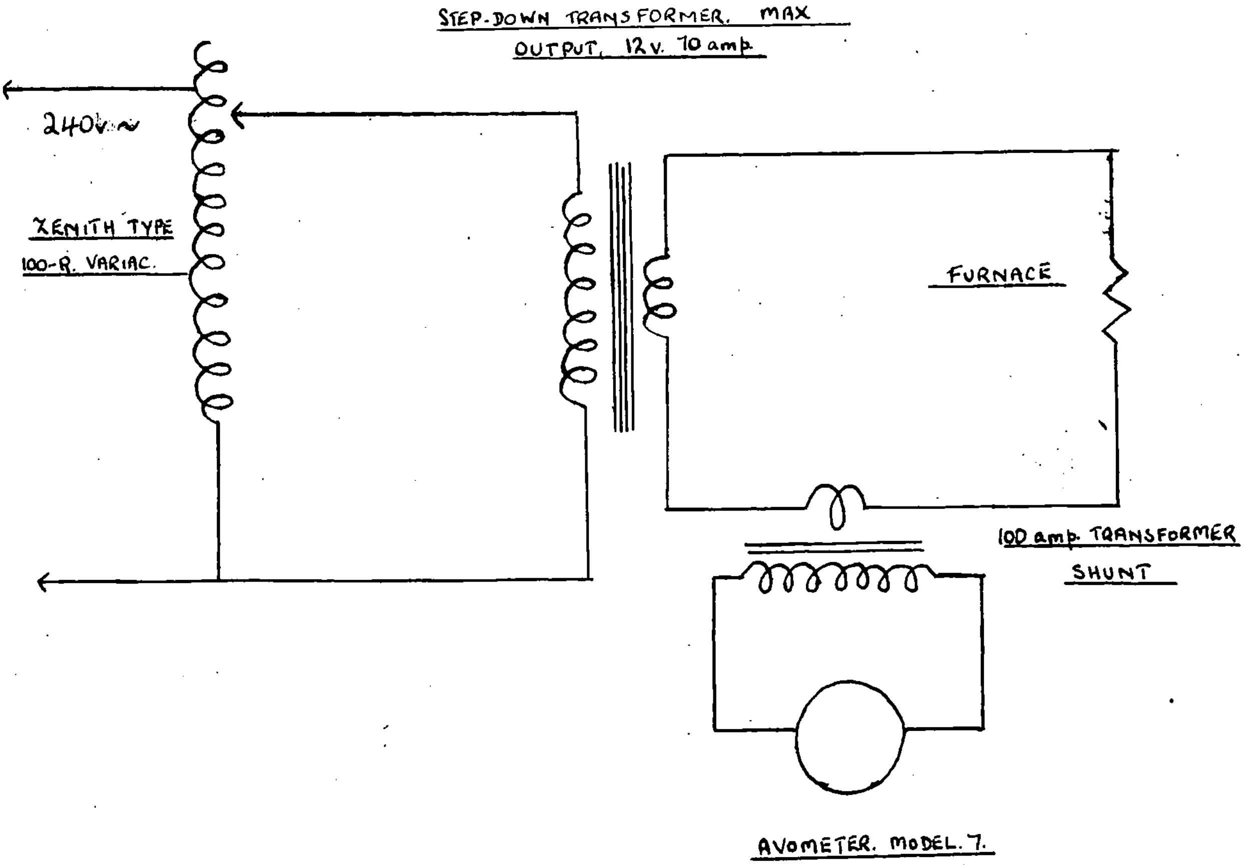
APPENDIX 3

Steel Fusion Furnace - Circuit Diagram.



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