[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Accommodation Coefficient of Hydrogen on Iron

BY H. H. ROWLEY AND W. V. EVANS

Introduction

The concept of the accommodation coefficient as a measure of the completeness of heat exchange between a gas and a solid body was introduced by Knudsen[1] and has since been studied experimentally by numerous investigators. It was found that the accommodation coefficient is dependent not only on the nature of the gas but also to a large extent upon the condition of the solid surface.

Most of the previous experiments concerned the accommodation coefficient of light gases, such as helium and hydrogen, on the surfaces of heavy metals like platinum and tungsten. Earlier work[2] showed that the accommodation coefficient of hydrogen on a platinum surface freed from ordinary contamination was 0.22 at room temperature and that with decreasing temperature it rose to a value of 0.37 at 110°K. A similar rise was noted by Blodgett and Langmuir[3] for hydrogen on a tungsten surface. This negative temperature coefficient is contrary to the results obtained for helium[4] and to certain theoretical expectations.[5] The anomaly was explained by the presence of two types of adsorption layers: at room temperature the hydrogen was atomically adsorbed (active adsorption) giving rise to a more firm, rigid (smoother) surface and thus a lower accommodation coefficient; at the temperature of liquid air, the more loosely bound, molecular adsorption prevailed and the resulting rougher surface favored better heat exchange and consequently a higher accommodation coefficient.

The present work was undertaken to determine whether this rise was characteristic for hydrogen and also to determine whether a metal of lighter mass had any appreciable effect on the value of the accommodation coefficient. To determine this, the heat exchange of hydrogen at an iron surface was determined over a temperature range from 120–450°K. The method used was essentially the measurement of the amount of heat given up by an electrically heated wire at relatively low pressures of hydrogen.

Experimental

Apparatus.—The apparatus was practically the same as that used previously in determining the heat exchange of hydrogen on a platinum surface.[2] The cell consisted of a fine iron wire (over 99.9% pure) with a measured diameter of 0.0128 cm. stretched along the axis of a vertical Pyrex glass tube 1 cm. in diameter and about 23 cm. in length. The ends of the iron wire were silver soldered to 0.03-mm. tungsten leads which in turn were sealed through the glass. The lower lead-in wire was sealed through the side of the cell about 3 cm. from the bottom and the lower portion of the iron wire formed into a loop from which was suspended a glass weight filled with mercury. This weight not only served to keep the wire centered in the tube but also to take up the slack when the wire was heated and prevent its touching the walls and becoming contaminated.

The cell was sealed to a regular vacuum system containing a manometer, McLeod gage, hydrogen reservoir, mercury diffusion pump, Hy-vac oil pump, appropriate freezing-out traps and phosphorus pentoxide tubes. The hydrogen used was obtained by the electrolysis of dilute sodium hydroxide solution followed by diffusion of the hydrogen into the reservoir through an electrically heated palladium tube.

In order to eliminate the cooling effect of the tungsten leads, the resistance of the iron wire was not measured directly but the potential drop on the wire was determined between two potential leads of 0.05-mm. platinum wire firmly wrapped about the iron wire and connected to a Leeds and Northrup type K potentiometer through two extra tungsten leads sealed into the sides of the cell. The section of wire between the potential leads was 6.21 cm. in length and located in the middle of the wire as far removed from the lead in wires as possible.

The current passing through the wire was determined by means of an accurate milliammeter placed in the circuit. The temperature–resistance curve was determined by letting pure hydrogen at a pressure of 10–20 mm. into the cell which was immersed in a liquid bath at the proper temperature and passing a small current through the wire, sufficient to give an accurate potential reading but not enough to heat the wire above the temperature of the bath. Separate experiments showed that even with thirty milliamperes flowing, there was no appreciable rise of temperature. Twenty milliamperes was the current used for all calibrations.

Condition of the Wire.—The wire was carefully cleaned and placed in position, care being taken not to touch the wire with the fingers after cleaning. When the cell was constructed and sealed to the apparatus, the wire was

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[1] M. Knudsen, *Ann. Physik*, **34**, 593 (1911).

[2] H. H. Rowley and K. F. Bonhoeffer, *Z. physik. Chem.*, **B21**, 84 (1933).

[3] K. Blodgett and I. Langmuir, *Phys. Rev.*, **40**, 78 (1932).

[4] J. K. Roberts, *Proc. Roy. Soc.* (London), **A129**, 146 (1930); **A135**, 492 (1932).

[5] C. Zener, *Phys. Rev.*, **37**, 556 (1931); **40**, 335 (1932); Jackson and Mott, *Proc. Roy. Soc.* (London), **A137**, 703 (1932); Jackson and Howarth, *ibid.*, **A142**, 447 (1933).

further cleaned by alternately heating in hydrogen and in vacuum at a temperature of not over 900°K., a treatment which should reduce any oxide formed and remove the resulting water. This cleaning process was repeated at frequent intervals throughout the course of experiments. This was the condition of the wire during most of the experiments and a wire so treated is referred to as a "normally" clean wire. The glass cell, freezing-out traps and connecting tubes were also baked out in electric ovens and frequently torched with a Bunsen flame in order to remove adsorbed and occluded gases that might affect the results.

Some later experiments were performed in which the wire was glowed for considerable time in vacuum just before the measurements in an effort to dislodge the adsorbed hydrogen layer which was believed to be present under the above conditions. It was found that after heating, the resistance of the wire at the bath temperature changed—sometimes considerably. At first, it was believed that this change was due to strains in the wire caused by uneven annealing and an attempt was made to relieve these by glowing at about 900–1000°K. in hydrogen for a period of several hours. This treatment did not seem to correct the difficulty. A separate series of experiments seemed to indicate very clearly that this change in resistance was not due to absorbed hydrogen, which is in agreement with work of Sieverts.[6] Inasmuch as the glowing wire reached a temperature of 1000–1200°K., the change in resistance was probably due to incomplete changes in the internal structure of the iron which is known to exist in at least three modifications, α-, β-, γ-iron and which have different resistances. This incomplete change caused different parts of the wire to have different resistances and hence when the wire was heated in vacuum (to avoid any possible Busch effect[7]) it glowed unevenly. This uneven heating might be due to variations in the diameter of the wire,[8] but since the dark places in the wire showing varying resistances shifted, this could not be the answer.

However, numerous calibrations of the temperature–resistance curve over the temperature range used for the experiments showed all these curves to have essentially the same slope, so that by determining the resistance of the wire at the temperature of the bath for each experiment, the temperature–resistance curve for that run could be found, even though the resistance of the wire at 274°K. varied from 0.110 ohm/cm. to 0.082 ohm/cm. Due to this irregularity, the temperature of the wire as read from the calibration curve was the average temperature of the section measured.

Calculation of the Accommodation Coefficient.—The method of calculation was the same as that used for determining the accommodation coefficient of hydrogen on platinum[2] and evolved the following formula

$$\alpha = \frac{\sqrt{2mk/\pi} \times 10^7}{dk\ 1332} \times \frac{W_c \sqrt{T_a}}{(\beta + {}^1/_2)p(T - T_a)}$$

where m is mass of molecule (3.32×10^{-24} g. for hydrogen), k is the Boltzmann constant (1.371×10^{-16} ergs/deg.), d is the diameter of wire (0.0128 cm.), p is pressure in mm., T is temperature of the wire, T_a is temperature of the incident gas molecules. Since, at the pressures used, the mean free path of the hydrogen molecules equals or exceeds the radius of the cell, the temperature of the incident molecules can be taken as equal to the temperature of the cell walls or the bath temperature. W_c is the energy loss per second from the wire in watts/cm. and is calculated from the potential drop along 6.21 cm. of the wire and the current flowing. βk is the specific heat at constant volume per molecule expressed in ergs/deg. K. When hydrogen is cooled to low temperatures, the specific heat approaches that of an ideal monatomic gas and β has the value 1.5 at 45°K.; at higher temperatures, the specific heat increases to values characteristic of diatomic gases and $\beta = 2.44$ at 273°K.[9] The values of β used when T_a was below 273°K. were those for the average temperature of the wire and the bath. Though β changes rather rapidly in this temperature range it was believed to be a better approximation of the true value than the value at either the wire or the bath temperature. It might be noted here that substitution of the other values did not materially change the type of curve obtained.

The pressure was measured with a McLeod gage, the mercury vapor being kept from the cell by means of liquid air or solid carbon dioxide–acetone traps. Since the measurements were never at room temperature, there is, according to Knudsen,[10] a pressure difference between the cell and the McLeod. In the pressure range used in these experiments where the quotient (diameter of connecting tube d)/(mean free path)λ has a value between 1.5 and 6, the following empirical formula holds according to Roberts[4]

$$p_1 - p_2 = (\lambda_0 \times 10^4/7.28\ d)\ (T_1 - T_2)$$

where λ_0 is the mean free path at 273°K. and 760 mm. and taken as 1.8×10^{-5} cm. for hydrogen. The pressures were corrected with this formula for all bath temperatures.

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(6) A. Sieverts, *Intern. Z. Metallog.*, **3**, 37 (1913).

(7) H. Busch, *Ann. Physik*, **64**, 401 (1921); A. Farkas and H. H. Rowley, *Z. physik. Chem.*, **B22**, 335 (1933). This effect is frequently noted when a fine wire is heated in a gas at low pressures. Under certain conditions, the even temperature distribution along a wire becomes suddenly unstable and the wire takes on an uneven temperature; some sections may be glowing while others are at room temperature, though the average temperature of the entire wire may not change appreciably from its previous value.

(8) Actual measurements of sections of the wire taken at random failed to show any marked deviation from 0.0128 cm.

(9) "International Critical Tables."

(10) M. Knudsen, *Ann. Physik*, **31**, 205 (1910); O. Reynolds *Phil. Trans.*, **170**, 727 (1879).

Experimental Procedure and Data

Surface of Wire "Normally" Clean.—After treating the wire and getting it in a "normally" clean condition, the cell was completely immersed in a constant temperature bath. Five different bath temperatures were used during the experiments: liquid air at 88°K., acetone–solid carbon dioxide at 195°K., ice water at 273°K., petroleum oil bath at 325 and 373°K. Pure hydrogen was let into the apparatus at a pressure of about 0.025 mm. of mercury and accurately measured with the McLeod gage. A known current from a six-volt storage battery was then passed through the cell and the potential drop along the wire measured. From these data the resistance and hence the temperature of the wire could be found. About five minutes was allowed for the cell to come to thermal equilibrium. Four or five measurements were made during each trial, the temperature of the wire ranging from 30 to 100° above that of the bath. Typical data for the various bath temperatures are given in Table I.

In a separate series of experiments, the heat lost from the wire by metallic conduction and radiation was determined for each bath by evacuating the cell and recording the energy necessary to bring the wire to a temperature 30–100° above that of the bath. Values from these curves were always subtracted from the total energy input in order to determine the amount of heat actually carried away from the wire by the gas molecules. Check determinations at various times indicated that this correction factor was constant for any one bath and wire temperature.

TABLE I

ACCOMMODATION COEFFICIENT OF HYDROGEN ON A "NORMALLY" CLEAN IRON WIRE

Press., mm.	T, °K. wire	Watts/cm.	β	α
Bath temp., 88°K.				
0.0230	119	0.001316	1.76	0.555
.0230	122	.001509	1.77	.580
.0230	130	.001785	1.79	.550
.0223	133	.001810	1.81	.530
.0230	137.5	.002073	1.84	.530
.0230	147	.002418	1.86	.515
.0223	152	.002487	1.87	.500
.0230	157.5	.002810	1.88	.505
.0230	171.5	.003310	1.93	.485
.0223	181.5	.003480	1.96	.465
.0230	190.5	.004006	1.98	.465
.0230	205	.004509	2.03	.450
.0223	215.5	.004621	2.06	.435
Bath temp., 195°K.				
0.0175	229	0.000679	2.31	0.410
.0175	236.5	.000818	2.32	.405
.0200	237	.000884	2.32	.380
.0175	243.5	.000932	2.33	.395
.0200	247.5	.001096	2.33	.375
.0175	250.5	.001052	2.34	.385
.0175	259	.001197	2.35	.380
.0200	262	.001377	2.35	.365
.0175	270.5	.001381	2.37	.370
.0200	274	.001597	2.37	.360
.0175	282	.001586	2.38	.365
Bath temp., 273°K.				
0.0240	317	0.000416	2.47	0.315
.0250	320	.000883	2.47	.305
.0250	325	.000995	2.47	.310
.0240	328.5	.000985	2.47	.300
.0250	330	.001091	2.47	.310
.0250	335	.001174	2.47	.305
.0240	339	.001187	2.47	.305
.0250	340	.001306	2.47	.315
.0250	347.5	.001413	2.47	.305
.0240	349.5	.001370	2.47	.300
.0240	356.5	.001509	2.47	.305
.0250	357.5	.001619	2.47	.310
Bath temp., 325°K.				
0.0245	358.5	0.000582	2.48	0.310
.0225	362.5	.000603	2.48	.315
.0245	367.5	.000742	2.48	.315
.0225	371.5	.000741	2.48	.310
.0245	377	.000886	2.48	.305
.0245	383	.001006	2.48	.310
.0225	390	.001005	2.48	.300
Bath temp., 373°K.				
0.0240	416.5	0.000707	2.49	0.320
.0235	418	.000694	2.49	.310
.0240	424	.000802	2.49	.310
.0235	424.5	.000791	2.49	.305
.0235	431.5	.000905	2.49	.310
.0240	432	.000912	2.49	.305
.0240	439	.001005	2.49	.300
.0235	439	.001008	2.49	.305
.0240	446.5	.001115	2.49	.295

Attempts to Obtain Bare Surface.—It appears quite certain that the "normally" clean surface is actually covered with adsorbed hydrogen. Patterning after the work of Roberts[4] and Mann,[11] a similar technique was employed in attempting to obtain an iron surface free from adsorbed hydrogen. The wire which had been cleaned of ordinary contamination in the usual way, was glowed at 1000–1100°K. for varying periods of time in vacuum. The temperature of the wire was quickly lowered to a value about 80° above that of the bath and the time noted. Pure hydrogen at the proper pressure was introduced as soon as possible (within one minute) after re-

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(11) W. B. Mann, *Proc. Roy. Soc.* (London), **A146**, 776 (1934).

ducing the current and readings taken at frequent intervals for twenty to thirty minutes. It was found that after about thirty minutes of glowing in vacuum the values of the accommodation coefficient dropped appreciably, giving 0.35 at 180°K. and 0.18 at 351°K. Further half-hour periods of heating at 1000–1100°K. failed to lower these values.

In an attempt to lower the values still further, the wire was heated to 1000–1100°K. in a vacuum for twelve hours. During this heating the resistance of the wire changed markedly as noted above. Using the same technique as before, the accommodation coefficient was found to be 0.21 at 346°K. and failed to change by further fifteen minute periods of heating in vacuum. The slightly higher value obtained might well be due to a change of surface caused by prolonged glowing.

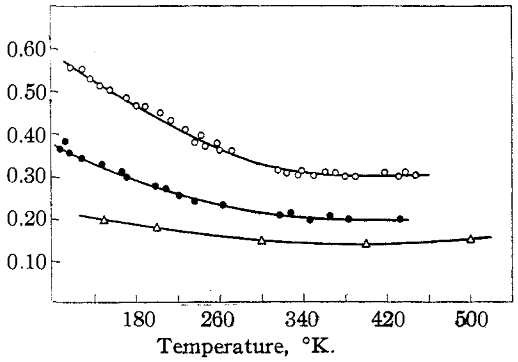

Fig. 1.—Change of accommodation coefficient with temperature: ○, iron wire saturated with hydrogen; ●, platinum wire recently glowed; △, tungsten wire specially cleaned.

Some runs were also made in which the wire was heated in hydrogen. In a typical experiment it was found that according to the measurements of the first few minutes, the accommodation coefficient rose quite rapidly. It is interesting to note that in some cases after this first sharp rise the values remained fairly constant for twenty to thirty minutes though showing a definite tendency to increase. In certain other cases, the increase was more rapid though nowhere near as great as during the first few minutes as shown in Table II. Upon letting the wire stand in contact with hydrogen at room temperature for several hours, the regular value of 0.31 was always obtained.

Table II

Increase of Accommodation Coefficient with Time

Bath temperature, 273°K.

Minutes	1	2	3	6	17
α	0.172	0.196	0.209	0.210	0.211
Minutes	1	2	3	4	6
α	0.130	0.205	0.228	0.236	0.238
Minutes	10	15	30	60	
α	0.245	0.250	0.263	0.278	

Discussion of Results

The values of the accommodation coefficient obtained for a "normally" clean iron wire follow quite closely those of hydrogen on a platinum surface, rising considerably as the temperature of the wire is decreased. The relatively higher values obtained with iron might be due to the smaller mass of the iron, since according to the theory of Baule[12] the energy exchange by collision between gas molecules and surface atoms of a solid body is more complete the smaller the difference in mass between the colliding particles. However, it seems more probable that the higher value is due to adsorbed layers on the surface. This is further substantiated by the fact that shortly after glowing the iron wire, the values of the accommodation coefficient are practically the same as those for a platinum surface which had been similarly treated.

With respect to the increasing accommodation coefficient with decreasing temperature, it is interesting to compare three different sets of values obtained at low temperatures. In Fig. 1 are plotted the values for a "normally" clean iron wire, a platinum wire that had been recently glowed[2] and a tungsten wire with which special pains had been taken to obtain a perfectly clean surface.[3] It is significant that in all cases there is a decided upward trend below 350°K., being greatest in the case of the iron and least in the case of tungsten. Recent work of Gregory[13] with platinum surface also shows a definite rise from 500 to 300°K. though not as great as that obtained at lower temperatures. This general rise in all cases would tend to substantiate the suggestion made in the previous paper[2] that two types of adsorption are causing this effect. According to certain theoretical considerations,[5] if the condition of the surface remains unaltered, the accommodation coefficient should decrease with decreasing temperature. That this is the case above approximately 500°K. appears to be shown by work of Blodgett and Langmuir[3] and others. In this range it might be assumed that the hydrogen was atomically adsorbed. Below

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[12] B. Baule, *Ann. Physik*, **44**, 145 (1914).

[13] H. S. Gregory, *Proc. Roy. Soc.* (London), **A149**, 35 (1935).

this range, a second type of adsorption begins to take place, possibly a molecular adsorption on top of the atomic adsorption. This second type, being more loosely bound, would form a rougher surface and hence bring about a better exchange of energy between the gas molecules and solid. For a range of about 150°, this increasingly rough surface would offset the drop in the accommodation coefficient due to decreasing temperature and give values more or less constant such as actually found between 350 and 500°K. As the temperature was lowered still further, this molecular adsorption would become predominant and cause an actual rise in the accommodation coefficient. If such is the case, the values should reach a maximum and then drop sharply. Since no supply of liquid hydrogen was available, it was impossible to test this experimentally. The more ready adsorption of hydrogen on iron might explain the steeper rise at low temperatures than that observed with platinum or tungsten.

It might appear that this rise at low temperatures was caused by applying the pressure correction when the bath was not at room temperature. When the bath was below room temperature this correction, which amounted to 0.005 mm. at liquid temperatures, was subtracted from the pressure as read on the McLeod. This would tend to cause a rise in the calculated values. However, even if this correction were ignored, which we did not feel justified in doing, the curve still showed a decided upward trend giving values of 0.41 at 150°K.

It would appear that in all cases, even with the tungsten surface which had been carefully cleaned, there was adsorbed hydrogen on the wire to a greater or less extent. The value of 0.31 might be taken as the accommodation coefficient of hydrogen on a bright iron surface saturated with hydrogen at 350°K. It is interesting to compare values of the accommodation coefficient of hydrogen on various surfaces in this temperature range as shown in Table III. In all the cases chosen, the condition of the surface might be termed "normally" clean, *i. e.*, no special attempt had been made to get rid of adsorbed hydrogen. Considering the wide difference in the substances used and also the noticeable effect of rough surfaces, it is surprising to find the values of the accommodation coefficient so nearly the same. This fact seems to indicate that in all cases the solid surface was covered with adsorbed hydrogen and that the heat exchange was between hydrogen gas molecules and an adsorbed hydrogen surface. When a special technique is used to remove this hydrogen layer, lower values are always obtained, *i. e.*, 0.11 for platinum,[11] 0.14 for tungsten,[3] 0.18 for iron, but it is believed that even in these cases there is some adsorbed hydrogen. Langmuir[3] and others also postulated adsorbed layers in these cases.

TABLE III

ACCOMMODATION COEFFICIENT OF HYDROGEN ON VARIOUS SURFACES

Investigator	Surface	Temp. of surf. °K.	α
Knudsen[14]	Platinum	273	0.315
Knudsen[1]	Platinum	273	.26
Soddy and Berry[15]	Platinum	335	.25
Gregory[13]	Platinum	389	.25
Rowley and Bonhoeffer[2]	Platinum	350	.21
Soddy and Berry[15]	Palladium	(335)	(0.25)
Blodgett and Langmuir[3]	Tungsten	400	.22
Hughes and Bevan[16]	Nickel	437	.25
Chapman and Hall[17]	Silver	373	.25
Knudsen[1]	Glass	300(?)	.26
Rowley and Evans	Iron	350	.31

In the experiments where an attempt was made to dislodge this adsorbed hydrogen from the iron surface, the rapid rise of values during the first few minutes (see Table II) might be construed to mean a very rapid adsorption during the first few minutes such as Mann found on platinum.[11] Though this may be true, it appears certain that the wire and cell were not at thermal equilibrium much under three or four minutes after glowing the wire. Since the correct calculation of the accommodation coefficient by this method depends upon thermal equilibrium, values taken before this time have no great significance.

Summary

1. The accommodation coefficient of hydrogen on a bright iron surface saturated with hydrogen has been determined for the temperature range 120–450°K. and found to be 0.31 at the higher temperatures and rising steadily below 350°K. to 0.55 at 120°K.

2. This rise with decreasing temperature has been compared to similar results obtained with platinum and tungsten surfaces and discussed

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(14) M. Knudsen, *Ann. Physik*, **6**, 129 (1930).

(15) F. Soddy and A. J. Berry, *Proc. Roy. Soc.* (London), **A83**, 254 (1910); *ibid.*, **A84**, 576 (1911).

(16) D. R. Hughes and R. C. Bevan, *ibid.*, **A117**, 101 (1928).

(17) D. L. Chapman and W. K. Hall, *ibid.*, **A124**, 578 (1929).

on the basis of two distinct types of adsorbed hydrogen.

3. Comparison of the accommodation coefficients obtained by numerous investigators on different surfaces leads to the conclusion that the exchange of energy between hydrogen gas molecules and an adsorbed layer of hydrogen was measured in each case.

4. An attempt to remove this adsorbed layer lowered the accommodation coefficient from 0.31 to 0.18 at 350°K.

EVANSTON, ILLINOIS RECEIVED JULY 22, 1935

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Some Fluorinated Chlorobenzenes[1]

BY HAROLD SIMMONS BOOTH, HOWARD M. ELSEY[2] AND PAUL E. BURCHFIELD[3]

A survey of the literature revealed descriptions of the preparation of only ortho[4] and para-chlorofluorobenzene.[5] In order to complete the series of monochlorofluorobenzenes the preparation of meta-chlorofluorobenzene from meta-chloroaniline was undertaken.

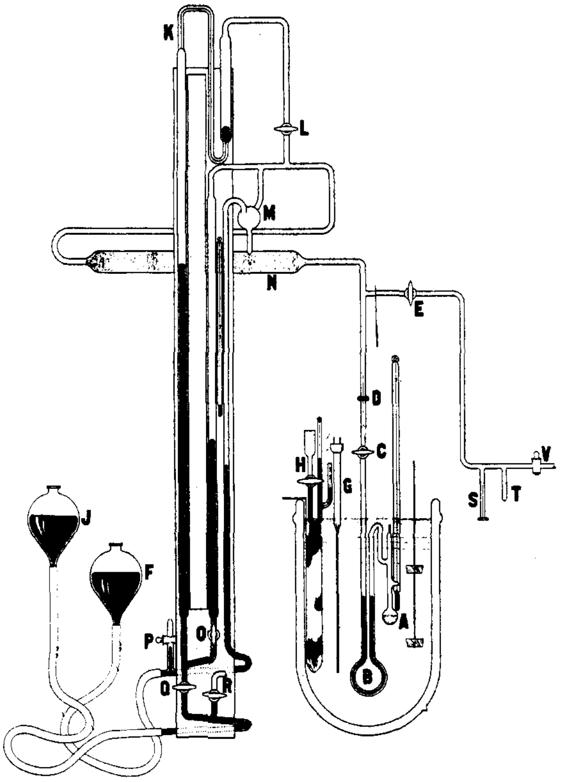

Fig. 1.

De Crauw[6] reported the preparation of 2,4,5-trichlorofluorobenzene from meta-fluoroaniline by several steps. De Crauw stated that a fluorine atom cannot be introduced into the benzene ring ortho to chlorine. The preparation of 2,4,6-trichlorofluorobenzene was attempted in order to extend the knowledge of this class of compounds and to discover whether or not the Balz and Schiemann reaction would effect the introduction of fluorine ortho to chlorine. In addition 2,4,6-trichlorofluorobenzene was successfully prepared from 2,4,6-trichloroaniline.

Experimental

Method of Determining Vapor Pressures

The apparatus for the determination of vapor pressure used in this research consisted of a modified "static isoteniscope,"[7] a suitable thermostat equipped with automatic and manual heat controls, and a modified Germann barometer,[8] shown in Fig. 1.

For the measurement of vapor pressure, a carefully purified sample was introduced into the bulb (A) the volume of which was approximately 2 cc. One arm of the bulb was connected to one side of the short U-manometer (B), the other arm was sealed to a tube (T) connected to a Hyvac pump. The second side of the U-manometer was provided with a stopcock (C) and a flat joint (D) and could also be connected by means of the flat joints (D) and (S) to the Hyvac pump. Both sides of the U-manometer were simultaneously evacuated for some time, and the mercury was carefully heated to its boiling point under the reduced pressure so that residual gases entrapped by the mercury were driven out.

When the mercury cooled, a small part of the sample was condensed on it in (B) and redistilled off in order to completely wash out any residual permanent gases in the sample chamber. The tube (T) connecting the sample bulb to the vacuum system was sealed off while the liquid in A was cooled in liquid air, and the other side of the small manometer was closed by means of stopcock (C).

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(1) From a portion of a thesis submitted by **Paul E. Burchfield** to the Graduate School, Western Reserve University, June, 1934, in partial fulfilment of the degree of Doctor of Philosophy..

(2) Manager of Chemical Division, Westinghouse Research Laboratories, East Pittsburgh, Pa.

(3) Holder of the Westinghouse Fellowship in Chemistry, 1932-1934.

(4) Rinkes, *Chem. Weekblad*, **11**, 360, 952 (1914).

(5) Wallach and Heusler, *Ann.*, **243**, 219 (1888); Swarts, *Rec. trav. chim.*, **35**, 131 (1915).

(6) De Crauw, *ibid.*, **48**, 1061 (1929).

(7) A. Smith and A. W. C. Menzies, THIS JOURNAL, **32**, 1412 (1910).

(8) A. F. O. Germann, *ibid.*, **36**, 2456 (1914).