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THESIS.

SPECIFIC HEAT AT CONSTANT PRESSURE OF HYDROGEN, NITROGEN, AND THE MIXTURE $N_2 + 3H_2$; VARIATION WITH PRESSURE UP TO 200 ATMOSPHERES.

The thesis is one of the reports prepared on work done in the Munitions Inventions Department Laboratories at University College, London, under the direction of the late Dr.H.C.Greenwood.

A summary of results is set out on p.1.

In an introductory section (p.p.2 & 3) is given the relation of the problem treated to the general problem (ammonia synthesis) of the laboratory and an account of earlier and related work by Lussana, Holborn & Jakob, & G.W.Todd.

Under the heading, "Report of Experiments" (pp 3-7) an account of the choice of the method used, and a description of the several parts of the apparatus, are given together with statements of the methods of manipulation & calibration, and a representative set of observations. In connection with this last it should be noted, that, while all the readings taken during the actual passage of the gas through the apparatus are given, only the last few of the preliminary "cooling period", and the first few of the final "cooling period" are shown.

The section "Calculations & Results" (pp 7-12) contains a statement of the method of treating the observed valves & sets out the Results obtained from them. The actual observed Cp valves and the corresponding pressures are shown (pp 8, 9 & 11) under the names of the relative gases in the columns headed Cp (obs.) and P of the tables headed "Tabulation of Results etc" I II & III;

in the case of air the observed values & pressures are given in a separate table on p.11. It is shown (p.9) that the Cp valves for H_2 & N_2 are additive for the mixture 74.5% H_2 + 25.5% N_2 and the actually observed valves for this mixture are then corrected (p.10) for the ideal mixture 75% H_2 + 25% N_2 ie. $3H_2 + N_2$.

The results are then discussed (pp 11 & 12) and the significance of the air figures is pointed out.

STATEMENT OF THE AUTHORSHIP OF THE THESIS "SPECIFIC HEAT AT CONSTANT PRESSURE OF HYDROGEN, NITROGEN, & THE MIXTURE $N_2 + 3H_2$; VARIATION WITH PRESSURE UP TO 200 ATMOSPHERES" BY

VICTOR E.PARKE.

On having the problem apportioned to me by Dr.Greenwood, I searched & digested the relative literature available at the Patent Office Library, London (see in particular "References" p 13 of Thesis) and on this search & digest are based both the choice of the method & apparatus for the work & the criticism of other work (pp 2,3 & 12).

The device of direct measurement of the gas entry & exit temperatures was used in Dr.Todd's earlier experiments, but I have no certain knowledge of the origin of it. Dr.Greenwood & I shared the design of the four-way pieces etc for housing the couples.

The whole of the observations, save only the potentiometer readings (gas entry & exit couples) which could not be done by the same observer as controlled the experiment,

the experimental control and arrangement and the calculations are my own.

To the extent therefore above set out, I declare that the work is mine.

July, 1919. Amm: Syn: No:113.

SPECIFIC HEAT AT CONSTANT PRESSURE OF HYDROGEN, NITROGEN, AND THE MIXTURE $N_2 + 3H_2$; VARIATION WITH PRESSURE UP TO 200 ATMOSPHERES.

SUMMARY OF RESULTS.

The experiments were carried out at a mean temperature of about 60°C. and the following results obtained:

(1) C_p increases regularly with increase of pressure in each case studied, and the variations are represented by the following equations:-

Hydrogen, $C_p = 3.418 + 4.27 \times 10^{-4}P$ see P. 8
Nitrogen, $C_p = 0.2475 + 2.45 \times 10^{-4}P$ see P. 9
Mixture, $C_p = 0.804 + 3.00 \times 10^{-4}P$ see P. 10

P. Represents absolute pressure in atmospheres.

These are accurate to 0.3% in the case of Hydrogen and to 0.5% in the other cases. The formulae are in terms of gram atmospheres and calories. These equations may be written in terms of atmospheres and C.H.U. per 1000 cubic ft. free gas at 20°C. viz.,

Hydrogen $17.87 + 2.23 \times 10^{-3}P$ see P. 10

Nitrogen $18.01 + 1.78 \times 10^{-2}P$ "

Mixture $17.78 + 6.65 \times 10^{-3}P$ "

(2) Within the range and accuracy of the present work the values are additive for mixtures of nitrogen and hydrogen.

(3) The following values are obtained from the equations above:

Pressure		Specific Heat.		
Abs.	Gauge	Hydrogen	Nitrogen	Mixture.
0	--	3.418	.2475	.804
1	0	3.418	.2477	.804
51	50	3.439	.2600	.819
101	100	3.461	.2722	.834
151	150	3.482	.2845	.849
201	200	3.503	.2968	.864

(4) As a "control", determinations of C_p for air were made from time to time and results agreeing well with those of Holborn & Jakob 1) were obtained (p.11). This agreement was found at the lowest pressures,

1) All references explained on P. 13.

studied so that the present work has cleared up the discrepancy between the value of 0.237 obtained at ordinary pressure by Witkowski 2) and others by the Regnault method, and the value of 0.241 obtained by Holborn and Jakob and others by the Callendar method. In the present experiments a modified Regnault apparatus (see Fig:1) was used, and agreement was obtained with the figures from the Callendar method.

INTRODUCTORY.

General.

The present experiments were undertaken on account of the unsatisfactory nature of previous work on this subject which is of great importance in connection with the synthetic production of ammonia by the Haber process. The thermal balance in the catalyst system depends on the relation between the heat of the reaction and the heat carried away from the system by the warm gases leaving the heat-interchanger. It will readily be appreciated that as the autothermicity or otherwise of a given catalyst furnace depends on the difference between these two quantities, an uncertainty of say 10% in the specific heat is an important matter. Unlikely as it may seem, it can be stated without exaggeration that the uncertainty as to the pressure coefficient of the specific heat at constant pressure of hydrogen, for example, made the absolute value uncertain to the extent of some 20% at 100 atm.

The matter is also of importance in connection with the use of calorimetric flow meters for the determination of the rate of flow of high pressure gases, through conduits, and in relation to determinations of the coefficient of heat-transfer between high pressure gases and solid surfaces.

Previous Work.

The only direct measurements of the specific heats of gases under high pressure are due to Lussana 3) and to Holborn and Jakob 1) respectively.

Lussana worked chiefly with air but also with hydrogen and carbon dioxide. He used the Regnault method and his apparatus was designed to permit of the circulation of a small quantity of gas a large number of times. But as the sketch given by Lussana himself and copied by Preston 4) is specially stated to be diagrammatic only, it is difficult to go into detail in description or to criticise adequately. The following points however are emphasised by Lussana in his own description:- The gas is contained in one of two cylinders the other of which contains mercury and can be adjusted to put any desired pressure on the gas and to drive it through the apparatus. After completing the circuit the gas collects in the second cylinder, taking in turn the place of the mercury which has displaced it from the first. After passing a manometer the heater is reached. This is an air bath containing the long heating coil and having a jacket heated by steam or petrol vapour. The temperature of the air bath is taken on a mercury thermometer and is assumed to be the entry temperature of the gas to the calorimeter; by preliminary experiments Lussana claims to have justified this assumption.

The calorimeter is of copper standing in an air space inside a double vessel, the annulus being full of lagging. The mean calorimeter temperature is taken as the mean gas exit temperature from the calorimeter, and here again it is claimed that previous experiments have justified this procedure (on this point see p.12). In the original form of the apparatus the calorimeter was protected from the heater

by an insulating slab, and the naked gas pipe passed over the top of this and entered the calorimeter by the lid. Later, however, the slab was made a part of the actual wall of the calorimeter and the pipe passed through it 1 mm. below the water level.

For his results see p.12

Holborn and Jakob 1) used a modification of Callendar's 5) continuous flow method for liquids which is described with a sketch in their paper.

The calorimeter is a nickel steel cylinder 45 cm. long, 9 cm, dia, and .5 cm. wall with domed ends, at one of which the gas enters by a 4.5 cm. pipe, leaving at the other by a 3.5 cm. pipe. The gas enters at a constant temperature, about 18°C. which is measured by a resistance thermometer, and then passes an electric heater inside the calorimeter, which gives to it a quantity of heat which can be exactly measured. It is now directed by baffles along the calorimeter wall and issues at a second constant temperature also measured by a resistance thermometer. The calorimeter is surrounded by an air jacket which is itself surrounded by a jacket of boiling water

For fuller detail on Previous Work see Amm. Syn. No.72.

Finally reference should be made to some preliminary determinations carried out in this laboratory by Dr. G. W. Todd in 1918. The method of mixtures was used as in the present investigation, the apparatus being somewhat similar in type to that now employed, but the temperatures of the gas entering and leaving the calorimeter were measured only by thermocouples on the exterior of the tubes and the calorimetric arrangements were much less elaborate. The experiments sufficed to indicate that the high pressure coefficient found by Lussana for hydrogen was certainly erroneous but a considerable rise was still observed. The main object was, however, to give, very rapidly, approximate data for immediate use; and this object attained, the problem has now been attacked in a much more searching manner. This step was the more necessary as calculations based on Witkowski's compressibility data had indicated a very small pressure coefficient in the case of hydrogen. As a result the values given below are forthcoming.

The value of the accurate treatment of the problem is evident from the statement that the specific heat of hydrogen at constant pressure under 200 atms. is now found to be 3.503, i.e., the pressure coefficient is almost negligible; the experiments of Lussana had indicated a value of 3.788 for 30 atms., giving a mean rise of .013 per atm., and the previous rough experiments by Dr. Todd had given a value of 4.1 at 100 atms., giving a mean rise of .007 per atm.

REPORT OF EXPERIMENTS.

The Regnault method offered several advantages over the Callendar method from the point of view of the present work. The apparatus is more compact, for no circulator is necessary; the duration of determinations is less, for there is nothing corresponding to the long time (3 hrs) needed for the Callendar apparatus to attain a steady temperature distribution; and the quantity of gas measured is comparatively small. Futher, it is clear from the work of White 6) that the Regnault method is amply capable of the accuracy required and is at no disadvantage compared with the Callendar method in the matter of number, difficulty, uncertainty or magnitude of corrections.

The Apparatus (see Fig: I).

Purified gas is stored at high pressure in the Cylinder A

and delivered from it (through a $CaCl_2$ drier for pressures less than 50 atm.) via the fine adjustment valve B and the four-way piece C, with pressure gauge D, to the heater E. The heater, 9" dia. and 9" deep, with well-fitting wooden lid and short chimney contains water which is kept boiling by a ring burner and heats the gas as it traverses the copper coil FF,(3/16" O/D, 18 s.w.g. and 30 ft. long,) to a temperature which is read by the thermojunction at G.

Measurement of Gas Temperatures.

G (see Fig:II) is a $\frac{1}{2}$" length of $\frac{1}{4}$" bore M.S. tubing with M.S. plugs screwed and soldered into the ends, leaving 3/16" space between them. To minimise heat conduction along the tubing to the calorimeter, the gas enters and leaves by steel hypodermic tubing $\frac{1}{16}$" O/D, soldered into the plugs, and the arms of the couple (copper and constantan, 30 and 31 s.w.g.) enter by similar tubing soldered in radially. In an appendix sketches in detail are given of this part and of the joints at the ends of the couple arms, with a description of the fixing of the couples.

In order to avoid loss of heat from G. it is housed in a brass tube H. $3\frac{1}{4}$" long and $1\frac{1}{2}$" in dia. slotted to admit the couple arms and set in a tapered boss I, which allows free circulation of water around it. The mouth of H is closed loosely with cotton wool. The small piece of hypodermic tube which projects into E is heavily "tinned" with solder to avoid rusting.

The Calorimeter.

From G the gas passes to a copper coil JJJ, $\frac{1}{8}$" O/D and 1/16" bore, about 40 ft. long, contained in the calorimeter and kept free from the walls by three pieces of glass tubing about $\frac{1}{8}$" O/D closed at both ends; which permits of free circulation of the calorimeter water. The calorimeter K is a copper vessel $4\frac{1}{2}$" dia. and 6" deep, through the wall of which passes the hypodermic tube G, leaving so that the whole of JJJ can be covered with water. A motor-driven stirrer L ensures uniformity of the water temperature which is read on a Beckman thermometer M.

K stands on hard fibre wedges in the double vessel N, the outer part of which is of 9" dia. and 9" deep and the inner 6" dia. and $7\frac{1}{2}$" deep. This vessel is kept full of water by a lead from the main and a draw off to a water pump; a safety overflow is provided. N. is perforated to take the boss I of E. and so allow N and E to be brought close together. A layer of felt surrounds N, with a special pad between I and its seating. For rigidity N and E are bound round with iron wire. The calorimeter thus has an air jacket of $\frac{3}{4}$" surrounded by a water jacket of $1\frac{1}{2}$" (the double vessel N) kept at uniform temperature by the stirrer P. From the calorimeter the gas reaches the second thermocouple 4-way Q, which is a duplicate of G except that the gas enters and leaves it by copper tubing, for there is no longer any question of vitiation of calorimeter results by heat conduction as at G.

Leaving Q, the gas passes by the 4-way piece R, with gauge S, to the fine adjustment valve T, where the speed of flow is regulated, and then via the stop-valve U to the rate gauge V.

Measurement of the Gas.

The gas used in the determinations was of course dry, and in general, on releasing the pressure at the valve T for collection, some alteration of temperature was observable. As the apparatus was at first fitted up, the gas passed directly from V to the gas holder where it was confined over water,

and the result was that about 12 hours were necessary for steady conditions of temperature and moisture to be attained, an unsatisfactory state of affairs from the point of view of accuracy. Consequently, a hot water bubbler W, was introduced to moisten the gas at a temperature above that at which it would be measured; and W was followed by a coil X of compo in a bath of water at about 7°C. above the room temperature. With these adaptations steady conditions were reached in 1 - 1½ hrs.

Course of an Experiment

The apparatus is first filled with gas to the pressure to be used and the valves all shut. E is filled, preferably with hot water, to a little below H, and the Bunsen lit. While E is heating up, the calorimeter water is weighed in, the water feed for N turned on, the stirrers started, and the Beckmann put in position. When N is full the draw off is adjusted to keep the Boss I under water, and the temperature is allowed to steady. By the aid of a thermometer of open scale it is possible to keep the temperature of N constant to 0.1°C. Just before the start of the actual experiment, the heater E is filled up (submerging H): this method of heating E being necessary at high pressures, as the soft solder joint between copper coil FF and hypodermic tubing will not stand long continued boiling, but frequently blows out.
E very shortly boils again and is kept vigorously boiling throughout the experiment.

The cold junctions of the couples are immersed in ice, and the binding screws connecting couple leads and flex are put in water baths at air temperature and kept constant to within 0.2°C.

After a test of the potentiometer attachments a preliminary cooling period is taken with one minute readings of the Beckmann. The gas pressure to be used in the succeeding determination being on the apparatus during this period. The gas is then turned on at about 30ft^3 per hr., and readings of the Beckmann taken every half minute and of the couples alternately every minute till about 5 cu. ft. of gas have passed. The gas is then shut off, A & B being kept open, so that the pressure is maintained in spite of any slight leak, and a second cooling period taken with Beckmann readings every minute till steady cooling conditions are reached. The time of gas flow is 10 to 15 minutes.

Successive experiments on one day are carried out with the same quantity of water but the calorimeter is thoroughly dried out each evening.

Calibrations of Thermocouples, Thermometer, and Gauges.

The couples were calibrated, using as standard temperatures the Boiling Points of water, benzene and acetone, and the Transition point of sodium sulphate; the cold junctions were always in ice. It was found that the results obtained were fitted (to 0.1% accuracy) by the equation:

$$\log_{10} t = .9196 \log_{10} E + 1.4311$$

The gasholder was calibrated from a glass vessel containing about .56 cu.ft. which was in turn calibrated by a 2-litre measuring cylinder, the volume of which was checked by weighing the water it delivered.

The Beckmann thermometer was specially checked at the N.P.L. and a table of corrections supplied for use over the desired range. Gauges were calibrated against a standard calibrated at the N.P.L.

Average Quantities

Gas passed about 5 ft^3 free gas

Fall of gas temp. " 80°C.

Water equiv. of calorimeter		80.9 gms.
Total water equivalent	About	1200 gms.
Rise of calorimeter temp.	"	3°C.
Correction for cooling	"	2% on that rise

To minimise the cooling correction, the temperature of the water put into the calorimeter was such that, in general, during the first cooling period, the calorimeter was gaining heat and during the second cooling period losing heat.

Observations.

The scheme of observations has already been stated, and a representative set is given below. It will be noticed that the readings of the exit couple rise regularly while those of the inlet couple are constant.

The rise of the Beckmann is uniform during the transfer period and stops about one minute after the gas flow.

During the experiment the pressure falls off about 6 atm. and the pressure drop between the gauges is .5 atm., except for pressures below 10 atm. when it rises to 1.5 atm.

Example of Determination

Date 2.4.19. Gas: Nitrogen Run No.4.

Couples

Time H.M.	Exit (m.v.)	Time h.m.	Inlet. (m.v.)
4 13	0.581	4 12	3.965
15	655	14	4.150
17	699	16	4.150
19	708	20	4.145
23	725	24	4.145
25	735	26	4.155
27	750	28	4.025
29	585	30	3.936

The period of gas passage is shown between the short lines

Mean values.
Inlet 4.149 m.v.
Exit .724 m.v.
Temperatures.
Inlet 99.9°C
Exit 20.1°C
Fall in gas temperature 79.8°C

Pressures and Calorimeter Temperatures

Time H.M.	Temp.	Calorimeter mean temp.& cooling rate in cooling periods(obs) minute cooling correction in transfer period(calc)	Pressure Inlet (atm.)	Pressure Exit (atm)	Bath Temp. (vessel N)
4 14	0.675	period mean temp, 0.662°C			
15	.679	mean cooling rate, -0.0050°C (obs)			
.5	.682		59	59.5	18.6
16	.700	Transfer: cooling - .0049 °C (calc.)	58.5	59	
.5	.810				
17	.927	37	58.5	58.5	18.6
.5	1.043				
18	.156	26			
.5	.272		58.0	57.5	
19.	.430	15			
.5	.530				
20	.630	5			18.6
.5	.735		56.5	56.5	
21	.852	+ .0004			
.5	.965		56	56	
22	2.090	+.0016			18.6
.5	.205				
23	.325	27	55	55	
.5	.430				18.6
24	.550	37			
.5	.640				18.6

* The gas current was started at 4 hrs 15.5 mins.

Pressures and Calorimeter Temperatures (contd.)

25	.760	Transfer period; +.0047			
.5	.870	minute Cooling (calc.)	54	54	
26	.980	57			
.5	3.095		53.5	53.5	18.6
27	.230	69			
.5	.320		53	53	
28	.455	79			
.5	.520				
29	.521	82			
.5	.517	3rd Period mean temp	53	53	
30	.514	3.488; mean cooling			
31	.507	rate +0.0080 °C			
32	.497				

Total Cooling (Transfer period)

-.0132
+.0418
+.0286

Calorimeter Temperatures

	Initial	Final
~~Corr~~ Beckmann	.682	3.521
	.017 (corrn)	.045 (corrn)
	.699	3.566
. . Rise		2.867
Cooling corr.		.029
Net. Rise		2.896

Water Equivalent

Mass of vessel and water	1322.43 g
Mass of vessel empty	173.86
Water charge	1148.57
W.E. of Calorimeter	80.9
Total Water Equivalent	1229.5

Pressure on Gas in Holder

Tension of Water vapour; at 13°C, 11.2 m.m; at 14.3°C, 12.2 m.m;
Barometer 761.5 " 761.5 "
Holder gauge 1.5 " 1.5 "
Net pressure on Gas, 1st Reading 751.8 " ; 2nd Reading 750.8 "

Gas Holder

First Reading	5.300 at	13.0°C	
Second Reading	.190	13.0°C	4.20 p.m.
	.144	14.3	5.34 p.m.
	.143	14.4	6.16 p.m.

Gas Volume

1st Reading 5.300, Vol. of gas .200, corrd. .201, at N.T.P. .189 cu.f
2nd Reading .144, " 5.356, " 5.343, 5.016 cu.f

. . Gas passed 4.827 cu.ft. = 170.9 g

Specific Heat

170.9 g Nitrogen, cooling 79.8°C heat 1229.5 g water 2.896°C

. . $C_p = \frac{1229.5 \times 2.896}{170.9 \times 79.8} = .2611$

Mean Pressure

Obs. 55.9, corrd. 58.0 Absolute 59.0 atm.

CALCULATIONS & RESULTS

Calculations

For any one run these are quite simple. The cooling correction is obtained by plotting mean cooling rate and mean temperature during the two cooling periods and joining the points be a straight line. Assuming Newton's Law to hold this gives at once the minute cooling rate at each temperature. The total value of the cooling correction is rarely over 2% on the total

rise in the calorimeter.

No correction is made for the Joule-Thomson effect. Of the total of about 80 feet of fine copper tubing between the gauges only 40 ft. is between the couples. Besides this, it is well known that changes in diameter of a duct are often the most important causes of pressure drop, and of the ten such changes between the gauges in the present apparatus only three are between the couples. Again the Joule-Thomson coefficient diminishes with rise in pressure. The Joule-Thomson effect is therefore negligible.

All the results for each gas were collected and the "most probable" equation found by the method of least squares.

Tables are given below showing the experimental values and those calculated from the "most probable" equations and their differences. The table given on p.1 is also repeated.

Tabulation of Results & Calculation of Most Probable Equation

I

Hydrogen

C_p(obs).	P atm.	C x P	P^2	C_p(calc)	diff.(obs-calc)
3.502	195.3	683.9	38150	3.501	+ .001
3.504	192.4	674.2	37020	3.500	004
3.494	171	597.4	29240	3.491	003
3.468	160.7	557.2	25810	3.486	- .018
3.497	143.6	502.1	20620	3.479	+ .018
3.461	111	384.1	12320	3.465	- .004
3.485	107	372.9	11450	3.464	+ .021
3.451	82.2	283.6	6757	3.453	002
3.424	76.8	262.9	5899	3.451.	- .027
3.455	64	221.1	4097	3.445	+ 010
3.416	52	177.6	2704	3.440	- .024
3.456	45	155.5	2025	3.437	+ .019
3.435	38.7	132.9	1497	3.434	001
3.425	11.4	39.0	130	3.423	002
48.473	1451.1	5044.4	197719		mean. 011.

If equation is $C_p = kP + m$

we have $48.473 = 1451.1\ k + 14m$

and $5044.3 = 197719k + 1451.1\ m$

which gives $C_p = 4.27 \times 10^{-4} p + 3.418$

The column headed C_p (Calc.) is obtained from this equation and similarly in tables II & III.

II

Nitrogen.

C_p obs.	P abs.	C_p calc.	Diff obs.-calc.
.2937	183	.2924	+ .0013
.2893	172	.2897	-.0004
.2843	161	.2870	- 27
.2841	153.5	.2852	- 11
.2829	143	.2826	+ .0003
.2729	98	.2716	13
.2737	92	.2701	36

III

Mixture 74.5% H_2 + 25.5% N_2

C_p obs.	P abs.	C_p calc.	Diff. obs.-calc.
.854	192.5	.850	+ .004
.854	188	.848	6
.849	184	.847	2
.849	177	.845	4
.832	171	.843	- .011
.833	155	.838	- 5
.840	145.5	.837	+ .003

contd.

Tabulation of Results of most probable equation (contd.)

II (contd.) Nitrogen.

C_p obs.	P abs.	C_p calc.	Diff. obs.-calc.
.2611	59	.2620	- .0009
.2619	52	.2603	+ .0016
.2557	44	.2583	- .0026
.2511	20.5	.2525	- 14
.2510	16	.2514	+ .0003
.2515	15	.2512	- .0004
.2499	7.8	.2494	+ .0005
		mean	.0013

C_p Equation = $.2475 + 2.45 \times 10^{-4}p$

III (contd.) Mixture 74.5% H_2 + 25.5% N_2

C_p obs.	P abs.	C_p calc.	Diff. obs.-calc.
.828	129	.831	- .003
.829	122	.829	000
.821	108.2	.824	- .003
.818	101	.822	- 4
.811	77	.815	- 4
.819	70	.813	+ 006
.809	43.7	.805	4
.796	7.6	.794	2
		mean	.004

C_p Equation = $.792 + 3.00 \times 10^{-4}p$

Additivity of C_p Values.

I

74.5% H_2 + 25.5% N_2 mixture.

(1 gm. contains .1735 g H_2 + .8265 g N_2)

P abs. atm.	C_p mix.	C_p H_2	C_p N_2	C_p mix.	Diff.
0	.792	.5929	.2046	.797	.005
1	.792	.5929	.2047	.798	6
51	.807	.5965	.2149	.811	4
101	.822	.6006	.2250	.825	3
151	.837	.6040	.2352	.839	2
201	.852	.6077	.2453	.853	1

The first three C_p columns contain values obtained from the equations, the first for 1 g of the mixture, the second for .1735 g H_2, the third for .8265 g N_2. The fourth C_p column is the sum of the second and third. The column headed "Diff" shows differences between the two C_p Columns for the mixture.

II. C_p for the ideal mixture $N_2 + 3\ H_2$. obtained from observed values.

In view of the additivity of the C_p values as shown under I above, the following table has been calculated from the values observed for the 74.5, 25.5 mixture by adding for each pressure the C_p value for .0038 grams hydrogen and subtracting that for .0038 grams nitrogen. This gives values corresponding to a gas composition .1773 g H_2 + .8227 g N_2 i.e 75% H_2 + 25% N_2 by volume or $3H_2 + N_2$

Press Abs. Atm.	C_p Mix.
0	.804
1	.804
51	.819
101	.834
151	.849
201	.864

The Ideal Mixture $N_2 + 3H_2$

These values are comprehended in the equation.

$C_p = 804 + 3.00 \times 10^{-4} P$.

Collected results calculated from equations.

I

Pressure (atm.)		Specific Heat.		
Abs.	gauge	Hydrogen.	Nitrogen.	Mixture.
0	-	3.418	.2475	.804
1	0	3.418	.2477	.804
51	50	3.439	.2600	.819
101	100	3.461	.2722	.834
151	150	3.482	.2845	.849
201	200	3.503	.2968	.864

N.B. The last column is calculated for the ideal mixture, $N_2 + 3H_2$ and not for that actually tested, which had 74.5% H_2 + 25.5%N_2.

II

When calculated for atmospheres and C.H.U. per 1000 cu.ft. free gas at 20°C. the above table gives:

Pressure (atm.)		Specific Heat.		
Abs.	gauge.	Hydrogen.	Nitrogen.	Mixture.
0	-	17.87	18.01	17.78
1	0	17.88	18.02	17.78
51	50	17.99	18.91	18.11
101	100	18.10	19.81	18.45
151	150	18.21	20.70	18.78
201	200	18.32	21.59	19.11

The corresponding equations are:

Hydrogen $17.87 + 2.23 \times 10^{-3} p$

Nitrogen $18.01 + 1.78 \times 10^{-2} p$

Mixture $17.78 + 6.65 \times 10^{-3} p$

At 760 m m and 20°C, 1000 cu.ft. of Hydrogen weigh 5.229 lbs.
Nitrogen " 72.749 "
Mixture " 22.109 "

Control Values. (Air).

Pressure (abs) Atm.	C_p obs.	C_p calc.
149	.2818	.2829
94	.2667	.2687
72.5	.2617	.2626
55	.2566	.2574
6	.2428	.2431

The third column is obtained from the equation given by Holborn & Jakob.

Discussion of Results.

These tables give a linear rise of C_p with pressure for hydrogen and nitrogen, and while it is to be expected that higher powers of P than the first would appear in a perfectly exact equation, the accuracy with which the Holborn-Jakob[1] results, in which the effect of higher powers is small but evident, have been reproduced gives ground for the belief that the coefficients of such powers would be very small indeed.

The equations obtained are: (C_p in calories per gram. and P in atmospheres)

Hydrogen $C_p = 3.418 + 4.27 \times 10^{-4}p$

Nitrogen $C_p = .2475 + 2.45 \times 10^{-4}p$ see pp. 8-9

The observations are good to 0.3% for hydrogen, and 0.5% for nitrogen.

In the case of a sample of the reaction mixture, a linear rise was also observed and the equation is

$$C_p = .792 + 3.00 \times 10^{-4}p$$ see p.9

On analysis this mixture showed 74.5% (by volume) hydrogen and 25.5% nitrogen, and thus 1 gramme of it contained .1735 g H_2 and .8265 g N_2. Tables are given showing how the sums of the C_p values for these quantities of the two gases compare with the C_p values for the mixture as determined from the equation just stated. It appears from this table that within the accuracy limits of the present work, the C_p value of the mixture is the sum of the C_p values of its components under the same conditions. The agreement is better at high pressures. Hence a table has been calculated for the ideal 3 : 1 mixture on the assumption that the C_p values are additive, and it is represented by the equation :

$$C_p = .804 + 3.00 \times 10^{-4} \times p.$$

Reference has been made to the work of Lussana[3] and Holborn & Jakob [1], and a short account of their methods given.

Lussana's value of C_p for air at ordinary pressure is in good agreement with those of other workers by the Regnault method, but the rise of C_p with pressure observed by him is much higher than that of Holborn & Jakob and than that calculated by Witkowski from his compressibility data. Besides this, his tables of values of C_p for air published in successive years are somewhat inconsistent. Further, it is worth noting that in figures specially set out by him,[7] the rise in temperature of his calorimeter is only 0.1°C. to 0.2°C. in all, and of that 25-50% is due to heat reaching the calorimeter otherwise than from the gas. All his values then must be accepted with some reserve.

Holborn & Jakob worked on air alone and their results are shown to be in accord with the best known determinations of the Joule-Thomson effect. These results have been used as a "control" in the present work, and it has been found possible to reproduce them, even as low as at 6 atmospheres at will.

Incidentally, this fact disposes of the difference outstanding between the results obtained by the Regnault method at ordinary pressure, .237, and that by the Callendar method, .241, see Table, p.11 The reason for this is that previous workers by the Regnault method assumed the temperature of the gas entering their calorimeter to be that of their heater, and that of the gas leaving to be the mean temperature of the calorimeter. By putting thermo-junctions actually in the gas entering and leaving (see figs.) it is found that this is not so, and in particular the exit temperature is about .5°C. above the mean calorimeter temperature. In the Callendar method too, measurements of entry and exit temperatures are actually made.

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July, 1919.

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Appendix.

Method of putting the Couples in place and Making the Joints at Ends of Couple Arms in 4-way pieces, G and Q.

A diagrammatic sketch is given with letters to elucidate this description p. 16 (Fig II) The requirements are to put the junctions in place in A and to have the couples insulated from the fourway piece, and the joints at E and F good to 200 atms. The couples were copper - constantan- copper, the copper being connected with flex to the potentiometer. The outside junction was undone, a piece of drawn glass capillary slipped over each of the remaining wires, and the junction pulled into place using a third piece of glass capillary slipped on one of the free ends as a guide. To make sure that the junction, which is bare, is actually in A and free from the walls, one end of the couple and one Delta Metal end (E or F) are put in series with a dry cell and voltmeter. If the glass capillaries are pulled quite up to the junction on each side, contact can only be made by the junction touching the walls of A or the couple arms B or C. Insulation therefore shows that the junction is in A as required. This test is repeated at each stage.

The capillary on the constantan is now cut off flush with the end of the D.M. (Delta Metal) thread, E. say. After a little practice this can be done accurately with a glass knife without disturbing the couple. The wire is next tinned over about $\frac{1}{4}$ inch just outside E, and a hard fibre washer 3/16" dia. slipped on up to E. (Soft fibre was found unsatisfactory as it contains Zinc Chloride which conducts on screwing up).

To make a gas-tight joint with the wire a D.M. washer 5/32" dia. and 3/64" thick, drilled with a hole 1/16" dia. is next slipped on, the hole having been previously filled with solder and pierced again to allow the wire to pass. If necessary, a little extra solder can be put on the tinned part before slipping

on the D.M. washer. The joint is made by putting the D.M. washer in place and warming it on the edge with a small flame. The solder then runs and unites with the tinned part of the wire. It is necessary to have sufficient solder but no excess, and the washer should be centrally set on the wire, if not, and especially for the second joint, a paper collar should be slipped on the D.M. washer.

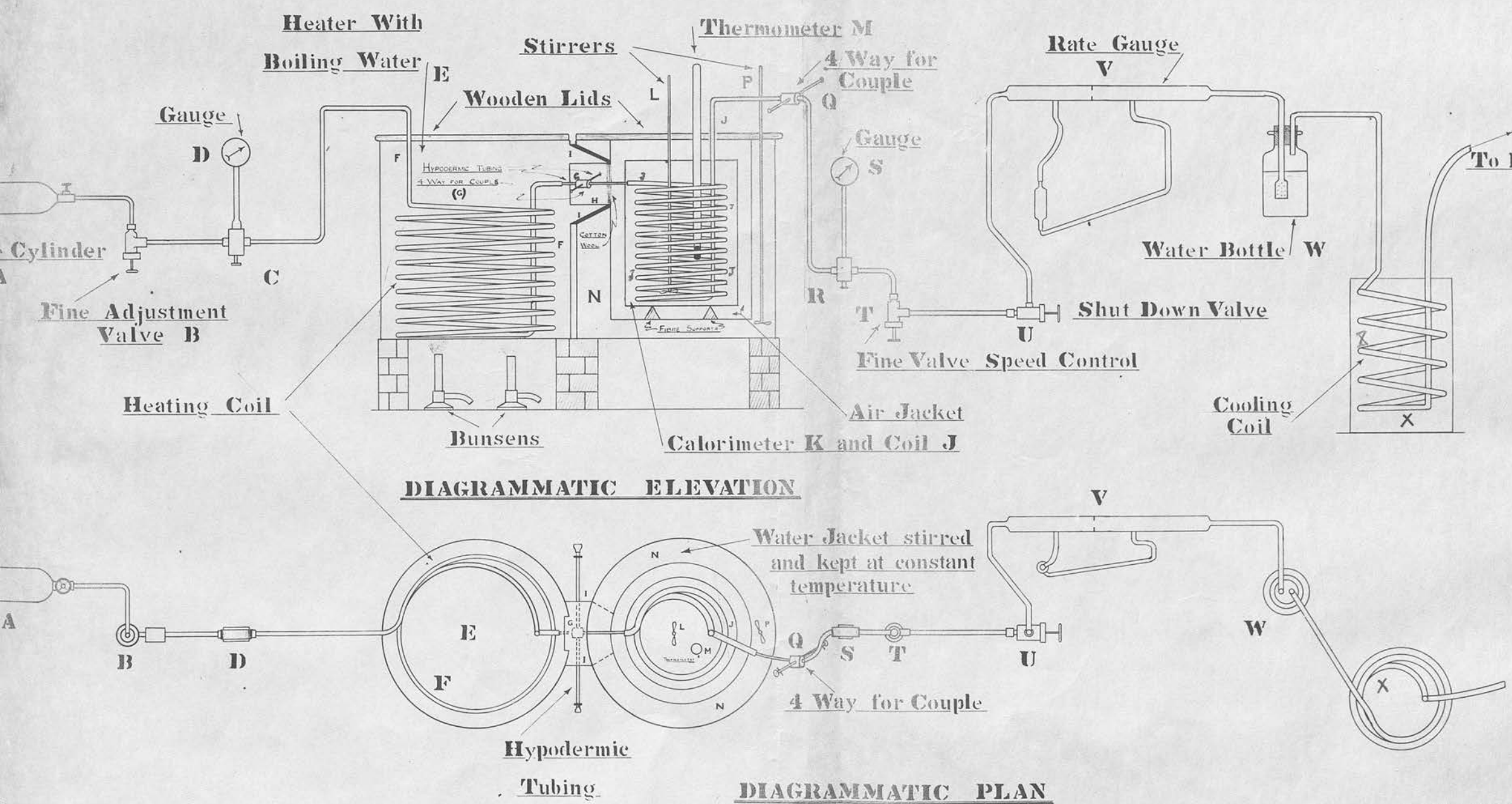
The first fibre washer insulates the D.M. washer from the D.M. end E, and a second one is now slipped on to insulate it from the knurled head which is next screwed up tight. Contact between the wire and the knurled head is prevented by a second short length of glass tubing outside the second fibre washer.

The special difficulty with the second joint is that, on screwing up tight, the couple sags slightly and may make contact. This is avoided by making the second piece of capillary as wide as possible and taking care that it is quite flush with the end of the screw, F, say.

If these joints are to stand long, it is advisable to coat the whole piece with paraffin wax, as otherwise moisture will ruin the insulation.. Once done up these joints can very rarely be undone without either breaking the wire or rupturing the junction.

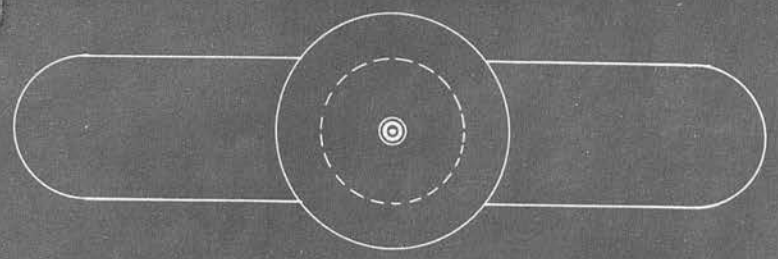
As constantan is less easy to solder and more easy to break than copper, it is best to make the constantan joint first and undo it last. Breakages are then more frequent in the copper which is more safely replaced. The alternative is to have a stock of calibrated couples to succeed each other on breakage.

SPECIFIC HEAT OF COMPRESSED GASES

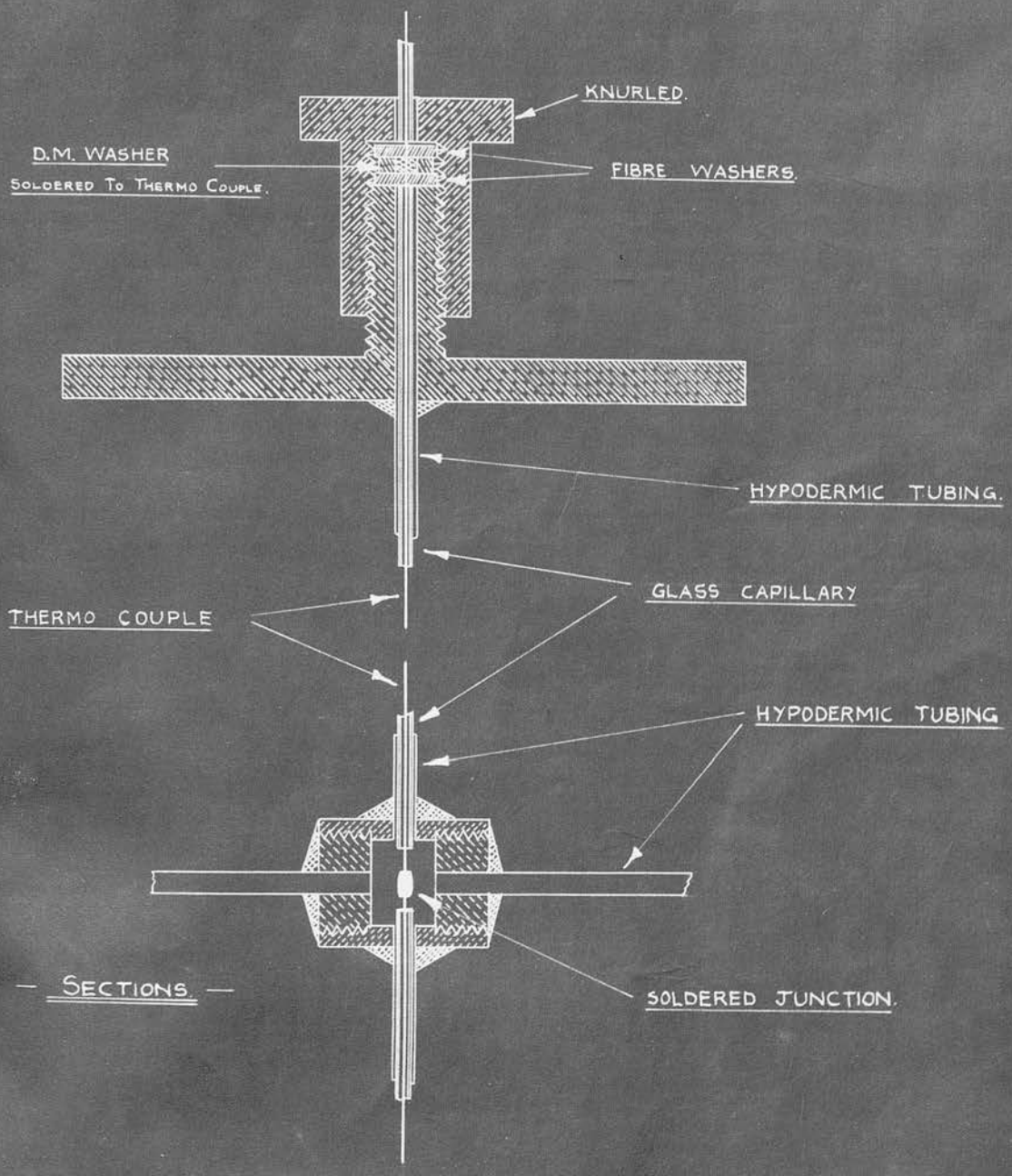


MID 2440

Fig I



- PLAN. -

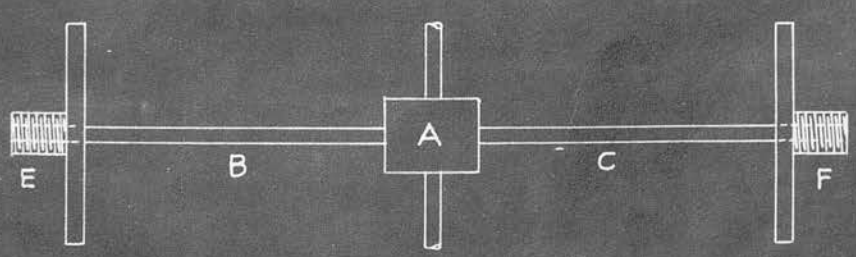


- SECTIONS. -

- GAS TEMPERATURE MEASUREMENT -

- DETAIL OF FOUR-WAY PIECE WITH COUPLE CONNECTIONS. -

- TWICE ACTUAL SIZE. -



DIAGRAMMATIC ARRANGEMENT.

M.I.D. 2539.

Fig II