# THE ABSORPTION OF GASES BY METALS



### THE ABSORPTION OF GASES BY METALS.

by

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I. <u>GENERAL</u> <u>INTRODUCTION</u>.

One of the outstanding problems of physical chemistry, which have , as yet, received no satisfactory solution, is that of solubility. The work of **\***an<sup>•</sup>t Hoff contributed largely to the advancement of our knowledge of the subject, but, although we have a fairly accurate knowledge of how a substance will act in solution, we are as yet unable to arrive at any satisfactory estimate of the solubility of one substance in another.

Solid solutions are in a still less advanced state. The most convenient kind of solid solution for purposes of investigation is one in which the solute is a gas. The existing data on the absorption of gases by solids are very vague and conflicting. An allied phenomenon, that of diffusion of gases through solids, is also in an unsatisfactory state as far as accurate knowledge is concerned.

Accordingly it was decided to investigate thoroughly the absorption and diffusion for one particular gas in some one metal. Oxygen and silver were chosen as it was known that oxygen would 'dissolve in silver and would diffuse through it.

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Silver has the advantage of being inexpensive compared

to platinum and metals of that group and is easily pur-

ified, while oxygen is easily obtainable in a fair degree

of purity.

The diffusion of oxygen through silver has already been investigated at McGill University by Johnson and Larose <sup>1</sup>.

This thesis is concerned with the absorption of the same gas by silver. An attempt will be made in a later section to correlate the phenomena of diffusion and absorption.

II. HISTORICAL INTRODUCTION.

In 1863, Deville and Troost<sup>2</sup> showed that hydrogen gas can diffuse through red hot platinum or iron, but that the cold metals are quite impervious to the gas. They suggested that the permeability was caused by a kind of porosity. They said that this new porosity was entirely due to the expansive agency of heat opening up intermolecular spaces in the metal.

In 1866, the experiments of Deville

and Troost were brought to the attention of Graham<sup>3</sup>. Graham could not detect any signs of the passage of oxygen,nitrogen,chlorine,steam,or several other gases through a piece of platinum at a full red heat. He found,however,that when certain metals are heated in hydrogen,more or less of the gas is absorbed and retained as the metal cools,forming a kind of solid solution of the gas in the metal. His experimental procedure and results were as follows:

A small piece of the metal under investigation was heated in a porcelain tube,glazed inside and out. The tube was heated to redness

and exhausted. Hydrogen was then allowed to pass over the heated metal and the metal was allowed to cool in the same gas. The tube was then evacuated. It was then slowly heated and evacuated, and the gas evolved was collected over mercury and measured. He found

Platinum4	•7	volum	es
Palladium4	95.	5 <b>'</b>	,
Copper0	•6	,	,
Gold0	•5	,	,
Silver0	•9	,	<b>9</b>
Iron	.2	,	,

Palladium, therefore, of all the

metals, appears to possess the power of absorbing hydrogen in the highest degree. The volume of gas absorbed by the metal was found to depend on its con-The gas absorbed by the metal is retained dition. very tenaciously and it can be recovered only by heating the metal to redness in vacuuo. Hence, Graham added,

It appears necessary to recognize in palladium a new property, a power to absorb hydrogen at a red heat, and to retain gas at a temperature under redness for an indefinite time. It may be allowable to speak of this as a power to occlude (shut up) hydrogen, and the result as the occlusion of hydrogen by palladium.

#### Graham's results led to a consid-

erable interest being taken in this new property. At

first the majority of the investigators confined their

attention to hydrogen.

The fixation of the gas was found to be more energetic if the metal under investigation were used as a negative electrode during electrolysis, and hydrogen thus liberated at its surface in the nascent state. Thus Thomas<sup>4</sup> showed that if palladium be employed as negative electrode during the electrolysis of acidulated water, the metal may become supersaturated with the gas and dissolve over 935 times its volume of gas, the amount actually dissolved varying with the strength of the current. The excess is quickly evolved when the current ceases.

On account of the very large volume of gas which it absorbs, palladium has been much more thoroughly investigated than any other metal.

Neumann and Streintz<sup>5</sup> found that the physical state of the palladium had a large effect. Thus wroaght palladium dissolved 376-643 volumes

wire	,,
sponge	,,
fused	,,

Favre<sup>6</sup> found that the heat of occlusion of hydrogen by palladium was the same for the same

7.

amount of hydrogen at all stages of the absorption, and hence he assumes that the hydrogen forms an alloy with the palladium. This idea of an alloy was first suggested by Graham<sup>7</sup> He supposed that the gas during the process of absorption condensed to a solid metal, which then alloyed with the palladium. He gave the name hydrogenium, to the hypothetical metal in order to emphasize its metallic character. It was argued that the metallic character of the occluded hydrogen is shown by the fact that if a plate of palladium be charged electrolytically with hydrogen, and subsequently immersed in a solution of copper sulphate, the metal is soon covered with a film of metallic copper.

 $CuSO_4 + 2H = H_8SO_4 + Cu$ 

Solid hydrogen, however, was found

by Dewar to have rather the properties of a non-metal than a metal - its specific gravity for example is 0.076, which is only 1/8 that calculated for the absorbed hydrogen in palladium.

Graham<sup>7</sup> also suggested from the change in density of palladium when it occludes hydrogen, that the compound PdH is formed. Troost and Hautefeuille<sup>8</sup> conclude that the compound Pd<sub>g</sub>H is formed.

Hoitsema<sup>9</sup>, basing his opinion on the experiments of Roozeboom and himself, concludes that no compound is formed (on account of the sloping

character of the absorption isotherms); he suggests

that a mixture of two different solid solutions are is

formed.

## Holt, Edgar, and Firth<sup>10</sup> conclude

from their own investigations that hydrogen is occluded by palladium in two ways, (1) in an adsorbed layer of high vapour pressure which can be easily removed by evacuation, and (2). as an absorbed gas which is nonuniformly distributed in the body of the metal. As the temperature rises the pressure of the absorbed gas increases, whilst the adsorbed layer diminishes, Sieverts<sup>11</sup> has extended measure-

ments up to the melting point of palladium and finds that on liquefaction the occlusion falls off to about one half.

Wolf<sup>12</sup> measured the electrical

conductivity of palladium and decided as follows: (a).The conductivity diminishes proportionally to the occluded quantity of hydrogen as long as the hydrogen is being merely dissolved.

(b).It diminishes asymptotically as long as the chemical compound Pd2H is being formed (i.e. between 40 and 600 volumes of gas per volume of palladium). (c).After this,further hydrogen dissolves in the Pd2H and the conductivity diminishes again proportionally to the additional quantity of hydrogen occluded. Holt<sup>13</sup> concludes that the rate

of solution of hydrogen by palladium is not a simple

function of the concentration of the gas. The rate curves consist of two portions which are interpreted as referring to solution in two different forms of the metal. In spite of the extensive investigation of the occlusion of hydrogen by palladium, the problem of the state of the occluded gas is, as yet by no means solved. The palladium-hydrogen system, however, does not appear to be a typical one. Most of the metals which absorb gases absorb only a relatively small amount.

In addition to the pure metal, several investigations have been made on palladium alloys. Graham<sup>3</sup>, and Berry<sup>14</sup> have measured the solubility of hydrogen in palladium-gold alloys. Berry found that the decrease in the amount of occluded hydrogen is a simple function of the proportion of gold in the alloy, but that the occluding power of the alloy vanishes when the proportion of palladium falls below 25%.

Sieverts and Jurisch<sup>15</sup> have extended these observations over a greater temperature range,viz.138-820°C. They have also employed palladium-silver and palladium-platinum alloys. All proportions of platinum were found to diminish the solubility of hydrogen in the alloy. Hydrogen is

10.

comparatively insoluble in silver, but the addition of silver to palladium raises the solubility until a maximum is reached at about 40% silver. At 130° this alloy dissolves about four times as much hydrogen as pure palladium. The solubility diminishes with increasing proportions of silver above this limit and becomes zero with alloys containing over 70% of silver.

#### Absorption of Hydrogen by Other Metals.

Platinum has been shown by various observers to absorb hydrogen. The results are, however, far from consistent. Graham<sup>3</sup> obtained an absorption of 3 to 4 volumes depending on the physical state of the metal. Neumann and  $Streintz^5$ found 0.8 to 1.5 volumes for platinum foil, and from 1.5 to 49 volumes for platimum sponge. Similar results were obtained by Annelli<sup>16</sup>. Berliner<sup>17</sup> found large values for the absorption of hydrogen by platinum, reaching as much as 271 volumes, his work,  $\sigma$ however, was inaccurate and his results have been dis-Berthelot<sup>18</sup> showed that platinum black credited. absorbed large quantities of hydrogen, but that most of it was due to the presence of oxygen in the black. Mond, Ramsay, and Shields<sup>19</sup> found

that platinum foil did not take up any hydrogen or oxygen at a white heat. Platinum sponge absorbed 2.1 volumes of oxygen and 3.0 volumes of hydrogen. Platinum black gave up oxygen on heating to  $300-400^{\circ}$ it also gave some  $CO_{g}$ . It absorbed 309 volumes of hydrogen, of which about 120 were truly absorbed, while the rest combined with the oxygen present to form water. In vacue platinum black still held

about 35 volumes of hydrogen.

Sieverts<sup>20</sup> found a very small absorption of hydrogen by platinum foil. Gutbier and Maisch<sup>21</sup> obtained similar values to those of Mond,Ramsay,and Shields. Varied results have been obtained

for the other metals of the platinum group. Cailletet and Collardeau<sup>22</sup> say that iridium and ruthenium can take up hydrogen during electrolysis. Rother<sup>23</sup>, and Finkener and Fisher<sup>84</sup> state that while ordinary iridium does not occlude much hydrogen, under a prolonged cathode bombardment it can take up as much as 800 volumes. Gutbier, Ottenstein, and Weise<sup>25</sup>, however, found that finely divided iridium absorbs a considerable amount of hydrogen at low temperatures, 113 volumes at -30°, this falls off rapidly as the temperature is raised and at 49° the absorption is only 38 volumes.

Wilm<sup>26</sup> and Erlen<sup>27</sup> state that rhodium absorbs more hydrogen than does palladium. Quenessen<sup>28</sup>, however, finds no absorption. Sieverts, Jurisch, and Metz<sup>29</sup> find a very small absorption.

#### Other Metals.

The majority of the other metals

12.

have been investigated, some of them by several work-

ers. The most noteworthy feature of the results

obtained is their general lack of certainty and the

enormous discrepancies between the results of diff-

erent investigators, working under apparently the same

conditions.

According to Sieverts and his co-

workers, hydrogen is not dissolved by thallium, aluminium, zinc, lead, bismuth, antimony, cadmium, tungsten, silver, or gold, while copper, nickel, and iron do dissolve the gas. Skinner, however, <sup>30</sup> finds that alum-

inium absorbs hydrogen in vacuum tubes. This, however, is hardly comparable with the usual absorption process. Neumann and Streintz<sup>5</sup> obtained an absorption of 1.1 to 2.7 volumes with sheet aluminium under the usual condit-Hodgson<sup>31</sup> confirms Skinner's result, and also ions. finds that zinc and lead absorb hydrogen under the same Neumann and Streintz find 0.11 to 0.15 conditions. volumes for lead, and a trace of absorption for zinc. Streintz later found that reduced lead occludes a considerable amount of hydrogen<sup>32</sup>. Cantor<sup>33</sup> confirmed Shields<sup>34</sup> found that hydrogen diffuses this. through an iron plate used as a negative electrode in He then substituted a lead plate and got no a cell. depression of the mercury in his manometer. This. however, is not an absolutely definite proof that lead does not absorb hydrogen. Boettger<sup>35</sup> obtained the

13.

## Caron<sup>36</sup> confirmed Sieverts result

and got no absorption of hydrogen by tin even in the

molten condition. Boettger, however, found that tin

when used as the cathode in an electrolytic cell absorbs

a small amount of the gas.

Caron found that molten antimony

absorbs hydrogen and spits on solidifying. Neumann and Streintz, on the other hand, found no trace of absorption.

Heald<sup>37</sup>, contrary to Sieverts, obtained a condiderable absorption of hydrogen with a thin film of cadmium.

Neumann and Streintz found a fairly large absorption of hydrogen by gold, although Sieverts was unable to detect any. They obtained 1.4 volumes with gold leaf and 37 to 46 volumes with precipitated gold. The latter result, however, seems very doubtful.

Carveth and Curry<sup>38</sup> report the occlusion of 250 volumes of hydrogen by electrolytically deposited chromium.

Troost and Hautefeuille<sup>8</sup> obtained evidence of the occlusion of hydrogen by manganese; and also found that the presence of manganese increased the solubility of hydrogen in iron. On the other hand Wedekind and Veit<sup>39</sup> obtained practically no occlusion of hydrogen by manganese.

Winkler<sup>40</sup> says that beryllium,

manganese, yttrium (and zirconium take up hydrogen when

their oxides, intimately mixed with magnesium, are heated,

but that magnesium alone does not absorb the gas.

The experimental conditions are obviously such that

this statement is practically worthless as far as

furnishing reliable evidence of the absorption of hydrogen by these metals is concerned.

Van der Berghe<sup>41</sup> finds that

molybdenum does not absorb hydrogen.

Sieverts<sup>20</sup> reports that cobalt absorbs from 0.1 to 0.5 volumes of hydrogen and Boettger fonds that a cobalt cathode absorbs hydrogen during electrolysis.

Roscoe<sup>42</sup> states that vanadium prepared by reduction sometimes contains as much as 1.3%of hydrogen by weight. Similar results were obtained by Muthmann, Weiss and Riedelbauch<sup>43</sup>.

Bolton<sup>44</sup> found that tantalum, prepared by reduction contained hydrogen. He also found that niobium absorbed hydrogen. Piriani<sup>45</sup> confirmed this for tantalum and found 0.3 volumes of hydrogen at a red heat and more at higher temperatures. Muthmann<sup>46</sup> obtained a similar result. Sieverts and Bergner<sup>47</sup> found that the solubility decreased as the temperature increased. They obtained an absorption of 420 mg. per 100 grams of metal at 20°C. This fell to 40 mg. at 700°C. The amount absorbed varied as the square

15.

root of the pressure, pointing to an absorption as hyd-

rogen atoms rather than as molecular hydrogen.

Numerous investigations have found

no evidence of any absorption of hydrogen by mercury.

Winkler<sup>40</sup> considers it unlikely

Sieverts and Bergner<sup>47</sup> obtained a

that titanium absorbs hydrogen.

small occlusion of hydrogen by uranium. Their sample, however,was very impure and the result therefore is by no means conclusive evidence that uranium absorbs hydrogen. The rare earth metals have been

investigated by Winkler<sup>40</sup>, Matignon<sup>48</sup>, Muthmann<sup>46</sup>, and Zhukoff<sup>49</sup>. All of them have found that cerium and lanthanum absorb large quantities of hydrogen. Winkler and Matignon found evidence of the absorption of hydrogen by thorium, and Matignon by samarium, neodymium, and praseodymium. Nothing definite is known of the behaviour of the other rare earth metals.

Troost and Hautefeuille<sup>8</sup> found that potassium and sodium absorb hydrogen. Moissan<sup>50</sup> found that 126 volumes of the gas were absorbed between 200 and 400° by potassium and 237 volumes by sodium between 300 and 421°. In addition, Mey<sup>51</sup> found that sodium and potassium absorb hydrogen when used as cathodes in a discharge tube. Chrisler<sup>52</sup> found that sodium and potassium and alloys of the one with the

other, absorb hydrogen when used as anodes in a glow current. Newman<sup>53</sup> found that a sodium-potassium alloy absorbed hydrogen when used as either the anode or the cathode in a discharge tube. Matignon found that lithium absorbed no hydrogen." Soddy discovered that calcium absorbed large quantities of gases and he patented its use as an absorbent in the production of high vacuua.

The earlier results obtained with nickel are very conflicting. According to Troost and Hautefeuille<sup>55</sup> 0.2 volumes of hydrogen are occluded by finely divided nickel. Neumann and Streintz<sup>4</sup>, however, find a much larger absorption, namely 16.9 to 17.6 volumes. Hempel and Thiele<sup>56</sup> find no absorption whatsoever. Baxter<sup>57</sup> obtained an absorption of from 2 to 10 volumes of hydrogen. Meyer and Altmeyer<sup>58</sup> in 1908 obtained at 360°C an absorption varying from 5.5 volumes at 1/15 of an atmosphere to 50 volumes at 4/5 atmos, Sieverts<sup>59</sup> found 0.18 volumes at 200°C increasing gradually to 0.98 at 1023°C. Sieverts was working with nickel foil instead of finely divided nickel and his results are probably fairly close to the true values for the solubility.

More recently, on account of the interest taken in nickel as a catalyst in hydrogen-

17.

ation processes, the adsorption of hydrogen by nickel has been studied by Gauger and Taylor<sup>60</sup> and by Taylor and Burns<sup>61</sup>. They have worked with very finely divided nickel, reduced at a low temperature. The surface in this case is very large and the values obtained, which are considerably higher than those of Sievefts, are probably mainly due to adsorption rather than true solution. It is also possible that the nickel they used, which was prepared by reduction from the oxide, was not completely reduced and hence chemical action took place, the oxide being reduced by the hydrogen.

The absorption of hydrogen by copper has been investigated by Sieverts<sup>20</sup> who found that from 0 to 4.8 volumes were absorbed, the absorption increasing with increasing temperature. There is a sharp break at the melting point, molten copper absorbing slightly more hydrogen than the solid metal. Sieverts and Krumbhaar<sup>62</sup> also showed that the solubility of hydrogen in copper is not affected by alloying the copper with moderate amounts of silver. Gold. tin, and aluminium, however, diminish the absorption, while nickel and platinum increase it. Taylor and Burns<sup>61</sup> and Pease<sup>63</sup> have investigated the adsorption of hydrogen by copper.

Sieverts has also investigated the solubility of hydrogen in iron.<sup>64</sup> The amount

18.

absorbed is small but increases regularly to 0.4mg per 100 grams of iron at  $900^{\circ}$ C. On the change from alpha to beta iron there is no noticeable change in the curve. Above  $900^{\circ}$  the beta changes to the gamma form and a sharp break occurs. After this

the absorption increases faster than before and is 1.08 mg per 100 grams at the melting point. On melting there is an abrupt change and 2.5 mg. are absorbed by the liquid iron at the melting point. The solubility of hydrogen in the molten iron again increases as the temperature is raised. The previous history of the iron has no appreciable effect. The hydrogen absorbed is not all recovered by heating It seems as if there were a chemical in vacuuo. reaction going on as well as simple absorption. The amount of gas absorbed varies as the square root of Neumann<sup>65</sup> used Sieverts method the pressure. and obtained practically the same results. Ryder<sup>66</sup> finds practically no absorption of hydrogen by steel. His work, however, is not very accurate.

A considerable absorption of hydrogen by thin metal films has been reported by Heald<sup>67</sup>. This, however, is probably due more to adsorption than to absorption since there is a very large area of surface. Baker<sup>68</sup>, however, finds no absorption of hydrogen by a film of iron under iden. tical conditions.

19.

## Hughes<sup>69</sup> found that iron wire

in the presence of atomic hydrogen became brittle.

On heating it recovered its flexibility. This is

apparently due to the occluded gas.

The results in the literature on the absorption of hydrogen by silver are very conflicting. Graham<sup>70</sup> found that silver heated and cooled in an atmosphere of hydrogen occluded 0.2 volumes of the gas. Silver reduced from the oxide occluded 0.9 volumes. Neumann and Streintz<sup>71</sup> were unable to detect any absorption of hydrogen by silver. Le Chatelier<sup>78</sup> stated that silver absorbed hydrogen at 600° and that the melting point of the metal is lowered 30° in an atmosphere of hydrogen. This lowering of the melting point seems to be rather excessive.

Baxter<sup>57</sup> found an absorption of 0.5 to 2.8 volumes of the gas.

Richards and Wells<sup>73</sup> investigated the solubility of hydrogen in silver in order to determine if it introduced any appreciable error into atomic weight work. They found no measurable absorption. Baxter and Parsons<sup>74</sup> investigated the problem from the same point of view. They found that the total weight of the occlude**d** gases was 0.00063% of the weight of the silver. Of this a considef-

20.

able amount was hydrogen.

## Sieverts<sup>20</sup> obtained a small ab-

sorption, but his results are far from conclusive and

do not show very good agreement with one another.

Heald<sup>67</sup> found a small absorption of hydrogen by silver films on glass. Baker<sup>68</sup> finds none at all. Soddy and Mackenzie<sup>75</sup> observed an absorption of hydrogen by silver when used as an electrode in a discharge tube. Chabrier<sup>76</sup> found that silver would readily absorb a considerable amount of hydrogen which had been made active in an apparatus somewhat resembling an ozonizer. The absorbed gas was readily given up when the action was stopped.

D.P.Smith<sup>77</sup> has classified the occlusion of hydrogen by metals from the point of view of the Periodic Law. Thus if we consider Table I we see that there are three distinct types of metal-hydrogen combination

(1) SbH<sub>3</sub> for example. This is a non-metallic volatile compound. In it the hydrogen atoms are probably positive and the antimony negative.
(2) KH. This is a non-metallic crystalline, volatile compound. Here the hydrogen is negative and the potassium positive.

(3) The palladium-hydrogen type. This is metallic

21.

#### in nature. The composition is variable and it is

probably a solid solution rather than a compound.

#### TABLE I.

ABSORPTION OF HYDROGEN BY THE ELEMENTS.

H																	
Li				-							Be	В	C	N	0	F	Ne
Na											Mg	Al	Si	P	S	Cl	Ar
K	Ca	o Sc	o Ti	x Vd	X Cr	x Mn	x Fe	x Co	x Ni	x Cu	Zn	o Ga	Ge	As	Se	Br	Kr
Rb	Sr	Yt	Zr	x Cb	Mo		o Ru	Rh	x Pd	Ag	Cd	o In	Sn	Sb	Te	I	Xe
Cs	Ba			x Ta	W		o Os	Ir	x Pt	Au	Hg	<b>T</b> 1	Pb	Bi			
	Ra																
CLASS							CL	ASS II							CI	LASS	5

x = definite absorption found

o = no definite absorption found

= not investigated, or very conflicting results.

In addition to the elements

shown above, some of the rare earth metals have been shown to absorb hydrogen as previously mentioned. Smith uses this periodic classification to connect the power of the metal to absorb hydrogen with its magnetic suscept-

ibility. This is not very conclusive as it would agree equally well with any other periodic property. There seems to be no doubt, however, from the preceding table that the absorption of hydrogen by metals is a property of a somewhat periodic nature, Absorption of Gases other than Hydrogen and Oxygen.

Various other gases are also absorbed by metals. No systematic study of their absorption has been made, but a considerable mass of observations exists in the literature.

Iron has been more largely investigated in this connection than any other matalxon account of the importance of occluded gases in the steel industry. Sir Henry Bessemer<sup>78</sup> in a paper in the Journal of the Iron and Steel Institute in 1881, refers to his original observation in 1856, that large quantities of carbon monoxide are given off when iron is heated in Alleman and Darlington<sup>79</sup> also found that vaculo. large quantities of carbon monoxide and nitrogen were absorbed by iron alloys. Graham<sup>80</sup> found that meteoric iron contained about 0.3 volumes of nitrogen. Neumann<sup>81</sup> reported a considerable absorption of nitrogen by iron, amounting to as much as 21.03 mg. perbloo grams of iron at 981°C. After this the solubility decreases This is presumagain as the temperature is raised. ably a case of chemical action rather than one of true Falcke<sup>82</sup> found that carbon monoxide is solution.

23.

absorbed by iron at 500 to 600°C. Ryder<sup>66</sup> stated

that nitrogen was not absorbed at high temperatures.

He found that carbon dioxide was absorbed. Carbon mon-

oxide is absorbed but decomposes above 900°C.

Mond, Ramsay and Shields<sup>83</sup>

liscovered that platinum black gave up oxygen and carbon

dioxide on heating. The carbon dioxide, however, may have been due merely to the oxidation of organic matter present in the platinum black.

Sieverts and Krumbhaar<sup>62</sup> found that carbon monoxide and carbon dioxide were absorbed by copper and that carbon monoxide was absorbed by nickel. Nitrogen was not absorbed by gopper, nickel, iron or silver. Caron<sup>••</sup> reported that molten copper absorbed carbon monoxide and spitted on solidification. Sieverts and Bergner<sup>85</sup> observed the solution of sulphur dioxide in copper and in alloys of copper with gold, silver, of platinum. They said that it seemed to form Cu<sub>2</sub>S and Cu<sub>2</sub>0 Soret<sup>86</sup> found that electrolytic copper contained a small amount of carbon dioxide and carbon monoxide, with a considerable amount of hydrogen.

Berthelot<sup>87</sup> stated that nitrogen was absorbed by the rare earth metals. This is a case of chemical action, however, the nitride of the rare earth metal being formed.

Bolton<sup>88</sup> found that niobium absorbs nitrogen and oxygen but this is also a case of chemical combination.

24.

#### A large number of observers have

found that the rare gases, helium, neon, etc., are not absor-

bed by metals. Nitrogen also is not absorbed, except

in cases where a well defined compound is formed.

In the case of metals used as

electrodes in discharge tubes however, the majority of gases, including nitrogen and helium, are absorbed. Thus Chrisler<sup>89</sup> found that in vacuum tubes the following metals absorbed gases ÷

> Silver....H<sub>2</sub> Mercury....H<sub>2</sub>,He Sodium....H<sub>2</sub>,He,N<sub>2</sub> Potassium....H<sub>2</sub>,N<sub>2</sub>

Soddy and Mackenzie<sup>75</sup> found under the same conditions that aluminium, silver and sodium absorbed hydrogen, helium, Mey<sup>51</sup> reported that carbon monoxidevand nitrogen. sodium and potassium absorb nitrogen and hydrogen when Vegard<sup>90</sup> found that 0, HCl, used as cathodes. HBr Mand H were absorbed by cathodes of varbous mater-Skinner<sup>30</sup> observed the absorption of hydroials. gen and nitrogen, but not helium, by aluminium and magnes-Bolton<sup>44</sup> found that a tantalum cathode ium anodes. absorbed hydrogen, oxygen and nitrogen. Hodgson<sup>31</sup> found that various gases were absorbed in Giessler tubes:

> Oxygen.....by Al,Cu,Zn,Be Hydrogen....by Zn,Al,Cu,Pb Nitrogen....by Al,Cu,Pb

#### Helium.....by Cu,Al.

#### The conditions in cases of ab-

sorption such as this are however, entirely different from

the ordinary cases, and the results are not comparable. The absorption in these cases has been explained in a

variety of ways. Vegard claims that the gas is absorbed by the disintegrated particles of the cathode. Hodgson, and Soddy and Mackenzie explain it on much the Riecke<sup>91</sup> claims it is due to the occsame basis 😁 lusion of the gas in the cathode itself. Mey says that the gas 'attacks the cathode chemically. Skinner, Hodgson, and Chrisler claim that the phenomenon is due to the chemical ar mechanical action of the Willows<sup>93</sup> suggests that the gas gas on the anode. acts chemically on the glass. He found that the absorption was greatest with soda glass, less with lead glass and least with Jena glass. Swinton<sup>94</sup> suggests the occlusion of the gas by the glass. Hill<sup>95</sup> explains it by the chemical action produced by the formation of active nitrogen due to the discharge.

#### The Absorption of Oxygen.

In addition to hydrogen and the other gases previously mentioned, the absorption of oxygen by metals has aroused considerable interest. Graham<sup>3</sup> found that the following metals absorbed oxygen:

26.

Other silver samples varied, one giving as much as 8.0 volumes of 0

Neumann<sup>96</sup> found the following

absorptions:

The platinum group of metals

have been investigated in some detail by Mond, Ramsay and Shields<sup>97</sup>. They found no absorption of oxygen by platinum foil at a white heat. Platinum sponge gave up 2.1 volumes of oxygen on heating. Platinum black gave up oxygen and carbon dioxide, the carbon dioxide apparently being derived from organic matter. Most of the oxygen came off between 300 and 400°C. The absorption of oxygen increased with increasing temperature and pressure. They also determined the heat of occlusion of oxygen by platinum. With palladium they found an absorption of 969 volumes. This did not come out in vacuto at a red heat, so that it is no doubt due to oxidation, probably the oxidation of dissolved hydrogen.

27.

## Engler and Wohler<sup>98</sup> state that

platinum probably forms a true compound with oxygen, similar to palladium, or else a mixture of compounds, PtO and PtO<sub>2</sub>.

## Lucas<sup>99</sup> attributes the absorp-

tion of oxygen by platinum to the presence of iridium. He says that pure platinum absorbs no oxygen. Magnus<sup>100</sup>, however, claims that platinum, palladium and iridium all absorb oxygen.

Goldstein<sup>101</sup> says that the platinum electrode of a Geissler's tube rapidly absorbs oxygen when at a red heat.

Kern<sup>102</sup> found that a small amount of oxygen 0.025 to 0.05 volumes is absorbed by This is given up on heating in vacuuo. steel. Graham<sup>3</sup> obtained 2.8 volumes of gas containing about 4% oxygen, by heating a sample of meteoric iron in vacuto.

Regnault<sup>103</sup> states that mercury dissolves a small amount of oxygen. Amagat<sup>104</sup>. however, found no evidence of this between 0 and 100° even at a pressure of 420 atmospheres. Matthiessen and Vogt<sup>105</sup> say that as silver when molten absorbs oxygen and spits on solidifying, and mercury does not spit on solidifying, therefore mercury does not ab-This evidence is obviously not of sorb oxygen. much value.

28.

## Leblanc<sup>106</sup> says that molten

litharge absorbs oxygen and gives it up on solidifying.

#### The results with oxygen and

silver are conflicting.

Molten silver has been known for a long time to absorb oxygen from the air and to 'spit' it out again on solidifying. This fact was first mentioned by Suetonius in the 1st Century. Lucas in 1819 showed that it was due to oxygen. One year later Chevillot<sup>107</sup> found that 8 grams of silver gave up 7.8 c.c. of oxygen on solidifying. Later Gay Lussac found that 22 volumes were given Levol<sup>109</sup> discovered that if 1/3 its out. weight of gold were added to the silver when molten, the oxygen was given up and the silver did not spit on solidification. Chevillot found that 15% of copper would also prevent the spitting. Hautefeuille and Perrey<sup>108</sup> found that the metal also spits in an atmosphere of phosphorus vapour.

Sieverts and Hagenacker<sup>110</sup> investigated the solubility of oxygen in molten silver quantitatively. They found that about 20 volumes were absorbed. The absorption decreases as the temperature increases, being greatest at the melt-The amount of gas absorbed was found ing point. to vary as the square root of the pressure, pointing to the solution taking place as atomic oxygen or as

29.

Donnan and Shaw<sup>111</sup> verified the results Ag\_O. of Sieverts and Hagenacker.

Dumas<sup>112</sup> was the first to show that a portion of the oxygen is retained by the metal He obtained 57 c.c. of oxyon solidification.

gen from 1 kilogram of silver in six hours at 500 to 600°. No more came out at higher temperatures even on prolonged heating.

Brauner<sup>113</sup> showed that the silver prepared by Stas' method contains very little oxygen,(0.04 volumes), and that it had no influence on the atomic weight determinations of Stas. Richards and Wells<sup>114</sup>, however,

showed that the silver contained about the amount which had been found by Dumas, i.e. from 0.6 to 1.8 volumes of oxygen.

Plattner from experiments on the action of oxygen on silver made in 1856 concludes that at ordinary temperatures solid silver has very little affinity for oxygen, but at moderately high temperatures silver is oxidised by gaseous oxygen, and the silver oxide which is formed at that temperature is volatile, while at lower temperatures the oxide is resolved into silver and oxygen. He adds that spitting is more likely to be due to the solution of  $A_{5_2}$ O in the silver than to O<sub>2</sub> itself. There are three possible cases as pointed out by

30.

## Donnan and Shaw<sup>111</sup> :

(1). If the gas is dissolved as  $O_2$  and if Henry's Law of Absorption be valid, the concentration of the

dissolved oxygen will be proportional to the partial

pressure of this gas, provided the molecules have the

same complexity in the gaseous and liquid states, i.e.

diatomic molecules, In that case the partial pressure of the free oxygen and the concentration  $C_{o_3}$ of the gas in the solution will be in equilibrium when  $p = K_1 C_{o_3}$ , where K is a constant. Hence  $\frac{p}{C_{o_3}} = K_1$ 

i.e. the absorption varies as the pressure. This is  
not true. Hence the oxygen is not dissolved as 
$$0_{g}$$
,  
(2). Suppose the dissolved gas is in the atomic  
condition. We have the equilibrium  $0_{g} \neq 20$ .  
Then by the law of Mass Action,

$$C_{\circ_2} = K_2 C_2^2$$

but Henry's Law is valid for the dissolved diatomismolecules of oxygen. Hence

 $p = K_{1}C_{0} \text{ or } p = KC_{0}^{2}$ where K is a constant equal to K K 12. This is in agreement with the results of Sieverts and Hagenacker and of Donnan and Shaw. (3). If the oxygen is present as Ag<sub>2</sub>0, we have  $Ag_{2}0 = 2Ag + 0$ and

0<sub>2</sub> = 20.

So that as before the absorption varies as the square

root of the pressure. Hence we cannot distin-

guish between combination to form  $Ag_{\mathbf{g}}$  and solution of oxygen in the atomic state.

Donnan and Shaw suggest that

silver melted in air is a dilute solution of Ag<sub>2</sub>O and is stable in spite of the high dissociation pressure of the oxide; on account of its small concentration. As the metal solidifies, the silver oxide virtually insoluble in the solid silver, is rejected from solution and dissociates explosively, causing the mass to sputter.

Some support is lent to this view by the comparison between copper, silver, and gold. As Donnan and Shaw remark, 'It is interesting to compare the solubilities of oxygen in copper, silvery and In the case of copper the solid oxide Cu 0 gold. can separate from the solution, since the dissociation pressure of Cu O at the melting point is quite low. In the case of silver, the solid phase Ag 0 cannot separate owing to its very great oxygen dissociation pressure, although Ag 0 can probably exist in dilute solution in molten silver. Finally in the case of gold, the affinity between this metal and oxygen has become so low that even a very dilute solution of gold oxide in the molten gold would correspond to

32.

an oxygen pressure many times greater than that of

the atmosphere. This comparison may perhaps lend

more support to the view that the oxygen present in

- molten silver exists as dissolved silver monoxide."
  - The ability of solid silver to

take up oxygen at a red heat was first cited by Graham<sup>3</sup> in his classical investigation. The quantity of oxygen occluded varied with the form of the silver, silver wire occluded 0.75 volumes, silver reduced from the chloride 0.9 volumes, and heavy rolled silver 1.4 volumes. Silver reduced from the oxide took up as much as 6 to 8 volumes of oxygen. For a similar preparation, Neu-

mann<sup>5</sup> found 4.1 to 5.4 volumes.

In their investigations on the specific gravity of the metal Kahlbaum and Sturm<sup>115</sup> found that a silver wire glowing in air showed an increase in weight due to the absorption of oxygen, but they note that on additional heating in vacuto the weight did not change any further.

A small absorption of oxygen by silver was finally established by Berthelot<sup>116</sup>. He heated silver foil from 200 to 500° in a sealed tube with oxygen.

Guye and Germain<sup>117</sup> and Baxter and his co-workers<sup>118</sup> have measured the occlusion of gases by silver from the point of view of their effect on atomic weight determinations. Baxter found that the gases totalled 0.00063% of the silver by weight. The work of Lewis<sup>119</sup> shows that if the absorption of oxygen is due to the formation of Ag<sub>g</sub>O, the silver oxide must be rendered stable by solution as it is existing under pressures far less than its dissociation pressure.

33.
Sieverts<sup>20</sup> obtained an absorp-

tion of about 0.3 volumes of oxygen by silver. The gas came out again on heating in vacuuo. His results, however, are not in agreement with one another and are far from conclusive. He says It seems as if the silver wire used took up both onygen and hydrogen, in either case only a fraction of the volume.''

#### The Absorption of Gases by Charcoal.

In addition to metals it has been shown that charcoal can absorb large quantities of gases. The amount absorbed increases very largely as the temperature is lowered. It is probable that adsorption here plays the principal part. The conditions here are however so different from those existing when a gas is absorbed by a metal, that we will not deal further with the subject.

#### The Diffusion of Gases through Metals.

Side by side with absorption and undoubtedly fundamentally connected with it is the phenomenon of the diffusion of gases through

The first instance of the diff-

usion of gases through metals mentioned in the lit-

erature is that of hydrogen through platinum which

was investigated by Deville and Troost<sup>120</sup> in 1863.

They found that hydrogen diffused through a platinum

tube 1 mm. thick at high temperatures.

They also found that the same gas would diffuse readily through iron<sup>121</sup>. Deville, to explain this phenomenon assumed that heat caused dilatation of the intermolecular spaces in the metal, resulting in Na porosity.

Cailletet<sup>122</sup> noticed that iron plates dipped into sulphuric acid became covered with blisters. These blisters were found to contain pure hydrogen. This is probably due to the fact that nascent or atomic hydrogen can diffuse at ordinary temperatures, while the molecular form will only diffuse at higher temperatures. The effect was not observeable with zinc.

Winkelmann<sup>123</sup> used an iron tube as a cathode in an electrolytic cell and got a very great diffusion of hydrogen into the tube.

Ryder<sup>66</sup> has investigated the diffusion of gases through iron fairly accurately. Carbon monoxide showed a chemical reaction above 950°C. Argon would not diffuse at temperatures up to 1100°. Hydrogen diffused appreciably at 200°, carbon monoxide at 400°, and nitrogen at 600°. The rate of diffusion of hydrogen was much greater than

35.

in the case of the other gases. The log. of the

rate of diffusion plotted against the log. of the

absolute temperature gave a straight line.

In the meantime the investigation of diffusion had been extended to other metals. Graham found that carbon dioxide, air, chlorine, hydrogen chloride and water vapour would not doffuse through platinum. Ammonia and hydrogen sulphide would not diffuse, but they were decomposed and the hydrogen passed through. Hydrogen was found to diffuse extremely rapidly through palledium. Graham considered that diffusion was preceded by liquefaction of the gas in the metal.

Ransay<sup>125</sup> in 1894, also investigated hydrogen and palladium. He discovered that the hydrogen as it leaves the metal is in an active state.

Richardson<sup>186</sup> examined the results

of other investigators theoretically and deduced a formula connecting thickness, pressure, temperature, and rate of diffusion. Together with Nicol and Parnell, he investigated the diffusion of hydrogen through palledium and obtained results in good agreement with his formula<sup>127</sup> The rate of diffusion was found to be proportional to the square root of the pressure.

36.

An extensive investigation on вł. the diffusion of hydrogen through palladium was made by Holt, Edgar, and Firth<sup>128</sup>. The experiments were carried out over a wide range of pressures. They were unable to find any relation between the pressure and the rate of diffusion. Drying the

hydrogen had no effect. The diffusion velocity varied with the physical state of the metal. They conclude that adsorption takes place prior to diffusion.

The diffusion of oxygen through silver was first mentioned by Troost<sup>129</sup>. Troost's work was not, however, very accurate.

Spencer<sup>130</sup> has recently measured the diffusion His results are fairly accurate and are in good agreement with those of Johnson and Larose<sup>1</sup> which are discussed later.

Sieverts<sup>20</sup> measured the rate of diffusion of a number of Gases through metals. He detected the diffusion of hydrogen through copper and nickel, and of oxygen through silver. He was unable to detect any diffusion of nitrogen . His apparatus was by no means sensitive and his results can only be taken as qualitative evidence of diffusion.

Lombard<sup>131</sup> and Deeming and Hendrics<sup>132</sup> have investigated hydrogen and nickel fairly accurately.

#### The only really accurate and

trustworthy investigation of the diffusion of gases

through metals is that of Johnson and Larose<sup>1</sup>.

They investigated the diffusion of oxygen through

silver of various thicknesses, from 375 to 650°C, and pressures of 15 to 76 cms. They found that the rate of diffusion was inversely proportional to the thickness, proportional to the square root of the pressure, and varied with temperature according to an equation of the form

 $D = A T^{\frac{1}{2}} e^{\frac{-b}{T}}$ 

where A is a constant

b is a constant

T is the absolute temperature

D is the rate of diffusion.

From their work they conclude that diffusion is preceded by dissociation of the gas. Their results will be discussed in detail later.

From the foregoing it is evident that the existing data on the absorption of gases by metals are highly inconclusive and contradictory. The only metals which have been investigated thoroughly are those of the platinum group. These, however, absorb such a large quantity of gas and behave

so differently from other metals that the results obtained are not comparable. As the phenomena of absorption and diffusion are apparently related to one another, it was considered of interest to investigate some metal of which the rate of diffusion had been accurately measured. In view of Johnson and Larose on silver, this metal was chosen for the absorption measurements. Accordingly a suitable apparatus has been devised and the absorption of oxygen by silver has been measured under varying conditions of temperature and pressure.

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#### III. DESCRIPTION OF APPARATUS AND EXPERIMENTAL PROCEDURE.

In principle the apparatus is extremely simple. A known volume of gas is introduced into a bulb of known volume which contains silver foil and which is connected to a manometer. At any temperature the pressure of the gas in-the bulb can be calculated from the gas laws. If any absorption takes place, the observed pressure will be less than the calculated value and the difference between the two pressures will be a measure of the absorption.

The apparatus as finally used is shown in Figure 7.

Three bulbs A, By and D are con tained in an electric furnace F, which is described The bulb A leads to a thermal regfully later. ulator D is part of a constant-volume gas thermometer. Both of these are described later. The third bulb B contains silver foil. All three bulbs are of Pyrex glass and are connected to the remainder of the apparatus, which is made of ordinary soft glass, by means of de Khotinsky cement. The bulb containing the silver is connected through the tap E with a manometer IJ. A pointer M is sealed into the top of the By means of the taps H and K either tube, J', the silver bulb or the gas thermometer may be connec-





## ABSORPTION APPARATUS.

ted to the manometer. The volumes of the tube J from the pointer  $M_{1}$  to the tap E the tube from the tap to the furnace and the bulb containing the silver are all known.

The tube  $\sqrt{J}_{A}$  is connected to one arm of a two-way taplo. The other arm of the tap leads through a phosphorus pentoxide tube to the gas reservoir R. The tube, S, leads to another twoway tap, U. One arm of U leads to a mercury container W, and the other leads through three phosphorus pentoxide tubes to the gas supply  $\sqrt{J}_{A}$  and the pumping system Y. The bulb  $\sqrt{J}_{A}$  is inserted to catch any mercury which may inadvertently be let through the tap  $\sqrt{U}_{A}$ .

In carrying out an experiment, the bulb containing the silver is connected to the pumping system by means of the taps  $E_0, U_1$  and  $Y_1$ , and the whole system is evacuated thoroughly. The taps,  $E_1$  and  $O_1$  are then closed. The tap,  $U_1$  is turned so as to connect S with the mercury reservoir  $W_1$  and mercury rises in S and completely fills it. The tap,  $O_1$  is then turned so as to connect S to the gas

41.

reservoir, R, the mercury reservoir is lowered and gas is drawn into S. S is then connected to the manometer tube J by means of the tap O and the mercury reservoir is raised, forcing the gas into J. The mercury is allowed to run up the tube after the gas till it takes up the position shown in the figure. The tap/0, is then closed, K is openedy and the tube J is thus connected to the manometer. The mercury is brought up to the lower pointer, Ny and the pressure is read in I. The volume of the tube from N to E is known (7.175 c.c.), the temperature of the room is read, and the volume of the gas in J can be calculated and corrected to Standard Conditions.

The tapyENs opened and the gas In The mercury level is admitted to the bulb B. is brought up to the pointer, My and the pressure read. The temperature of the furnace is determined by means of the gas thermometer. The pressure in the bulb falls until equilibrium is reached and then remains The absorption is then calculated as constant. described later under sample calculation

The temperature is then altered and the equilibrium pressure again determined. In this way a series of observations can be made at different temperatures without changing the gas in the bulb.

#### Measurement of Temperature.

The temperatures were measured

42.

by means of the ordinary type of constant-volume gas The bulb, D, of known volume, was thermometer. filled with 'nitrogen. The volume of the dead space from the pointer Gto the furnace was deter-In order to make a reading the  $tap_{H_{\pm}}$ mined.

is opened and the thermometer connecter to the manometer. The mercury level is then brought up to the pointer and the pressure read. The temperature of the room is also read.

- Then if V<sub>d</sub> is the volume of the dead space (from the pointer to the furnace),
  - V<sub>b</sub> is the volume of the bulb, D, and the tubing in the furnace,
  - T is the temperature of the dead space, i.e. room temperature,

$$P\left(\begin{array}{ccc} V_{b} + V_{d} \\ T_{b} + T_{d} \end{array}\right) = K$$

In the experiments made at lower temperatures, the bulb D was of Pyrex glass.

 $V_{b} \text{ was } 13.001 \text{ c.c.}$   $V_{d} \text{ was } 1.520 \text{ c.c.}$ The pressure P at 292°K was 30.45 cms, whence K = 1.514, so that P  $\left\{ \begin{array}{c} \frac{13.001}{T_{b}} + \frac{1.520}{T_{d}} \end{array} \right\} = 1.514$ 

Hence if the pressure and the temperature of the room are known, the temperature of the bulb can be calculated.

#### The thermometer was checked at

 $0^{\circ}$ C by means of melting ice, and at the boiling point of water. It agreed to within  $0.2^{\circ}$  at  $0^{\circ}$  and to  $0.15^{\circ}$  at  $100^{\circ}$ .

In the later experiments at higher temperatures the bulb of Pyrex glass was replaced by one of quartz. For this thermometer the equation was

$$P\left(\begin{array}{c} \frac{9.891}{T_{b}} + \frac{1.197}{T_{d}} \right) = 0.8460$$

This was checked as follows,  $0^{\circ}C....ice-water....error = 0.0^{\circ}$   $100^{\circ}C...boiling water...., , = +0.1^{\circ}$   $444.71^{\circ}C..boiling point of sulphur ,, = -0.1^{\circ}$ . Hence the temperatures are certainly accurate to within 1°.

In calibrating the thermometer at the boiling point of sulphur, the bulb was shielded by an asbestos cylinder and the procedure recommended by Meissner<sup>133</sup> was followed. Unless such precautions are taken, the observed value for the boiling point of sulphur may be two or three degrees out.

#### Electric Furnace.

#### The ordinary type of electric

furnace consisting of a platinum winding on a por-

celain tube was not found to be satisfactory. The

space in such a furnace is usually very limited, the temperature varies considerably along the furnace,

and also varies from the centre to the wall. The furnace shown in figure 2 was therefore constructed. A 15 inch length of 2 1/2 inch

iron pipe G, with a screw cap on the lower end, served as the interior tube. This allowed ample space for the three bulbs, and the high heat conductivity of the iron ensured an even temperature throughout. The iron tube was covered with

a layer of asbestos papers on which was wound 18 gauge wire the turns being about 1/4 inch apart. This was covered with another layer of asbestos paper.J. The tube was placed in a galvanized iron contained of about 8 inches diameter and packed in with loose as-A sheet of 1/4 inch asbestos board was bestos,H. used as a cover(E). After the glass or quartz tubes used in the experiments had been placed in position, the top of the furnace was completely covered with a layer of asbestos cement'. This made a practically air-tight cover and besides cutting down the heat los prevented oxidation of the iron pipe. After two years of use the furnace was still in perfect condition. The furnace would maintain a temperature of 1000°C with a current of 6 amperes at 110

45.

volts.

#### Temperature Regulation.

#### The thermal regulator used is



shown in FigureIII. The bulb B filled with air, is connected by capillary tubing to a small U-tube

into which are sealed two platinum electrodes E, and G, The U-tube is filled with mercury. When the furnace becomes too warm, the mercury is driven up and makes contact with the upper electrode. This short circuits the two electrodes and current passes through the relay, J. This pulls up the contact, K, and the resistance, N, which had been short circuited by the contact, K through the mercury cups, Ly is placed in the furnace circuit, cutting down the current to When the furnace cools down too far, the furnace. the contact at E is broken. Current ceases to flow through the relay, the contact, Kidrops down, and the extra resistance N is short circuited, thus increasing the current in the furnace. The extra resistance was adjusted so as to cut out about 10% of the total current being supplied to the furnace.

The resistance I of about 8 ohms, was placed across the terminals of the relay in order to eut down sparking. Current flows through this

continuously. When the relay is in operation, most of the current goes through the relay and only a little flows through the resistance, I due to the how resistance of the relay (2 ohms). When the relay is cut out the entire current goes through the





## THERMAL REGULATOR.



resistance. The result is that a spark is not formed at E,until the resistance of the spark gap is less than I,i.e. 8 ohms. Hence sparking is almost entirely eliminated.

In practice, the  $tap_{M}H_{M}$  is left open and the furnace is brought to the required temperature. The tap is then closed and the regulator comes into operation. By means of this regulator the temperature could be kept constant to within 1 to 2 degrees **G**entigrade.

#### Pumping System.

At the conclusion of an experiment, the tap K was shut and E opened (Fig. I). The twoway tap, 0, was then turned so as to connect the tubes J and S and the tap U so as to connect S to the mercury reservoir W. The reservoir was lowered and the mercury in J and S allowed to run out. Both two-way taps and the tap X were then turned so as to connect the bulb containing the silver to the pumping system, Figure IV.

The pumping system consisted of a first and a second stage Langmuir Mercury

Vapour Condensation Pump, B, and D, backed up either by a Hyvac Pump or, if it was desired to collect the gas pumped out, by a Toepler Pump, H. A M'Leod Gauge was used to indicate the pressure(M). If the tap F was opened and J shut, the Hyvac pump served as the forepump. If the reverse was the case the Toepler Pump was used. By opening or shuting K or L , the M Leod Gauge could be connected either to the line on the far side of the Langmuir Pumps and thus register the pressure in the apparatusyor to the Toepler Pump.

The M'Leod Gauge was sometimes used to measure the gas pumped out To accomplish this the tap U (Fig.I.) was left closedy and the system from there over was evacuated with the Langmuir and Hyvac Pumps. The tapyFywas then turned, cutting out the Hyvac Pump. The M'Leod Gauge was connected to the Toepler Pump and the The tap U (Fig. I ) was then pressure read. opened and the Langmuir Pumps were allowed to pump the gas in the bulb over into the Toepler Pump and Then, knowing the volume of the Toepler Gauge. Pump and Gauge, the volume of gas pumped out could be calculated. Usually, however, the quantity of gas to be measured was too large to be indicated on the M'Leed Gauge. In this case the apparatus described in the next section was used.

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If it was desired to collect

the gas pumped out the Hyvac Pump could not be used. In this case the whole system was first evacuated. It was then connected to the apparatus and the gas pumped into the Toepler by means of the Langmuir A small glass tube I (Fig.IV) filled with mercury, was then inverted over the open end of the discharge tube of the Toppler Pump. The pump was operated and the gas pumped out was collected in the tube by displacement of mercury.

By means of the Langmuir Pumps a pressure as low as 0.000001 m.m. of mercury could be obtained. (This does not include mercury vapour as it would not be indicated on the M'Leod Gauge.)

#### Gas Measuring Apparatus.

In those cases where the volume of gas to be measured was too large to be indicated on the M'Leod Gauge, the gas was pumped out and collected as described in the preceding section. It was then measured in the apparatus shown in Figure V.

The apparatus consisted of a

manometer tube, E, connected through the tap, F, to the tube, C, which contained a sealed in glass pointer, D. The lower end of this tube was connected through the tap, H, to a mercury reservoir, I. To the upper end of the tube, C, was sealed a capillary tube, bent

as shown in the figure, and containing the tap, B.

The volume from the pointer to the tap, B, was known,

( 3.382 c.c.). The open end of the capillary

tube dipped under the surface of mercury contained

in the reservoir,A.

In order to transfer the gas pump-

ed out to this apparatus, the open end of the small glass tube (Fig.IV) was immersed in a crucible filled The tube and crucible were then with mercury. placed under the surface of the mercury in Ayand the crucible was withdrawn The tube was then placed over the open end of the capillary. The tube  $\chi C_{\chi}$  and the capillary tube were at this stage entirely filled with mercury. The taps, B, and H, were opened and F closed and the reservoir I was lowered. The glass tube was pushed down till the top touched the point of the capillary tube; the gas was thus sucked over into C. When all the gas was in  $C_{\chi}$  the tap, B, was closed and F opened. The mercury surface was then brought to the pointer and the pressure was read in E. Then knowing the volume, pressure and room temperature, the volume of the gas under standard conditions could be calculated.

At the conclusion of each experiment the volume of gas pumped out was measured and compared with the volume of gas originally admitted to the bulb. In this way any leak could be detec-

50.

tedy and it could be ensured that all the gas absorbed by the metal had been removed. If, in any experiment, the initial and final volumes did not agree, the results were discarded.

#### Silver.

The silver used was in the form

of foil, of a thickness of about 0.15 m.m. Samples 1 and 2 were commercially pure silver. Analysis showed them to contain 0.02 % copper 0.001 % iron

0.005 % lead.

The presence of tin.bismuthyand antimony could not be detected in a 5 gram sample.

For samples 3 and 4 the above silver was further purified as follows<sup>134</sup> ÷

The metal was dissolved in nitric

acid and the solution was diluted with water and allowed to settle so that gold, tin, and antimony oxides, basic bismuth nitrate, silver sulphide, etc., would coagulate and permit the solution to be filtered. Silver chloride was precipitated from the filtered solution by the addition of hydrochloric acid. The silver chloride was boiled with hydrochloric acid and washed with hot distilled water until free from acid. It was then reduced to the metal by boiling it with a solution of invert sugar and sodium hydroxide.

The precipitate was thoroughly washed with hot distilled water and fused to a button in a crucible under borax. The button was cleaned by scrubbing it with sand and was then rolled into sheets 0.15 m.m. thick. The purified silver gave on analysis-- 0.004 % copper 0.001 % lead

with a trace of iron.

#### Nitrogen.

The nitrogen used was the ordinary commercial variety supplied in cylinders. The gas was bubbled twice through alkaline pyrogallate to free it from oxygen, then twice through concentrated It was finally stored in the gas sulphuric acid. reservoir over phosphorus pentoxide.

#### Oxygen.

The oxygen was also the commer-It was treated in the same manner cial variety. as the nitrogen except that the pyrogallate wash bottles were omitted.

#### Calibration.

The various parts of the apparatus, except the bulb containing the silver, were calibrated by weighing when filled with mervury. The

silver bulb was weighed when filled with distilled

water.

#### Experimental Procedure.

Prior to making an experiment, the furnace was raised to a temperature of about 550° C in the case of Pyrex glass apparatus, or 750° with The temperature was kept constant and quartz. the bulb was evacuated continuously for 6 to 8 hours. The tap between the bulb and the remainder of the apparatus was then closed and the silver allowed to remain in vacuuo over night. The next morning the bulb was again pumped out for about an hour.. The tap was then closed and gas from the reservoir was admitted to the tube and measured as previously des-The gas was then admitted to the bulb and cribed. after equilibrium was attained, the temperature and pressure were read. At high temperatures equilibrium was reached rapidly. At temperatures of 200° or less several days were required for equil-After equilibrium had been reached ibrium.. the temperature was altered, the bulb was allowed to stand till equilibrium had again been reached, and another reading was made.

At the higher temperatures, in

some cases, the temperature was kept constant, and

after each reading more gas was admitted. In

this way a series of observations at different press-

ures and the same temperature were made.

At the conclusion of an exper-

iment, the gas was pumped out of the bulb and measured; and the amount compared with the amount originally let in.

The long continued pumping out is absolutely essential in order to obtain consistent results. The last traces of the gas are only rexmoved very slowly from the silver. This point has, however, been overlooked by the majority of investigators.

#### <u>IV. PRELIMINARY RESULTS.</u>

The form of the apparatus described above is the final form in which it was used, and with which the results given here were obtained. Preliminary results were obtained with a simplified form of apparatus but they were not in good agreement with one another. This necessitated various changes.

Originally, a quartz, nitrogen filled, mercury (1).This, however, had a differthermometer was used. ent lag from that of the gas in the bulb and thus introduced an error. A still more serious error was due to the fact that as the bulb of the thermometer was small, it registered the temperature at one particular part of the furnace only. As the bulb containing the silver was much larger, if there were any uneveness in the temperature of the furnace, a fairly large error would be introduced. This error was serious because an accurate knowledge of the temperature is needed in order to calculate what the pressure would be if there were no absorption. The mercury thermometer was accordingly replaced by

a gas thermometer. The bulb of the gas thermometer

was made of they same size and shape as the bulb con-

taining the silver, and was placed next to it in the furnace. The result was that if there were any

tempefature variation in the furnace, the gas thermometer would indicate the mean temperature of the silver bulb, which is what is required for purposes of calculation. The use of the gas thermometer, therefore, automatically compensated for any irregularity in the temperature of the furnace.

(2). At first only the Toepler Pump was used in evacuating the bulb. The Langmuir Condensation Pumps, however, by giving a much higher vacuum, materially decreased they time necessary to pump all the gas out of the silver.

(3). Originally the tap between the silver bulb and the short arm of the manometer was left open during an experiment. It was found, however, that there was a very slow , steady drop in pressure amounting to about 1 m.m. per day. The only possible cause appeared to be oxidation of the mercury. This idea was supported by the fact that there was a small reddish brown deposit on the walls of the capillary tube just outside the furnacd.

A blank experiment was tried with an empty bulb and it was found that about 0.1 c.c. of gas disappeared in 10 days, but no oxidation was detectable if the bulb was kept at room temperature. This is presumably due to the oxidation of mercury vapour in the bulb. The oxide then distills out and condenses in the colder part of the apparatus, more mercury vapour diffuses in, and the process goes on continuously. By keeping the tap between the bulb and the nercury surface closed, the difficulty was overcome and no further drop in pressure was noticed.

(4). A further difficulty was met with in connection with the use of tap grease on the tap mentioned above. Blank experiments showed a slow but appreciable absorption of oxygen by the ordinary type of grease, consisting of rubber, paraffin, and vaseline. Vaseline alone showed no appreciable absorption, but it is not sufficiently viscous. A mixture of paraffin and vaseline was used and gave satisfactory results.

V. SAMPLE CALCULATION.

In order to illustrate how the calculations are carried out, one of the tables from the next section is given below.

#### TABLE XIX.

Tr <sup>o</sup> C	Ther. cms.	Press cms.	T°C	T <sup>o</sup> K	Press calc.	Press diff.	c.c. abs.	Vols. abs.
24.0	66.87	76.56	473	746	81.81	5.25	0.190	0.098
24.0	60.35	72.27	381	654	76.60	4.33	0.167	0.086
24.5	54.90	67.99	307	580	72.00	4.01	0.177	0.092
24.0	46.75	59.45	204	477	64.40	4.95	0.232	0.120

As shown above, the gas let in at the beginning of the experiment was sufficient to event a pressure of 34.40 cms in the tube from the



C.C.

Now the total volume of the

bulb and the dead space (from the upper pointer to the furnace ) is 5.222 c.c., hence at room temperature the above volume of gas would exert a pressure of  $\frac{3.240}{5.222} \times 76 = 47.30$  cms.

We have here a volume of gas the different parts of which are at different temperatures, but which is all at the same pressure. Now, from the Gas Laws,

$$\sum \frac{\underline{P} V}{\underline{T}} = \sum \frac{\underline{P} V_1}{\underline{T}_1} = K$$

Or, denoting the volume of the bulb by  $V_{b}$ , the volume of the dead space by  $V_{d}$ the temperature of the bulb( $^{\circ}K$ ) by  $T_{b}$ the temperature of the dead space (room temp.) by  $T_{d}$ the pressure of the bulb and dead space by P, we have,

$$P\left\{\begin{array}{ccc} V & V \\ \frac{b}{T_{b}} + \frac{d}{T_{d}} \right\} = K .$$

Or, inserting the actual values of  $V_b$  and  $V_d$  in this case,

$$P(\frac{3.668}{T} + \frac{1.554}{T}) = K.$$

# This equation will hold for any mass of gas in this

apparatus.

#### Now in this case at room temp-

#### erature, i.e. when the whole apparatus, bulb and dead

space, is at 24.0°C, the pressure would be 47.30 cms. Hence we can evaluate K for this particular amount of gas, (-3.668 - 1.554)

$$47.30\left(\begin{array}{c}3.668\\-297\end{array}+\frac{1.554}{297}\right) = \mathbb{R}$$

$$K = 0.830$$

Hence for this experiment we have the equation,

$$P\left(\begin{array}{ccc} 3.668 \\ \hline T_{b} \end{array} + \begin{array}{c} 1.554 \\ \hline T_{d} \end{array}\right) = 0.830$$

In the first line of the table we see that when the room temperature was  $24.0^{\circ}$ C and the gas thermometer reading was 66.87 cms, the pressure in the silver bulb was 76.56 cms. The gas thermometer reading is equivalent to a temperature of  $473^{\circ}$ C (see description of gas thermometer). Hence we have, expressing temperatures in  $^{\circ}$ K,

$$P\left(\begin{array}{ccc} 3.668 \\ - & - \\ 746 \end{array}\right) + \left(\begin{array}{c} 1.554 \\ - & - \\ 297 \end{array}\right) = 0.830 ,$$

whence the pressure which would be observed if there were no absorption is 81.81 cms.

The actual pressure observed is 76.56 cms., that is 5.25 cms.lower. So that an

## amount of gas sufficient to exert a pressure of 5.25 cms.in the apparatus (when the temperature of the bulb is 473°C and room temperature is 24°C) has disappeared. Bringing this to S.T.P., we have,

(1). For the bulb (at  $746^{\circ}$ K),

 $\frac{5.25 \times 3.668 \times 273}{76 \times 746} = 0.091 \text{ c.c.}$ (2). For the dead space (at 297°K),  $\frac{5.25 \times 1.554 \times 273}{76 \times 297} = 0.099 \text{ c.c.}$ 

Total volume of gas absorbed at S.T.P.= 0.190 c.c. The weight of silver contained

in the bulb was 20.315 grams. Taking the density of silver to be 10.5, this is equivalent to 1.93 c.c. of silver. Hence the number of c.c. of gas absorbed by 1 c.c. of silver under the conditions of the experiment is  $\frac{0.190}{1.93} = 0.098$ . That is 0.098

volumes of gas are absorbed by 1 volume of silver at 746°K and a pressure of 75.93 cms of mercury.

The calculations may be carried out in the same manner for the other temperatures shown in the table.

At the conclusion of the experiment, the gas was pumped out and measured as previously described. The volume of gas pumped out (at S.T.P.) was 2.981 c.c. The volume let in at the beginning of the experiment was 2.985 c.c.

These agree within the limit of the experimental

error, so that no leak occurred during the experim-

ent and all the absorbed gas was removed from the

silver.

<u>VI. EXPERIMENTAL RESULTS</u>

The first sample used was of commercially pure silver. It was used in a bulb constructed of Pyrex glass.

The second sample was also of commercially pure silver. The bulb used with it was of quartz. The results obtained did not agree with those obtained with the other three samples. The values obtained were very much higher and the absorption was practically independent of temperature or pressure. Apparently some oxidisable impurity was present. The results for nitrogen agreed with those obtained with the other samples and are given here. The results obtained with oxygen have been omitted.

Samples 3 and 4 were of specially purified silver and were used in quartz apparatus. In Table II are given the volumes of the bulb and of the dead space for the various samples.

#### TABLE II.

Sample	V <sub>b</sub>	V <sub>d</sub>	Apparatus	
I	3.668	1.554	Pyrex glass.	
II	7.335	1.855	Quartz	
III	7.750	1.655	<b>,</b> ,	
IV	8.301	1.574	<b>, ,</b>	

At the conclusion of the experiments with sample 1 in Pyrex apparatus, the bulb containing the silver was found to be coloured a dark brown. This was presumably due to the presence of colloidal silver in the glass. The silver lost 1.5 milligrams in weight during a period of alternate heating and cooling of about 4 months.

The quartz bulbs used with samples 2,3, and 4 all had a milky appearance. In addition to the milkiness there was a deposit of crystalline silver on the walls of the bulb. The silver after being in use for from 3 to 4 weeks lost from 0.1 to 0.2 grams.

No apparent change occurred in the silver except the development of a somewhat crystalline appearance on the surface due to the evaporation. The samples which were used at the higher temperatures sintered together to a considerable extent.

Except with sample 2 which behaved entirely abnormally, it is interesting to note that identical results were obtained with highly pure silver and with silver which contained considerably more

63.

impurity.

#### The observations are given in the

following tables and are discussed in the next section.

#### (A). RESULTS WITH NITROGEN.

#### TABLE III.

Tr	Ther cms.	Press cms.	T°C	T <sup>o</sup> K	Press calc	diff	Vols. abs.	
21.6	30.70	28.75	22.5	295.5	28.70	+0.05	-0.001	
22.6	49.42	40.94	236	509	40.80	+0.14	-0.004	
23.2	56.97	44.84	334	607	45.00	-0.16	<b>+</b> 0 <b>.</b> 004	
23.2	63.36	47.83	422	695	48.20	-0.37	+0.008	
23.2	72.95	53.07	561	834	52.70	+0.30	-0.006	

### TABLE IV.

65.

Sample 1.

Lower pointer reading	.38 cms.			
Room temperature2	21.3°C			
Volume of gas at room temperature,,,0	•933 c.c.			
Volume of gas at S.T.P	.855 c.c.			
Pressure(calculated)at room temperature.1	3.37 cms.			
K	•236			
Volume of gas pumped out (S.T.P.)0	.855 c.c.			

Tr	The <b>r</b> cms.	Press cms.	T <sup>o</sup> C	T <sup>o</sup> K	Press calc.	Press diff.	Vols. abs.	
21.3	65.13	22.65	447	720	22.80	-0.15	0.003	-
21.5	56 <b>.50</b>	20.65	328	601	20.82	-0.17	0.003	
22.0	48.84	18.75	229	502	18.83	-0.08	0.002	
17.5	30.23	13.17	17.5	290.5	13.28	-0.11	0.003	
# TABLE V.

Sample 1.

Lower pointer reading
Room temperature
Volume of gas at room temperature 0.771 c.c.
Volume of gas at S.T.P
Pressure(calculated) at room temp17.10 cms.
K0.3036

Volume of gas pumped out(S.T.P.)....0.703 c.c.

T r	Ther cms.	Press cms.	T <sup>o</sup> C	T <sup>o</sup> K	Press calc.	Press diff.	Vols. abs.
21.0	30.64	17.13	22.0	295	17.10	+0.03	-0.000
22.0	46.92	23.43	2 <b>0</b> 6	479	23.45	-0.02	+0.000
23.0	60.63	27.80	384	657	27.99	-0.19	+0.004
22.0	6 <b>6.</b> 37	29.47	465	738	29.62	-0.15	+0.003

66.

#### TABLE VI.

T r	Ther cms.	Press cms.	T <sup>O</sup> C	I <sub>O</sub> K	Press calc.	Press diff.	Vols. abs.
21.6	22.52	19.01	21.5	294.5	18.96	+0.05	-0.003
21.7	39.14	30.76	290	563	30.76	0.00	0.000
22.4	44.55	34.20	388	661	34.16	+0.04	-0.002
23.3	49.98	37.31	493	766	37.41	-0.10	0.005
24.0	54.20	40 <b>.10</b>	581	854	40.15	-0.05	0.002
24.0	59.50	43.02	701	974	43.00	+0.02	-0.001
24.1	65.85	46.29	850	1123	46.35	+0.06	-0.002

ويبهر ويترزجون المريبي بيرود مادا فبرعين المبتار في فلم بعن الفري المدواجي والمعن الكم الكموا الكما الأموي البوكالك أألف المتوري وي

# TABLE VII.

Sample 2.

Lower pointer reading14.77	cms.
Room temperature	C
Volume of gas at room temperature1.394	. C.C.
Volume of gas at S.T.Pl.295	C.C.
Pressure (calculated) at room temp11.52	cms.
K0.360	
Volume of gas pumped out (S.T.P.)l.300	• <b>C.</b> C.

T r	Ther. cms.	Press. cms.	T°C	T <sup>o</sup> K	Press. calc.	Press. d <b>bff</b> .	Vols. abs.	
21.0	22.50	11.54	21	294	11.52	+0.02	-0.001	
22.0	35.49	17.16	227	500	17.18	-0.02	0.001	
22.0	45.48	21.06	406	679	20.98	+0.08	-0.004	
23.1	53 <b>.91</b>	23.99	5 <b>7</b> 5	848	24.05	-0.06	0,003	
24.5	61.70	26.62	752	1025	26.72	-0.10	0.004	
21.2	22.52	11.53	21	294	11.52	+0.01	0.000	

# TABLE VII.

Sample 3.

Lower pointer reading17.90 cms	•
Room temperature	
Volume of gas at room templ.690 c.c	- -
Volume of gas at S.T.Pl.552 c.c	
Pressure (calculated) at room temp13.65 cms	•
K0.4355	
Volume of gas pumped out (S.T.P.)1.543 c.c	•

Tr	Ther. cms.	Press. cms.	T°C	T <sup>o</sup> K	Press. calc.	Press. diff.	Vols. abs.
24.0	47.60	26.72	446	719	26.62	+0.10	-0 <u>.</u> 002
24.2	41.41	23.63	330	603	23.60	+0.03	-0.001
23.0	35.00	2 <b>0.</b> 42	219	<b>49</b> 2	20.43	-0.01	0.000
20.4	22.40	13.53	20.5	293.5	13.50	+0.03	-0.001

# TABLE IX.

Sampl	e 3.						
Lower	pointe	r readi	ng			.28.15	cms.
Room	tempefa	ture	• • • • • •	• • • • •		.23.0°C	ů
Volum	e of ga	s at ro	om tem	perat	ure	.2.666	C.C.
Volum	e of ga	s at S.	I.P	• • • • •	• • • • • • •	.2.460	C.C.
Press	ure(cal	culated	)at ro	om te	mp	.21.53	cms.
K	• • • • • • •	•••••	• • • • • •	• • • • •	• • • • • • •	.0.685	
Volum	e of ga	s pumpe	d out	(S.T.	P.)	.2.468	с.с.
Tr	Thee. cms.	Press. cms.	T <sup>o</sup> C	T <sup>o</sup> K	Press. calc.	Press. diff.	Vols. abs.
23.0	22.50	21.39	23.0	296	21.54	-0.15	0.002
23.1	34.90	31.81	217	490	32.00	-0.19	0.002
23.0	43.02	38.21	359	632	<b>38.</b> 38	-0.17	0.001
22.5	49.40	43.21	481	754	43.15	+0.06	0.000

70.

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#### TABLE X.

Sample 4. Volume of gas at room temperature ...... 1.720 c.c. Pressure (calculated) at room temp......13.22 cms. Volume of gas pumped out(S.T.P.).....1.570 c.c. Tr TVK Press. Press. Vols. Ther Press. TC diff. abs. Cm S 🖕 calc. cms. 24.0 58.95 31.58 688 961 31.55 +0.03 0.000 24.4 51.60 28.13 528 801 28.10 -0.03 0.000 21.2 44.25 24.53 382 655 24.40 +0.13 -0.001 21.0 37.90 21.38 268 541 21.28 +0.10 -0.001 20.0 22.37 13.35 20 293 13.22 +0.13 -0.001

#### (B). RESULTS WITH OXYGEN.

#### TABLE XI.

Sample 1. Volume of gas at room temperature ..... 1.000 c.c. Pressure (calculated) at room temp.....14.53 cms. Volume of gas pumped out(S.T.P.).....0.930 c.c. Tr T<sup>O</sup>C TOK Press. Press. C.c. Vols. Press. Ther. diff. **ະຂ**ີບເຮ calc. ags. cme. cms. 728 24.63 2.26 0.083 0.043 22.0 65.65 22.37 455 21.0 59.25 20.90 365 638 23.03 2.13 0.085 0.044 509 20.30 2.62 20.0 49.36 17.68 236 C.118 0.061 22.0 71.17 22.75 535 308 25.92 3.17 0.113 0.059

# TABLE XII.

73.

Sample 1.

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Lower	pointe	r readi	ng		• • • • • • •	6.32	cms.	
Room	tempera	ture	••••	• • • • •		23.4	0 C	
Volum	ne of ga	s at ro	om te	mpera	ture	1.00	3 c.c.	
Volum	ne of ga	s at S.	T.P	• • • ū ū		0.92	бс.с.	
Press	sure (ca	lculate	d) et	room	temp	14.6	Q cms.	
K	• • • • • • •		• • • • •	• • • • • •	••••	0.25	8	
Volum	e of ga	s pumpe	d out	(S.T.	P•)		8 <b>c.c.</b>	
Tr	Ther. cms.	Press. cms.	T <sup>o</sup> C	T <sup>o</sup> K	Press. calc.	Press. diff.	C.c. abs.	Vols. abs.
T <sub>r</sub> 23.0	Ther. cms. 67.83	Press. cms. 23.24	т <sup>о</sup> с 486	т <sup>о</sup> к 759	Press. calc. 25.62	Press. diff. 2.38	C.c. abs. 0.096	Vols. abs. 0.050
T <sub>r</sub> 23.0 21.0	Ther. cms. 67.83 53.14	Press. cms. 23.24 19.68	T <sup>o</sup> C 486 283	т <sup>о</sup> к 759 556	Press. calc. 25.62 21.73	Press. diff. 2.38 2.05	C.c. abs. 0.096 0.088	Vols. abs. 0.050 0.046
T <sub>r</sub> 23.0 21.0 20.0	Ther. cms. 67.83 53.14 45.81	Press. cms. 23.24 19.68 16.97	T°C 486 283 192	T <sup>o</sup> K 759 556 465	Press. calc. 25.62 21.73 19.57	Press. diff. 2.38 2.05 2.70	C.c. abs. 0.096 0.088 0.128	Vols. abs. 0.050 0.046 0.066

#### TABLE XIII.

Sample 1. Lower pointer reading.....15.72 cms. Volume of gas at room temperature ..... 1.889 c.c. Volume of gas at S.T.P.....l.748 c.c. Pressure(calculated) at room temperature....27.50 cms. K..... Volume of gas pumped out (S.T.P.).....l.757 c.c. T<sup>o</sup>C T<sup>o</sup>K Press. Press. C.c. Press. T Abs. Ther. r calc. diff. abs. Vols. cms. cms. 44.85 542 815 0.172 0.089 22.3 71.65 49.75 4.90 0.119 **40**2 0.062 62.00 42.28 675 45.40 3.12 22.1 42.25 55.70 38.83 317 590 3.92 0.141 0.073 22.1 34.45 38.40 0.180 48.34 223 496 3.95 0.093 22.0

74.

#### TABLE XIV.

<sup>T</sup> r	Ther. cms.	Press. cms.	TC	Τ <sup>Ο</sup> Κ	Press. calc.	Press. diff.	C.c. abs.	Vols. abs.	
25.1	62.05	10.64	403	676	11.32	0.68	0.026	0.014	
28.0	70.26	10.93	52 <b>2</b>	<b>79</b> 5 <sup>.</sup>	12.35	1.42	0.051	0.026	
23.0	55.33	9.33	312	585	10.48	1.15	0.049	0.025	
24.5	<b>47.</b> 45	7.85	212	485	9.45	1.60	0.073	0.038	

NOTE. As the volume of gas used in this experiment

was very small, it was measured by bringing the mercury level to the upper pointer instead of the lower one and reading the pressure. The volume of the space from the upper pointer to the tap was 0.943 c.c.

#### TABLE XV.

Sample 1.

Tr	Ther. cms.	Press. cms.	T <sup>o</sup> C	T <sup>o</sup> K	Press. calc.	Press. diff.	C.c. abs.	Vols. abs.
24.0	65.37	6.15	451.	724	7.20	1.05	0.037	0.019
23.8	68.65	6.25	498	771	7.42	1.17	0.042	0.021
24.0	72.50	6.30	5 <b>5</b> 5	828	7.66	1.36	0.049	0.025
24.2	61.55	6.24	397	670	6.91	0.77	0.029	0.015
24.4	57.48	5.79	<u>3</u> 41	614	6.61	0.82	0.033	0.017
25.0	52.68	5.29	278	551	6.23	0.94	0.040	0.021

## TABLE XVI.

Sample ]

Lower pointer reading20	•48	cms.
Room temperature24	•0°C	•
Volume of gas at room temperaturel.	935	c.c.
Volume of gas at S.T.Pl.	780	C.C.
Pressure(calculated) at room temperature28	.19	cms.
K	495	
Volume of gas pumped out (S.T.P.)l.	790	c.c.

Tr	Ther. cms.	Press. cms.	T <sup>o</sup> C	T <sup>o</sup> K	Press. calc.	Press. diff.	C.c. abs.	Vols. abs.
24.0	65.33	44.82	450	723	48.00	3.18	0.118	0.061
23.8	61.17	42 <b>.94</b>	391	664	46.00	3.16	0.121	0.063
24.0	54.83	<b>39.</b> 63	<b>30</b> 6	579	42.80	3.17	0.133	0.070
22.1	48.62	35.49	227	500	<b>39.</b> 22	3•73	0.174	0.090
22.0	68.79	45.52	500	773	49.40	3.88	0.139	0.072

## TABLE XVII.

Sample	e 1.							
Lower	pointe	er readin	ng	• • • • •			.45.70	cms.
Room 1	tempe <b>r</b> a	ture		• • • • •		• • • • • • •	.26.5°C	
Volume	e of ga	as at roo	om te	mpe <b>r</b> a	ature		.4.310	c.c.
Volume	e of ga	is at S.	F.P	• • • • •		• • • • • • •	.3.930	C.C.
Pressu	ire(ca]	culated	) at	room	temp		.57.25	cms.
K	• • • • • • •	• • • • • • • •	• • • • •	• • • • •			.1.101	
Volume	e of ga	as pumped	l out	( <b>S</b> .1	<b>P.)</b>	• • • • • • •	•3•943	C.C.
					•			
Tr	Ther. cms.	Press. cms.	T°C	T <sup>o</sup> K	Press. calc.	Press. diff.	C.c. abs.	Vols. abs.
26.5	68.45	104.00	497	770	110.40	6.40	0.231	0.120
24.0	61.40	97.63	394	667	102.70	5.07	0.194	0.101
24.0 24.2	61.40 55.08	97.63 90.65	<b>394</b> 309	667 582	102.70 95.50	5.07 4.85	0.194 0.204	0.101 0.106

78.

### TABLE XVIII.

Sample 1.

Lower	pointe	r readi:	ng	• • • • •		• • • • • • •	.40.20	cms.
Room	tempera	ture		• • • • •		• • • • • • •	.28.0°C	
Volum	e of ga	s at ro	om te	mpera	ture	• • • • • • •	.3.800	C • C •
Volum	e of ga	s at S.	r.p	• • • • •	• • • • • • •		• 3• 443	C.C.
Press	ure(cal	culated	) at	room	tempera	ture	•55•30	cms.
K	• • • • • • • •	• • • • • • •	• • • • •	• • • • •	• • • • • • •	• • • • • • •	.0.960	
Volum	e of ga	s pumpe	d out	(S.T	.P.)		• 3 • 445	C.C.
T r	Ther. cms.	Press. cms.	T°C	T <sup>o</sup> K	Press. calc.	Press. diff.	C.c. abs.	Vols. abs.
26.5	68.30	89.70	493	766	96.35	6.65	0.237	0.123
25.0	60.55	84.05	384	657	89.00	4.95	0.186	0.093
23.0	53.60	75.70	284	557	81.00	4.95	0.208	0.108

21.1 47.65 69.49 214 487 74.75 5.26 0.247 0.128

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## TABLE XIX.

Sample	e 1.									
Lower	pointe	r readin	ng	• • • • •		• • • • • • •	.34.40	cms.		
Room	tempera	ture	• • • • •	• • • • •	• • • • • • • •		.24.0°C			
Volum	e of ga	s at roo	om·ter	nperat	ture	• • • • • • •	.3.240	C.C.		
Volum	e of ga	s at S.	r.p		• • • • • • •	• • • • • • •	2.985	C.C.		
Press	ure(cal	culated	) at :	room t	temperat	ture	47.30	cms.		
$K_{\bullet} = \frac{1}{2} \left( \frac{1}{2} - \frac{1}{$										
Volume of gas pumped out (S.T.P.)2.981 c.c.										
Volume	e of ga	s pumpe	l out	(S.T.	.P.)		2.981	C • C •		
Volum	e of ga	s pumpeo	d out	(S.T.	.P.)	• • • • • • •	2.981	C.C.		
Volumo Tr	e of ga Ther. cms.	s pumped Press. cms.	d out T <sup>o</sup> C	(s.t. T <sup>o</sup> k	P.) Press. calc.	Press. diff.	2.981 C.c. abs.	c.c. Vols. abs.		
Volumo T <sub>r</sub> 24.0	e of ga Ther. cms. 66.87	s pumped Press. cms. 76.56	d out T <sup>o</sup> C 473	(S.T. T <sup>o</sup> k 746	P.) Press. calc. 81.81	Press. diff. 5.25	2.981 C.c. abs. 0.190	c.c. Vols. abs. 0.098		
Volume Tr 24.0 24.1	e of ga Ther. cms. 66.87 60.35	s pumped Press. cms. 76.56 72.27	d out T <sup>o</sup> C 473 381	(S.T. T <sup>o</sup> K 746 654	P.) Press. calc. 81.81 76.60	Press. diff. 5.25 4.33	2.981 C.c. abs. 0.190 0.167	<pre>c.c. Vols. abs. 0.098 0.086</pre>		
Volumo Tr 24.0 24.1 24.5	e of ga Ther. cms. 66.87 60.35 54.90	s pumped Press. cms. 76.56 72.27 67.99	d out T <sup>o</sup> C 473 381 307	(S.T. T <sup>o</sup> K 746 654 580	P.) Press. calc. 81.81 76.60 72.00	Press. diff. 5.25 4.33 4.01	2.981 C.c. abs. 0.190 0.167 0.177	<pre>c.c. Vols. abs. 0.098 0.086 0.092</pre>		

# TABLE XX.

Sample	e l.										
Lower	pointe:	r readin	ng	• • • • •			39.90	cms.			
Room	tempera	ture		• • • • •			22.4°C				
Volume of gas at room temperature											
Volum	e of ga	s at S.	r.P	• • • • •			3.480	c.c.			
Press	ure(cal	culated)	) at :	room .	temperat	ture	,54.80	cms.			
$K_{\bullet$											
Volume of gas pumped out (S.T.P.)											
Volum	e of ga	s pumped	l out	(S.T	•P•)•••	• • • • • • • •	3.485	C.C.			
Volum	e of ga	s pumped	l out	(S.T.	•P•)		3.485	C.C.			
Volum Tr	e of ga Ther. cms.	s pumped Press. cms.	l out T <sup>o</sup> C	(S.T T <sup>o</sup> k	.P.) Press. calc.	Press. diff.	3.485 C.c. abs.	c.c. Vols. abs.			
Volumo T <sub>r</sub> 24.5	e of ga Ther. cms. 68.23	s pumped Press. cms. 90.90	l out T <sup>o</sup> C 492	(S.T T <sup>o</sup> k 765	.P.) Press. calc. 96.90	Press. diff. 6.00	3.485 C.c. abs. 0.214	C.C. Vols. abs. 0.112			
Volum T <sub>r</sub> 24.5 24.5	e of ga Ther. cms. 68.23 59.90	s pumped Press. cms. 90.90 84.41	l out T <sup>o</sup> C 492 374	(S.T T <sup>o</sup> K 765 647	.P.) Press. calc. 96.90 89.20	Press. diff. 6.00 4.79	3.485 C.c. abs. 0.214 0.188	C.C. Vols. abs. 0.112 0.098			
Volum T <sub>r</sub> 24.5 24.5 24.0	e of ga Ther. cms. 68.23 59.90 53.95	s pumped Press. cms. 90.90 84.41 77.83	l out T <sup>o</sup> C 492 374 294	(S.T T <sup>o</sup> K 765 647 567	.P.) Press. calc. 96.90 89.20 82.90	Press. diff. 6.00 4.79 5.07	3.485 C.c. abs. 0.214 0.188 0.212	<pre>c.c. Vols. abs. 0.112 0.098 0.110</pre>			

## TABLE XXI.

Sample 1.

Upper pointer reading	.27.85 cms.
Room temperature	,23,2°C
Volume of gas at room temperature	.0.345 c.c.
Volume of gas at S.T.P	.0.318 c.c.
Pressure(calculated) at room temperature	5.03 cms.
К	,0 <b>.0</b> 855
Volume of gas pumped out (S.T.P.)	.0.317 c.c.

Tr	Ther. cms.	Press. cms.	.T°C	T <sup>o</sup> K	Press. calc.	Press. diff.	C.c. abs.	Vols. abs.	
21.0	67.65	7.33	484	757	8.76	1.43	0.050	0.026	
22.0	60.16	6.91	37 <b>7</b>	650	8.14	1.23	0.046	0.024	
23.5	53.77	6.59	292	5 <b>65</b>	7.54	0.95	0.041	0.021	
24.0	48.45	5.90	225	498	7.03	1.13	0.052	0.027	

•

#### TABLE XXII.

Sample 3.

Volume of gas at room temperature ..... 0.615 c.c. Pressure (calculated) at room temperature.4.95 cms. Press. T<sup>o</sup>C<sup>.</sup> T<sup>o</sup>K Press. Press. C.c. Tr Ther. Vols. calc. diff. abs. abs. cms. cms. 24.0 55.78 8.63 615 888 10.94 2.31 0.119 0.043 More gas added. Volume added(T,).....0.745 c.c. Volume added S.T.P.....0.687 c.c. New Volume T<sub>r</sub>.....1.360 c.c. New volume S.T.P.....l.251 c.c. Press. T<sup>o</sup>C T<sup>o</sup>K Press. Press. C.c. Tr Ther. Vols. calc. diff. abs. abs. cms. cms. 24.8 56.08 20.53 621 894 24.27 3.74 0.192 0.069 More gas added. Volume added T .....l.875 c.c. Volume added S.T.P.....l.704 c.c.

84.

# TABLE XXII (continued)

T <sub>r</sub>	Ther. cm.s.	Press. cms.	T <sup>o</sup> C	T <sup>o</sup> K	Press. calc.	Press. diff.	C.c. abs.	Vols. abs.
22.0	56.60	51.33	633	910	58.00	6.67	0.344	0.124
More	gas add	ed.						
Volum	e added	Т	• • • • •	• • • • •	• • • • • • •		35 c.c.	
Volum	e added	S.T.P.	• • • • •	• • • • • •	• • • • • • • •	0.76	54 c.c.	
New v	olume T	* * * * * *	• • • • •	• • • • • •	••••		20 c.c.	
New v	olume S	•T•P•••		• • • • •		••••3•7	L9 c'.c.	
New K		• • • • • • •	• • • • •	• • • • •		1.02	20	
T r	Ther. cms.	Press.	T°C	Τ°Κ	Press. calc.	Press. diff.	C.c. abs.	Vols. abs.
22.0	56.10	64.24	621	894	71.50	7.26	0.374	0.135
Volum	e of ga	s pumpe	l out	(S.T	.P.)		.3.700	C.C.

#### TABLE XXIII.

Sample 3. Volume of gas at room temperature ..... 0.710 c.c. Pressure (calculated) at room temp.....5.73 cms. Press. T<sup>o</sup>C T<sup>o</sup>K Press. Press. C.c. Tr Ther. Vols. calc. diff. abs. abs. cms. cms. 21.8 59.60 9.63 703 976 13.48 3.85 0.188 0.068 More gas added. New volume T<sub>p</sub>.....l.618 c.c. New volume S.T.P.....l.509 c.c. New K.....0.416 Press. T<sup>o</sup>C T<sup>o</sup>K Press. Press. C.c. Tr Vols. Ther. calc. diff. abs. abs. cms. cms. 21.6 59.60 24.51 703 976 30.62 6.11 0.298 0.108

More gas added.

Volume added T\_.....1.482 c.c. New volume S.T.P.....2.881 c.c. New K.....0.800

## TABLE XXIII (continued).

Tr	Ther. cms.	Press. cms.	T <sup>o</sup> C	Tok	Press. calc.	Press. diff.	C.c. abs.	Vols. abs.
22.0	59.20	50.37	694	967	59.00	8.63	0.415	0.150
More	gas add	ed.						
Volum	e added	<sup>T</sup> <sub>R</sub>	• • • • •	• • • • •			336 c.c	•
Volum	e added	S.T.P.	• • • • •	• • • • •	• • • • • • •	1.	238 c.c	•
New v	olume T	r•••••		••••		••••4•	436 c.c	•
New v	olume S	•T•P•	• • • • •	• • • • •	• • • • • • •	4.	119 c.c	•
New K	• • • • • • •	• • • • • • •	• • • • •	• • • • •	• • • • • • •		142 °.	
T <sub>r</sub>	Ther. cms.	Press.	T°C	T <sup>o</sup> k	Press. calc.	Press. diff.	C.c. abs.	Vols. abs.
22.0	59.58	73.64	703	976	84.10	10.46	0.504	0.182

Volume of gas pumped out (S.T.P.).....4.139 c.c.

#### XXIV. TABLE

Sample	≥ 3•							
Lower	pointer	r readir	1g	•••••		•••••5	.31 cms	5.
Room t	cemperat	ture				2	4.0°C	
Volume	e of gas	s at roo	om te	mperat	cure	•••••	.501 c.	С.
Volume	e of gas	s at S.I	C.P.			•••••	.461 c.	. C .
Press	ire(calo	culated)	at	room t	temp	•••••4	•05 cms	5.
K		• • • • • • •				· · · · · · · · C	.128	
T <sub>r</sub>	Ther. cms.	Press. cms.	T <sup>o</sup> C	T <sup>o</sup> K	Press.	Press. diff.	C.c. abs.	Vols. abs.
24.0	63.80	4.83	800	1073	10.03	5.20	0.238	0.086
More a	gas adde	ed.						
Volume	e a <b>d</b> ded	T				· • • • • • • • C	.694 c.	. C .
Volume	added	S.T.P.				· · · · · · · C	.635 c.	. C •
New vo	olume T <sub>j</sub>					1	. <b>1</b> 95 c.	, C •
New vo	olume S.	.T.P				•••••	096 c.	, C .
New K.		• • • • • • • •				· • • • • • • • • • • • • • • • • • • •	• 306	
T <sub>r</sub>	Ther. cms.	Press.	T°C	T°K	Press. calc.	Press. diff.	C.c. abs.	Vols. abs.
24.1	63.81	14.93	800	1073	23.98	9 <b>.0</b> 5	0.415	0.150



## TABLE XXIV (continued).

Ther. cms.	Press. cms.	T°C	T <sup>o</sup> K	Press. calc.	Press. diff.	C.C. abs.	Vols. abs.
63.95	33.74	804	1077	47.60	13.96	0.640	0.231
gas adde	ed.		r de el in ∞				
added	T <sub>r</sub>				1.4	60 c.c.	•
e added	S.T.P.				].]	341 c.c.	•
lume T,						30 c.c.	,
olume S.	T.P					517 c.c.	•
						980.	
Ther. cms.	Press. cms.	T°C	T <sup>o</sup> K	Press. calc.	Press. diff.	C.c. abs.	Vols. abs.
62.77	59.93	7 <b>7</b> 6	1049	75.60	15.67	0.720	0 <b>.2</b> 59
	Ther. cms. 63.95 gas added added added olume T, olume S. Ther. cms. 62.77	Ther. Press. cms. $cms.63.95$ $33.74as added.added T_radded T_radded S.T.P.cms. T.P.cms. cms.62.77$ $59.93$	Ther. Press. $T^{\circ}C$ cms. cms. 63.95 33.74 804 gas added. added T <sub>r</sub> added S.T.P plume T <sub>r</sub> plume S.T.P Ther. Press. $T^{\circ}C$ cms. cms. 62.77 59.93 776	Ther. Press. $T^{\circ}C$ $T^{\circ}K$ <u>cms.</u> 63.95 33.74 804 1077 <u>gas added</u> . added T <sub>r</sub> added S.T.P. <u>olume T<sub>r</sub></u> <u>olume S.T.P.</u> <u>ther. Press.</u> $T^{\circ}C$ $T^{\circ}K$ <u>cms.</u> 62.77 59.93 776 1049	Ther. Press. $T^{\circ}C$ $T^{\circ}K$ Press. cms. $calc.63.95$ $33.74$ $804$ $1077$ $47.60aadded$ . $added$ $T_r$ . $added$ $T_r$ . added $S.T.P$ . $clume$ $T_r$ . clume $S.T.P$ . $cms.$ $T^{\circ}C$ $T^{\circ}K$ Press. cms. $cms.$ $calc.62.77$ 59.93 776 1049 75.60	Ther.       Press. $T^{\circ}C$ $T^{\circ}K$ Press.       Press. $calc.$ $diff.$ 63.95       33.74       804       1077       47.60       13.96         gas       added.         13.96         gas       added. $added$ Tr        1.4 $added$ S.T.P.        1.3 $olume$ Tr        3.8 $olume$ S.T.P.        3.5 $olume$ S.T.P. $for       To K       Press.       Press.         for       Calc.       diff.          for       Calc.       diff.          for       Calc.           for       Cal$	Ther.       Press. $T^{o}C$ $T^{o}K$ Press.       Press.       C.c.         63.95       33.74       804       1077       47.60       13.96       0.640         gas added.          e added $T_r$ 1.460       c.c.         e added $S.T.P$ 1.341       c.c.         e added S.T.P.        3.830       c.c.         olume $T_r$ 3.517       c.c.         olume S.T.P.         0.980         Ther.       Press.       T <sup>o</sup> K       Press.       Press.       C.c.         cms.       cms.       calc.       diff.       abs.         62.77       59.93       776       1049       75.60       15.67       0.720

#### TABLE XXV.

	T r	Ther. cms.	Press. cms.	T°C	T <sup>o</sup> K	Press. calc.	Press. diff.	C.c. abs,	Vols. abs.
-	23.0	50.20	36.61	497	770	39.72	3.11	0.175	0.063
	20.9	43.42	32.57	<b>3</b> 66	639	35.00	2.43	0.155	0.056
	21.0	35.88	26.82	234	507	29.70	2.88	0.216	0.078

## TABLE XXVI.

Sample 3.

Lower	pointe	r readi:	ng		• • • • • • • •	• • • • • • • •	.48.90	cms.
Room	tempera	ture					.24.0°C	
Volum	e of ga	s at ro	om te	mpera	ture		.4.610	C.C.
Volum	e of ga	s at S.	r.P	• • • • •			.4.248	C.C.
Pressure(calculated) at room temp								
K			• • • • •	• • • • •			.1.180	
Volum	e of ga	s pumpe	d out				.4.259	C.C.
T r	Ther. cms.	Press. cms.	T°C	ToK	Press. calc.	Press. diff.	C.c. abs.	Vols. abs.
24.1	47.60	68.24	446	719	72.15	3.91	0.231	0.082
24.0	53.45	73.44	566	8 <b>39</b>	79.54	6.10	0.323	0.116
23.3	43.20	62.88	362	635	66.45	3.57	0.228	0.082
24.0	35.11	51.50	220	493	55.50	4.00	0.304	0.112

90.

## TABLE XXVII.

Sample	e 4.							
Lower	pointe	r readi:	ng				.31.61	cms.
Room	tempera	ture			• • • • • • •	•••••	.22.5°0	<b>;</b>
Volum	e of ga	s atvro	om te	empera	ture	• • • • • • •	2.982	C.C.
Volum	e of ga	s at S.	r.P.		• • • • • • •	• • • • • • •	2.760	C.C.
Press	ure(cal	culated	) at	room	temp	• • • • • • •	.22.98	cms.
K		••••			•••••		.0.767	
Volum	e of ga	s pumpeo	i out		• • • • • • •	• • • • • • •	.2.760	C.C.
<sup>T</sup> r	Ther. cms.	Press. cms.	T <sup>o</sup> C	T <sup>o</sup> K	Press. calc.	Press. diff.	C.c. abs.	Vols. abs.
23.0	58 <b>.60</b>	46.45	68 <b>0</b>	953	54.60	8.15	0.411	0.139
23.0	60.80	45.53	732	1005	56.55	11.02	0.539	0.183
20.0	50.91	44.15	513	786	48 <b>.</b> 15	4.00	0.229	0.078

91.

### TABLE XXVIII.

Calculated Pressure.....7.55 cms.

Time (minutes)	Volumes absorbed	Log S/S-X	K	
1/4	0.002	0.040		
3/4	0.0035	0.074	gup and the sam and that the	
1 1/2	0.0045	0.096		
2	0.0055	0.122	0.011	
3	0.0065	0.149	0.016	
4	0.0075	0.176	0.019	
5	0.008	0.190	0.018	
7	0.0095	0.238	0.020	
9	0.0105	0.272	0.019	
12	0.012	0.331	0.019	
<b>1</b> 5	0.0135	0.397	0.020	
18	0.0145	0.449	0.019	
21	0.0155	0.506	0.019	
25	0.017	0.612	0.020	
30	0.018	0.700	0.020	
35	0.019	0.809	0.020	
Final	0.0225	865 mar		

# Mean = 0.0195





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#### TABLE XXIX.

Calculated Pressure.....13.94 cms.

Time (mins)	Volumes absorbed	Log S/S -X	K	
1/4	0.003	0.039		
1	0.006	0*080		
1 1/2	0.008	0.114		
2 3/4	0.011	0.162	0.022	
3 3/4	0.013	0.205	0.028	
5	0.014	0.235	0.027	
7	0.017	0.266	0.024	
9	0.019	0.360	0.027	
12	0.022	0.450	0.029	
15	0.024	0.535	0.029	
18	0.026	0.640	0.030	
21	0.027	0.681	0.028	
24	0.028	0.779	0.028	
27	0.0295	0.870	0.028	
30	0.0305	0.985	0.029	
35	0.031	1.080	0.028	
Final	0.034			

#### Mean = 0.028

C = 0.10

 $\sqrt{\frac{\mathbf{P}}{\mathbf{K}}} = 133$ 

## 94.

### TABLE XXX.

## 

Time (mins)	Volumes absorbed	Log S/S -X	K
1/4	0.007	0.042	
3/4	0.015	0.096	
1 1/2	0.021	0.142	
2	0.026	0.185	0.043
3	0.032	0.240	0.047
4	0.038	0.306	0.051
5	0.042	0.356	0.051
6	0.044	0.384	0.047
8	0.051	0.494	0.049
10	0.055	0.574	0.047
12	0.059	0.670	0.047
15	0.062	0.760	0.044
18	0.065	0.875	0.043
26	0.071	1.273	0.045
Final	0.075		

Mean = 0.047

## C = 0.10



#### TABLE XXXI

Time (mins)	Volumes absorbed	Log S/S - X	K
1/4	0.015	0.082	
1	0.025	0.147	
1 1/2	0.033	0.206	0.071
2 3/4	0.040	0.266	0.060
3 1/2	0.045	0.316	0.062
4 3/4	0.049	0.360	0.055
5 3/4	0.054	0.420	0.056
7	0.060	0.508	0.058
9	0.065	0.597	0.055
11	0.071	0.735	0.058
16	0.079	1.036	0.058
25	0.084	1.461	0.055
30	0.086	1.939	0.061
Final	0.087		

Mean = 0.058

C = 0.10

 $\frac{\sqrt{P}}{K} = 131$ 

## TABLE XXXII.

Time (mins)	Volumes absorbed	Log S/S - X	K
3/4	0.008	0.065	700 are test ant
1 1/4	0.014	0.119	147 147 484 44 48
2	0.018	0.160	*** == == == ==
3	0.024	0.232	0.044
4	0.028	0.286	0.046
5	0.031	0.331	0.046
6	0.035	0.400	0.050
8	Q.038	0.462	0.045.
10	0.040	0.508	0.041
12	0.0425	0.572	0.040
15	0.0465	0.703	0.040
18	0.050	0.860	0.042
21	0.052	0.985	0.042
25	0.0535	1.110	0.041
30	0.056	1.461	0.045
Final	0.058		

Mean = 0.042

#### C = 0.10



#### TABLE XXXIII.

Time (mins)	Volumes absorbed	Log S/S - X	K
1/4	0.014	0.082	مود موا مد
1	0.024	0.153	0.053
2	0.035	0.246	0.073
3	0.039	0.285	0.062
4	0.045	0.352	0.063
5	0.047	0.376	0.055
7	0.055	0.494	0.056
9	0.061	0.608	0.056
12	0.069	0.830	0.060
15	0.072	0.954	0.057
18	0.075	1.130	0.057
21	0.076	1.211	0.053
28	0.079	1.606	· <b>0.</b> 054
Final	0.081		

Mean = 0.057

 $C = 0.10 \qquad \qquad \sqrt{\frac{P}{K}} = 130$ 

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## TABLE XXXIV.

Time (mins)	Volumes absorbed	$\log S/S - X$	K	
1/4	0.008	0.054		
1	0.011	0.077		
2	0.017	0.124		
3	0.020	0.150	0.017	
4	0.021	0.160	0.015	
5	0.027	0.219	0.024	
6	0.031	0.264	0.027	
8	0.034	0.301	0.025	
10	0.040	0.385	0.028	
14	0.043	0.434	0.024	
18	0.050	0.576	0.026	
25	0.052	0:628	0.021	
30	0.059	0.879	0.026	
35	0.062	1.054	0.027	
40	0.063	1.133	0.026	
45	0.064	1.230	0.025	
60	0.065	1,355		



### TABLE XXXV.

Time (mins)	Volumes absorbed	Log <b>S/S -</b> X	K
1/2	0.012	0.122	
1	0.016	0.172	0.072
2	0.022	0.259	0.078
3	0.026	0.328	0.076
4	0.028	0.368	0.067
5	0.031	0.435	0.067
6	0.033	0.486	0.064
8	0.038	0.648	0.068
17	0.046	1.214	0.066
20	0.047	1.389	0.064
25	0.048	1.690	0.064
Final	0.049	••• •• •• ••	

Mean = 0.066

$$\sqrt{\frac{\mathbf{P}}{\mathbf{K}}} = 70.2$$

C = 0.10

#### TABLE XXXVI.

Time (mins)	Volumes absorbed	Log S/S - X	K	-
1/4	0.007	0.069		
1	0.017	0.190	0.090	
2	0.022	0.265	0.083	
3	0.028	0.380	0.093	
4	0.031	0.451	0.088	
6	0.037	0.640	0.090	
8	0.041	0.835	0.092	
10	0.044	1.080	0.098	
12	0.045	1.205	0.092	
15	0.046	1.380	0.085	
Final	0.048	ورون وندا الدن وي خط		

Mean = 0.090

$$\sqrt{\frac{P}{K}} = 61.7$$

C = 0.10

## TABLE XXXVII.

Time (mins)	Volumes absorbed	Log S/S - X	K
1/4	0.009	0.086	
1	0.020	0.222	
2	0.026	0.319	0.108
3	0.029	0.376	0.092
4	0.033	0.468	0.092
5	0.037	0.585	0.097
Ġ	0.040	0.699	0.099
8	0.043	0.855	0.094
10	0.046	1.096	0.100
12	0.047	1.222	0.094
Final	0.050		

$$\sqrt{\frac{P}{K}} = 57.4$$

 $\dot{C} = 0.10$
### Table XXXVIII.

Time (mins)	Volumes absorbed	Log S/S - X	K
1/4	0.007	0.065	
1	0.017	0.180	
2	0.020	0.221	0.030
3	0.022	0.252	0.030
4	0.026	0.319	0.039
5	0.029	0.377	0.043
6	0.030	0.398	0.040
8	0.035	0.522	0.045
10	0.037	0.585	0.043
12	0.040	0.698	0.045
15	0.042	0.796	0.042
18	0.044	0.920	0.042
21	0.046	1:096	0.040
25	0.047	1.221	0.043
Final	0.050		

Mean = 0.042

C = 0.16



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### TABLE XXXIX.

Time (mins)	Volumes absorbed	Log S/S - X	K
1/4	0.018	0.203	میں سے میں سے
1	0.026	0.339	
2	0.0315	0.464	0.037
3	0.033	0.504	0.038
4	0.035	0.566	0.044
5	0.036	0.602	0.042
6	0.037	0.640	0.042
8	0.039	0.728	0.042
10	0.040	0.778	0.039
12	0.042	0.903	0.043
15	0.043	0.982	0.039
18	0.044	1.079	0.038
21	0.046	1.379	0.049
Final	0.048		

Mean = 0.040

0 = 0.39





### 104.

### TABLE XL.

Time (mins)	Volumes ab <b>sor</b> bed	Log S/S - X	K
1/4	0.016	0.176	
1	0.029	0.403	1.00 COM - COM - COM - COM
2	0.033	0.505	0.027
3	0.034	0.535	0.028
4	0.0355	0.584	0.033
5	0.037	0.640	0.038
6	0.038	0.682	0.038
8	0.039	0.728	0.035
10	0.040	0.778	0.033
12	0.042	0.903	0.038
15	0.043	0.982	0.035
18	0.044	1.080	0.035
21	0.045	1.205	0.036
25	0.046	1.380	0.037
Final	<b>0.</b> 048	••••••••••••••••••••••••••••••••••••••	

Mean = 0.036

C = 0.45



بجري جدين محمل بجري سابق بالجار البري الجاري فالمتجاد ويتقافي فالمن الشيارات سارد والمجار المارك المراكفين

### 105.

### TABLE XLI.

Time (mins)	Volumes absorbed	Log S/S - X	K	a
1/4	0.024	0.301	But one and and are	
1	0.033	0:505		
2	0.035	0.566	0.043	
3	0.036	0.602	0.040	
4	0.037	0.640	0.040	
6	0.038	0.680	0.034	
8	0.040	0.778	0.037	
10	0.042	0.903	0.042	
12	0.043	0.982	0.042	
15	0.044	1.079	0.040	
18	0.045	1.204	0.040	
25	0.046	1.380	0.036	
Final	0.048			

Mean = 0.039

$$\sqrt{\frac{P}{K}} = 139$$

C = 0.48

### TABLE XLII.

106.

Time (mins)	Volumes absorbed	Log S/S - X	K
1/4	0.027	0.301	
1	0.036	0.486	
2	0.041	0.618	0.059
3	0.042	0.652	0.050
4	0.043	0.691	0.048
5	0.044	0.732	0.047
6	0.045	0.778	0.046
8	0.048	0.954	0.057
io	0.048	0.954	0.045
12	0.050	1.130	0.052
15	0.051	1.255	0.050
18	0.052	1.431	0.052
21	0.052	1.431	0.044
25	0.053	1.732	0.049
Final	0.054		

Mean = 0.049

C = 0.50



### TAELE XLIII.

Time (mins)	Volumes absorbed	Log S/S - X	K	-
1/4	0.029	0.334	<b>62</b> 6-1 6-1 6-1	
1	0.038	0.528	100 aut er un en	
2	0.042	0.652	المتل فيه عبد عمل	
3	0.045	0.778	0.066	
4	0.046	0.829	0.062	
5	0.047	0.886	0.061	
6	0.048	0.954	0.062	
8	0.049	1.033	0.057	
10	0.050	1.130	0.055	
12	0.052	1.430	0.071	
15	0.052	1.430	0.057	
18	0.053	1.731	0.064	
Final	0.054			

Mean = 0.061

 $\frac{\sqrt{P}}{K} = 89.5$ C = 0.58

### TABLE XLIV.

108.

Time (mins)	Volumes absorbed	Log S/S - X	K	
1/4	0.045	0.352		
1	0.063	0.654		
2	0.067	0.761	0.090	
3	0.070	0.866	0.095	
4	0.072	0.954	0.093	
5	0.074	1.062	0.096	
6	0.075	1.131	0.092	
8	0.077	1.306	0.091	
10	0.078	1.432	0.085	
12	0.079	1.608	0.086	
15	0.080	1.909	0.089	
Final	0.081			

Mean = 0.091

C = 0.58

 $\sqrt{\frac{P}{K}} = 89.3$ 

### TABLE XLV.

Time (mins)	Volumes absorbed	Log S/S - X	K
1/4	0.045	0.447	
1	0.055	0.669	
2	0.058	0.766	0.068
3	0.061	0.890	0.086
4	0.062	0.942	0.078
5	0.063	1.000	0.074
6	0.065	1.145	0.086
8	0.066	1.243	0.077
10	0.068	1.544	0.091
12	0.068	1.544	0.076
15	0.069	1.845	0.080
Final	0.070		

Mean = 0.080

C = 0.63

 $\sqrt{\frac{P}{K}} = 70.0$ 

### TABLE XLVI.

Time (mins)	Volumes absorbed	Log S/S - X	K
1/4	0.063	0.828	
1	0.066	0.966	0.096
2	0.068	1.092	0.111
3	0.069	1.171	0.100
4	0.070	1.267	0.099
5	0.071	1.392	0.104
7	0.072	1.568	0.100
10	0.073	1.869	0.100
Final	0.074		

Mean = 0.100

C = 0.87

 $\frac{\sqrt{P}}{K} = 55.6$ 

### TABLE XLVII.

Time (mins)	Volumes absorbed	Log S/S - X	K
1/4	0.102	1.256	<b>67</b>
1	0.104	1.431	0.141
2	0.105	1.556	0.133
3	0.106	1.731	0.137
5	0.107	2.033	0.149
Final	0.108		

Mean = 0.140

C = 1.29

 $\sqrt{\frac{P}{K}} = 41.6$ 

#### 112.

### <u>VII. DISCUSSION OF RESULTS.</u>

#### (A). SOLUBILITY OF OXYGEN IN SILVER.

The results obtained for the solubility of oxygen in silver are given in Tables XI to XXVII, and are plotted in Figures 6, 7, and 8.

Within the limits of experimental error the results were completely reproducible. There was no hysteresis effect, the solubility at any temperature being independent of the thermal history of the metal.

#### Variation of Solubility with Pressure.

The solubility at various temperatures is plotted against the pressure and against the square root of the pressure in Figures 6 and 7. The values are also given in Tables XLVIII LIV. The values given in these figures and tables were obtained by plotting the results of each experiment and interpolating, so as to be able to compare the results at the same temperattures. It is evident from the results that the solubility is proportional to the square root of the pressure.

The value of  $\sqrt{\frac{P}{Q}}$  (where P is the pressure and Q the absorption) is practically constant at any temperature.

There is, however, a drift at the lower pressures, the

amount absorbed being smaller than that given fra by



112 A.



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# Curve showing the variation of absorption with pressure at various temperatures.

. 6 .... 400°C

.





the above relationship. This deviation, however, is not noticeable at the higher temperatures.

### TABLE XLVIII.

Temperature.....200°C.

Pressure (cms)	Volumes absorbed	√ <u>P</u> Q
7•7	0.040	69
16.9	0.063	65
33 <b>•7</b>	0.100	58
34.1	0.101	58
59.4	0.121	63
68.0	0.132	62
69.6	0.118	69
79.0	0.143	63

### TABLE XLIX.

Pressure (cms.)	Volumes absorbed	V P Q
6.7	0.021	123
19.3	0.048	92
19.8	0.048	93
38.0	0,071	87

67.1	0.093	88
89.6	0.108	88

#### 

	TABLE	L.	
Tempera	ture	400°C	

Pressure (cms.)	Volumes ab <b>sor</b> bed	√ <u>₽</u> Q
6.2 .	0.015	164
20.5	0.041	111
21.8	0.045	104
42.3	0.062	104
43.0	0.062	<b>10</b> 6
72.6	0.085	101
85.6	0.094	99
86.2	0.096	98
98.1	0.100	99

## TABLE LI.

Temperature.....500°C

Pressure (cms.)	Volumes absorbed	
6.3	0.021	119
7.5	0.030	92
22.6	0.050	96
23.4	0.053	92

114.

36.6	0.063	96
43.6	0.074	89
45.5	0.072	94
104.4	0.121	85

### 115.

### TABLE LII.

## Temperature.....620°C

Pressure (cms.)	Volumes absorbed	√ <u>P</u> Q
8.6	0.043	68
20.5	0.069	66
45.3	0.111	58
51.3	0.124	60
64.2	0.135	60

## TABLE LIII.

## $Temperature.....700^{\circ}C$

Pressure (cms.)	Volumes absorbed	
9.6	0.068	46
24.5	0.108	46
48.0	0.153	46
50.4	0.150	47
73.6	0.182	47
	العلم بين هي هي من هي بين الله الله بين بين مي الله عن مي الله ا	
	TABLE LIV.	
J	Cemperature800°	C

Pressure	Volumes	√ P
(cms.)	absorbed	
می از مین افغان میکند. میرون میکن میکن با میکن با میکن با میکن با میکن و میکن و میکن میکن میکن میکن میکن میگر م میکن از میکن افغان میکن میکن میکن میکن میکن او میکن و میکن و میکن و میکن و میکن و میکن میکن میگر میگر میگر میگر		

4.8	0.086	25.5
14.9	0.150	25.7
33 <b>•7</b>	0.231	25.1
59.9	0.304	25.3

As has been previously pointed out, the fact that the absorption is proportional to the square root of the pressure means that the oxygen molecule when dissolved in the silver is broken up into two parts. No other inference as to the actual condition of the oxygen can be drawn from this fact. The oxygen may simply dissociate into atoms, it may dissociate into ions, or it may react with the silver to form AgO, or some other oxide of silver containing one atom of oxygen in the molecule.

The variation of the absorption of a gas by a metal with the square root of the pressure seems to be a phenomenon of a fairly general nature. The relation has been shown to hold for the absorption of hydrogen by fantalum<sup>47</sup>, Copper<sup>62</sup>, Iron<sup>62</sup> and nickel<sup>110</sup>, and for the absorption of Sulphur dioxide by copper<sup>85</sup>. Mond,Ramsay,and Shields, however,have found that this relationship does not hold for the absorption of hydrogen by palladium and platinum<sup>97</sup>

#### Variation of Solubility with Temperature.

The variation of the solubility

with temperature is shown in Figure 8 for oxygen pressures of 10, 20, 40, and 80 cms. The solubility curve shows a minimum in the neighbourhood of  $400^{\circ}$ C. The solubility increases as the temperature is lowered from  $400^{\circ}$ C to  $200^{\circ}$ C. On account of the extreme slowness of the process of solution at low temperatures, it was not practicable to make any measurements below 200°. It appears, however, from the form of the curve that the solubility should be considerably greater at room temperature than it is at 200°C.

The presence of the minimum in the solubility-temperature curve makes it virtually impossible to obtain any general relation expressing the variation of solubility with temperature over the entire range from 200 to 800°C. Above 400°, however, it was found that the equation 1/Q = K (930 - t), where Q is the absorption, K is a constant depending on the pressure, and t is the temperature in degrees Centigrade, fitted the experimental results fairly accurate-The reciprocal of the solubility is thus proporly. tional to the number of degrees the temperature is below 930°C. The melting point of silver is 960°C, but the melting point is loweredaby the dissolved oxygen. Le Chatelier<sup>72</sup> states that the absorption of hydrogen by silver causes a drop in the melting point of 30°. If the drop is as great in the case of oxygen, it seems justifiable to assume that the reciprocal of the solubility is proportional to the distance below the melting

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#### point. The constancy of K in the above equation is

illustrated in Tables LV to LVIII.

#### TABLE LV.

118.

Pressure.....20 cms.

Temperature	400°	500°	620 <sup>0</sup>	700 <sup>0</sup>	800°
Absorption	.041	•049	•069	.097	.175
K	21.8	21.1	21.4	22.3	22.8

### TABLE LVI.

Pressure.....35 cms.

K	29•7	26.7	30.4	30.4	30.5
77	00 7				70 5
Absorption	•056	.062	<b>.0</b> 98	.132	•235
Temperature	400 <sup>0</sup>	5 <b>00°</b>	62 <b>0</b> °	700 <sup>0</sup>	800 <sup>0</sup>

#### TABLE LVII.

#### 

Temperature.	400 <sup>0</sup>	50 <b>0°</b>	620 <sup>0</sup>	700 <sup>0</sup>	800°
Absorption	.067	.080	.121	.150	.278
K	35.5	34.4	37.5	34.6	36.2

### TABLE LVIII.

Temperature 400° 500° 620° 700° 800°

#### Absorption .0872 .104 .147 .185 .342 46.1 44.8 45.5 42.7 44.5 K

Effect of Thickness or Surface on Solubility.

The samples of silver used were of various thicknesses. Samples 1 and 4 were 0.15 m.m. thick, Samples 2 and 3 were 0.30 mm. The thickness of sample 4 was somewhat irregular.

No difference in the solubility due to the difference in thickness or surface was observed. Hence adsorption has no measurable effect at the temperatures used.

#### Effect of Traces of Impurities.

It has been already pointed out that the presence of small amounts of iron and copper in the silver had no effect on the solubility of oxygen in it.

#### (B). SOLUBILITY OF NITROGEN IN SILVER.

As may be seen from Tables III to X there is no measurable absorption of nitrogen by silver. This is to be expected as it has been found by a large number of observers that nitrogen is not absorbed by metals except in cases where a well defined

#### nitride is formed.



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Some sample absorption-time curves at various temperatures and pressures. 1.....690°C.....31.38 cms. 3.....560°C.....31.24 cms. 2.....508°C.....65.85 cms. 4.....280°C.....33.64 cms. 5.....400°C......32.18 cms.

FIGURE IX.

#### (C). RATE OF SOLUTION OF OXYGEN IN SILVER.

The rate of solution was also investigated and the results are given in Tables XXVIII to XLVII. Some sample absorption-time curves are shown in Figure IX.

#### Equation for Solution Velocity.

Consider a block of silver placed in an atmosphere of oxygen. Assume that the outer layer of the silver is immediately saturated with the gas in the dissociated condition. The process of solution will consist of the diffusion of gas from this saturated layer into the body of the metal. As the gas diffuses inwards from the surface layer, more gas will dissolve in it so as to keep it saturated. Let S be the saturation concentration, and X be the average concentration of gas in the body of the silver.

Then, according to Fick's Diffusion Law, the rate of diffusion inwards from the saturated surface layer will be proportional to the concentration gradient, that is proportional to (S - X). Hence we

have

$$\frac{\mathrm{d}x}{\mathrm{d}t} = K(S - X).$$

#### On integration this gives

$$\log \frac{1}{S - X} = Kt + I$$

where I is a constant of integration.

When t = 0, X = 0, so that  $I = \log 1/S$ .

Hence

$$\log \frac{S}{S-X} = Kt$$

or

$$K = \frac{1}{t} \left( \log \frac{S}{S - X} \right).$$

That is the rate of solution is proportional to the ratio of the saturation concentration to the amount of gas still to be dissolved.

As may be seen from Figures 10,11, and 12, log  $\frac{S}{S-X}$  plotted against t gives a straight line. The first two points, however, generally lie below the line, and the line does not pass through the origin as the foregoing equation would require. Apparently the first part of the gas is absorbed much faster than the equation would indicate. The process evidently proceeds in two stages. If we neglect the first two or three points on the curve and take into account the fact that the line does not pass through the origin, we obtain a corrected equation of the form

$$K_{t} = \frac{1}{t} \left\{ \log \frac{s}{s-x} - c \right\}$$

where K is a constant depending on the temperature and pressure, and C varies with the temperature but is indep-

endent of the pressure. This equation has been found

to give good agreement with the experimental results.

Effect of Pressure on Solution Velocity.

The variation with pressure of the constant K in the reaction velocity equation is shown in Tables 28-33 and 43-44. The results of Tables 28-33 are collected in Table 59 and are plotted in Figure 10.

#### TABLE LIX.

 Pressure	K	√ <u>P</u> K	C
7.55	0.0195	140	0.10
13.94	0.028	133	0.10
31.34	0.042	133	0.10
39.55	0.047	134	0.10
55.18	0.057	130	0.10
57.52	0.058	<b>1</b> 31	0.10

It will be seen that C is indepen-

dent of the pressure, while K, that is the slope of the line in Figure 10, varies as the square root of the press-This is to be expected. The process of solure. ution consists merely of diffusion of oxygen into the silver, and it has been shown by Johnson and Larose<sup>1</sup>

that the rate of diffusion of oxygen through silver is

proportional to the square root of the pressure.





Variation of solution velocity with pressure at 310°C.

1.....57.52 cms. 3.....31.34 cms. 2..... 39.55 cmd. 4..... 13.94 cms.

5.....7.55 cms.

Effect of Temperature on Solution Velocity.

The effect of temperature on the velocity of solution is shown in Tables 33-47. The results have been plotted in Figures 11 and 12 according to the equation previously derived.

At temperatures below  $390^{\circ}$ C,(that is below the position of the minimum in the solubilitytemperature curve), the value of C in the equation remains constant at 0.10, while K increases as the temperature is raised. Between 390 and 440°, C increases rapidly while K decreases. Above this temperature, C continues to rise as the temperature increases, and K increases slowly and regularly. In order to eliminate the effect of pressure, the values of  $\sqrt{P} / K$  instead of K are given, together with the values of C, in Table LX.

Temp.	√ <u>P</u> K	C	Temp. °C	$\sqrt{\frac{P}{K}}$	C
280	232	0.10	440	150	0.45
310	134	0. 10	450	139	0.48
337	70.2	0.10	465	114	0.50
375	61.7	0.10	508	89.4	0.58
390	57.4	0.10	56 <b>0</b>	70.0	0.63
400	135	0.16	605	55.6	0.87
43 <b>0</b>	139	0.39	690	41.6	1.29

TABLE LX.

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Variation of solution velocity with temperature at a pressure of 30 cms, (part 1). 1.....390°C 2.....375°C 4.....310°C 5.....280°C





Variation of solution velocity with temperature at a pressure of 30 cms. (part 2). 1.....690°C 4.....508°C 7.....430°C 2.....605°C 5.....465°C 8.....440°C 3.....560°C 6.....450°C 9.....400°C The peculiar behaviour of the value of K in the neighbourhood of 400°C makes it impossible to obtain any simple expression for the variation of the velocity of solution with temperature. The temperature coefficient is low, however, as would be expected in a process in which diffusion is the predominant factor.

#### Effect of Thickness or Surface.

Due to lack of time, no investigation of the effect of thickness on solution velocity has been made. As, however, the thickness has no measurable effect on the solubility, and as the rate of diffusion has been shown to be inversely proportional to the thickness<sup>1</sup>, it is probable that the same relationship holds here and that the rate of solution is inversely proportional to the thickness.

### <u>VIII. GENERAL DISCUSSION</u>.

The experimental results have been summarized in the foregoing section, and the effect of various factors on the solubility and the rate of solution has been discussed.

The explanation of the minimum in the solubility-temperature curve is difficult. Breaks in solubility-temperature curves have been found in the case of other metals, notably the solubility of hydrogen in iron. These breaks, however, in general merely affect the slope of the curve, and the solubility usually increases with increasing temperature both before and after the break. (Many) substances. however, when dissolved in water possess solubilities similar to that found in this investigation.

The fact that a sudden change occurs in the rate of solution at this temperature, seems to point to a transition of the silver from one allotropic form to another. There is also the possibility of a change in the manner of combination of the oxygen. The form of the solution velocity curve, as has been pointed

out, shows that the oxygen is apparently taken up in two

stages. At any rate it seems certain that two factors

enter into the reaction, one of which decreases as the

temperature is raised, while the other increases. The solubility-temperature curve actually obtained is thus the sum of these two effects. It is interesting to note in this connection that Holt<sup>135</sup> was obliged to assume two forms of palladium in order to explain his results on the rate of solution of hydrogen in it.

Above  $400^{\circ}$  the solubility varies regularly with the temperature and, as already pointed out, can be expressed simply by the equation 1/Q = K (930 - T).

The heat of solution can be calculated from the rate of change of the solubility with temperature. We know from thermodynamic considerations that

$$\frac{d \ln C}{dT} \neq \frac{U}{RT^2}$$

where C is the concentration of the saturated solution at a temperature T, U is the heat of solution,

R is the gas constant.

If we express the above solubility-temperature relationship in absolute temperatures, we have

$$Q = \frac{1}{1}$$



or

and



Hence we have

 $\frac{d \ln \left(\frac{k}{1203 - T}\right)}{dT} = \frac{U}{RT^{2}}$  $- \frac{1}{1203 - T} = \frac{U}{RT^{2}}$  $U = \frac{RT^{2}}{T - 1203} = \frac{1.98 T^{2}}{T - 1203} \text{ cal.}$ 

Hence we can calculate the heat of solution at any temperature above 400°C. Thus, for example, at 600°C we have

$$U_{00} = \frac{1.98 \times 873^2}{873 - 1203}$$
  
= - 4580 calories

At about 400°C the tangent to the solubility-temperature curve is horizontal and the heat of solution is zero. Below this temperature the heat of solution is positive.

From the rapid variation of the heat of solution with temperature, and the change in sign which it undergoes at 400°, it is apparent that the heat of solution is not merely the heat required to dissociate the oxygen molecule into atoms. Lewis<sup>119</sup> has calculated the heat of formation of  $Ag_{g}$  from measurements of the dissociation pressure. The heat of formation

does not change with temperature nearly as rapidly as the heat of solution calculated here. Hence, apparently, the process does not consist merely in the formation of  $Ag_{p}O_{p}$ . The variation of the solubility with the square root of the pressure shows definitely that a dissociation of the oxygen molecule takes place on solution. The actual condition of the oxygen after the dissociation has taken place cannot be definitely established. The two most likely possibilities are the solution of the oxygen atoms in silver as such, or the solution of the oxygen atoms in silver as such, or the solution of  $Ag^{8}O$ . At the temperatures investigated  $Ag_{g}O$  would be in existence at oxygen pressures far below its dissociation pressure. It is, however, possible that the fact that the  $Ag_{g}O$  would be in dilute solution would render it stable, even under such conditions.

There is also the possibility that the oxygen may be present in the form of ions. Thus Hartley<sup>136</sup> found that if gold were heated in oxygen at 370°C it became positively charged, while in hydrogen it became negatively charged. Apparently this charge was due to the gas leaving the metal in the form of ions. Ramsay<sup>137</sup> noticed the activation

of hydrogen which had diffused through palladium. It reacted with gases such as nitric oxide. This however

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might equally well be due to atomic hydrogen, rather than

to hydrogen ions.

### Langmuir<sup>138</sup> found that oxygen de-

creased the electron emission from a heated tungsten

filament, while nitrogen was inactive.

These phenomena, however, might all be explained on the basis of adsorption. They are all surface effects, and there seems to be no necessity for assuming ionized gas.

Other electrical phenomena give evidence against the idea of ions. Richards and Richards<sup>139</sup>, from the results of their investigation on the effect of a magnetic field on iron containing occluded hydrogen, concluded that the hydrogen was in the atomic condition and was not ionized. Richards and Behr<sup>140</sup> came to the same conclusion from the investigation of the E)M.F. of finely divided iron containing dissolved hydrogen. The evidence, therefore, does not seem to support the hypothesis of ionic dissociation.

Che mical affinity plays an important part in deciding whether a gas will be absorbed by a metal or not. Thus the rare gases which possess practically no residual field of force are not absorbed by any of the metals. Nitrogen, also, being relatively inert as far as chemical combination is concerned, is not absorbed, except in cases such as that of iron where a well defined nitride is formed.

129.

### The phenomena of absorption of gases

by metals and of diffusion of gases through metals must

be fundamentally connected. It is virtually impossible

to conceive of a mechanism for diffusion other than that of solution on the high pressure side of the metal and a subsequent giving up of the gas on the low pressure side. Apparently then, solution must precede diffusion and a gas cannot diffuse through a metal in which it is insoluble. That this conclusion is justified by experimental results is shown in Table 61<sup>1</sup>.

#### TABLE LXI.

#### GASES WHICH DIFFUSE THROUGH AND ARE ABSORBED BY

#### METALS.

Metal	Diffusion	No Diffusion	Absorption	No Absorption
Iron	H, N	Ar, He	H <sub>2</sub> , N <sub>2</sub>	Ar, He
Platinum	Н <b>8</b>	О я	H	о s
Palladium	H 2	He	H s	He
Silver	0 2	N z	0 <sub>2</sub>	N 2
Nickel	H 2	N <sub>g</sub> , CO	H 2	N <sub>z</sub> , CO
Copper	H 8		Hg	

Both the rate of diffusion of oxygen through silver, and the solubility of oxygen in silver,

have been found to be proportional to the square root of the pressure. Hence both phenomena point to a dissociation of the oxygen. The rate of solution of oxygen in silver is also proportional to the square root of the pressure. This is to be expected as the process of solution merely consists in the diffusion of the gas  $\gamma \rightarrow \gamma^{\gamma}$ into the metal. The solubility curve shows a minimum at 400°C. There is also a sudden change in the rate of solution at this point. It is therefore probable that the rate of diffusion would show an abrupt change at this point. Unfortunately no measurements have yet been made on the rate of diffusion below 400°C. The case of hydrogen and iron is somewhat analogous. Sieverts showed that there was a sharp rise in the absorption at 850°C, the transition point from Signa to beta iron, corresponding to a similar rise in the rate of diffusion observer by Ryder.

If we assume that diffusion is due to solution we can calculate the actual distribution of oxygen in a silver plate through which the gas is diffusing.



Press.=0

131.

#### Consider a plate of silver of 1

square cm. cross-section, and thickness T cms., through

which oxygen is diffusing from one side on which the press-

ure is P cms. to the other side which is kept evacuated.
Let the concentration of gas dissolved in the metal be C at the high pressure side and  $C_x$  at any distance x in from this side. The number of c.c. of oxygen diff-

using through per second , Q, is given by

$$Q = \frac{k \sqrt{P}}{T} \qquad \dots \qquad (1)$$

The amount of oxygen dissolved in the surface layer,  $C_0$ , will be given by

$$C_{o} = k_{1} \sqrt{P}$$

since the solubility varies as the square root of they pressure. Substituting for P in equation (1),we obtain

$$Q = \frac{KC}{T} \qquad (2)$$

This amount of gas must cross any plane in the metal per second.

The amount of gas diffusing towards the low pressure side at x is given by a similar expression to (2),

$$Q_{X} = \frac{K C_{X}}{T - X}$$

But since the total amount of gas

crossing any plane in the metal per second must be the

same, 
$$Q_x = Q$$
, so that  

$$\frac{KC_o}{T} = \frac{KC_x}{T-x}$$

or 
$$C_{x} = (\frac{T - x}{T}) C_{0}$$
 .....(3)

which gives the concentration of oxygen at any point in the plate.

We can also calculate the average velocity forwards of the voxygen atoms in any part of the plate. The amount of oxygen crossing per second any plane dx, a distance x in from the high pressure side, in a plate of thickness T is equal to the rate of diffusion of the gas through a plate of this thickness, say  $Q_m$  c.c. per square cm. per sec.

The average translational velocity, V, of the atoms of oxygen is equal to the number of atoms going through the layer per second multiplied by the thickness and divided by the number of atoms in the layer, that is

$$V = Q_{T} dx$$
$$\frac{dx \cdot C \cdot S}{1 \cdot C_{O}}$$

where S is the number of c.c. of oxygen dissolved by l cc. of silver at the pressure P. Whence we obtain

$$\mathbf{v} = \mathbf{o} \mathbf{c}$$



Hence

$$V = Q_T C_0 T = Q_T T$$
  
$$\overline{C_T T_x} S$$

Or, if Z is the rate of diffusion in c.c. per square cm. per second through a plate 1 cm. thick, we have

$$Q_{T} = Z/T$$

whence

$$V = \frac{Z}{S(T - x)}$$

From this we can obtain the average resultant velocity of the oxygen atoms through the plate at any point.

Thus, for example, at 500°C and a pressure of 76 cms. we have,

S = 0.104 c.c. per c.c. of silver

T = 0.0205 cms.

 $Z = 2.51 \times 10^{-9}$  c.c. per sq.cm. per sec. Hence we have:

(1). Velocity of entering gas (x = 0)

$$V = \frac{2.51 \times 10^{-9}}{0.104 (0.0205 - 0)}$$

= 1.18 x 10<sup>-6</sup> cms. per sec.

(2). Velocity at centre.(x = T/2)

 $= 2.36 \times 10^{-6}$  cms. per sec.

This is also the average velocity of the oxygen atoms through the whole plate.

IX. CONCLUSION.

From the foregoing discussion, certain conclusions may be drawn as to the mechanism of solution and diffusion in the case of oxygen and silver. The oxygen molecules are dissociated in the silver into atoms. These atoms then dissolve in the silver or react to form  $Ag_0$ .

The process of diffusion consists of the solution of gas in the metal, followed by a movement of the gas through the plate, by being dissolved on the high pressure side and given off on the low pressure side. This is accomplished either by the diffusion of the dissolved oxygen atoms, or by the handing on of the oxygen in Ag<sub>o</sub>O from one silver atom to the next.

The process of solution is similar to that of diffusion. The outer layer of the silver is kept saturated and gas diffuses from this layer into the interbor according to Fick's Law.

While no definite decision can be made as to whether the dissolved gas exists in the atomic state or as  $Ag_0$ , it appears to be more likely that it

is in the atomic condition.

The effect of temperature on the

solubility and the rate of solution points to the trans-

ition of the silver from one allotropic form to another

in the neighbourhood of 400°C.

The measurement of the rate of diffusion is difficult, while the rate of solution is comparatively easily determined. It is hoped that future work will establish the connection between the two and enable the rate of diffusion to be calculated from solution velocity measurements.

137.

### $\underline{\mathbf{X}}. \quad \underline{\mathbf{S}} \ \underline{\mathbf{U}} \ \underline{\mathbf{M}} \ \underline{\mathbf{M}} \ \underline{\mathbf{R}} \ \underline{\mathbf{R}} \ \underline{\mathbf{Y}} \ .$

- (1). An apparatus has been devised, by means of which accurate measurements of the solubility of gases in metals may be made.
- (2). The solubility of oxygen in silver has been measured over a wide range of temperature at various pressures.
- (3). The solubility is proportional to the square root of the pressure.
- (4). The solubility-temperature curve shows a minimum at 400°C. Above this the solubility is expressed by 1/Q = K(930 - T), where Q is the solubility and T is the temperature in °C.
- (5). The rate of solution of oxygen in silver has been measured over a considerable range of temperature and pressure. The equation K = 1/t (log S/S-X C) has been found to express the experimental results, where S is the saturation concentration, X is the amount dissolved atytime t, and K and C are constants.

(6). The rate of solution is proportional to the square

### root of the pressure. The variation with temp-

erature is complicated and has not been explained.

(7). By comparison with diffusion measurements, the concentration gradient and the average forward velocity of oxygen atoms in diffusion have been calculated. (8). The mechanism of diffusion and of solution has been discussed.

(9). Nitrogen has been shown to be insoluble in silver.

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