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Characteristic Equations for

Saturated & Superheated Steam

Mechanical Engineering

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CHARACTERISTIC EQUATIONS FOR SATURATED AND SUPERHEATED STEAM

BY

SIEBELT LUKE SIMMERING

B. S. University of Colorado, 1910

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

IN MECHANICAL ENGINEERING

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

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May 31st, 1913 190

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Siebelt Luke Simmering

ENTITLED Characteristic Equations for Saturated and Superheated Steam

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Master of Science in Mechanical Engineering

G. A. Goodenough
In Charge of Major Work

C. R. Richards
Head of Department

Recommendation concurred in:

Committee
on
Final Examination

247457

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Characteristic Equations for Saturated and Superheated Steam.

Introduction.

Prior to 1905, investigators studying the properties of steam had but little experimental information at their disposal. However, they were able to formulate equations which gave satisfactory results considering the limitations of the experimental data.

In 1905 Messrs. Knoblauch, Linde and Klebe[1] began an investigation involving the pressure, volume, and temperature measurements of steam. In 1906 Messrs. Knoblauch and Jakob[2], and later Knoblauch and Mollier[3], investigated the specific heats of superheated steam.

The data furnished by these experiments have been used as a basis for the general theory of steam by several investigators.

Professor G.A.Goodenough[4], of the University of Illinois, was probably the first to attempt to embody all of the experimental evidence into a self-consistent theory which would not be too difficult of application.

The purpose of this thesis is to present a review of the properties of steam based upon Professor Goodenough's investigation which appeared in the Journal of the American Society of Mechanical Engineers, and also including his more recent development which has not as yet appeared in printed form.

Part I.

Discussion of Sources of Information.

The relation between pressure and temperature of saturated steam was first investigated by V.Regnault in 1847. Some few years later A. Battelli brought forward a discussion of this same question and included the specific volumes of saturated and superheated steam.

To determine the validity of Battelli's discussion Knoblauch, Linde, and Klebe[1] conducted a series of experiments at the Royal Technical High School at Munich. These experiments extended over a period of three years and great care was exercised to eliminate errors and because of this, their results are considered to be very trustworthy.

To calculate the specific volumes, use was made of the Clapeyron-Clausius equation,

$$\frac{r}{u} = AT\frac{dp}{dT}.$$

The results of the Knoblauch, Linde, and Klebe experiments are shown graphically in Fig. 1.

If now from any proposed equation a set of values for $\left|\frac{dp}{dT}\right|_v$ be determined and compared with the slopes as calculated from Fig. 1, there exists at once a check as to the validity of the proposed equation. Examination of Fig. 1 however shows that too much emphasis need not be placed upon the slopes at the high temperature conditions since the experimental points were few and the temperature range

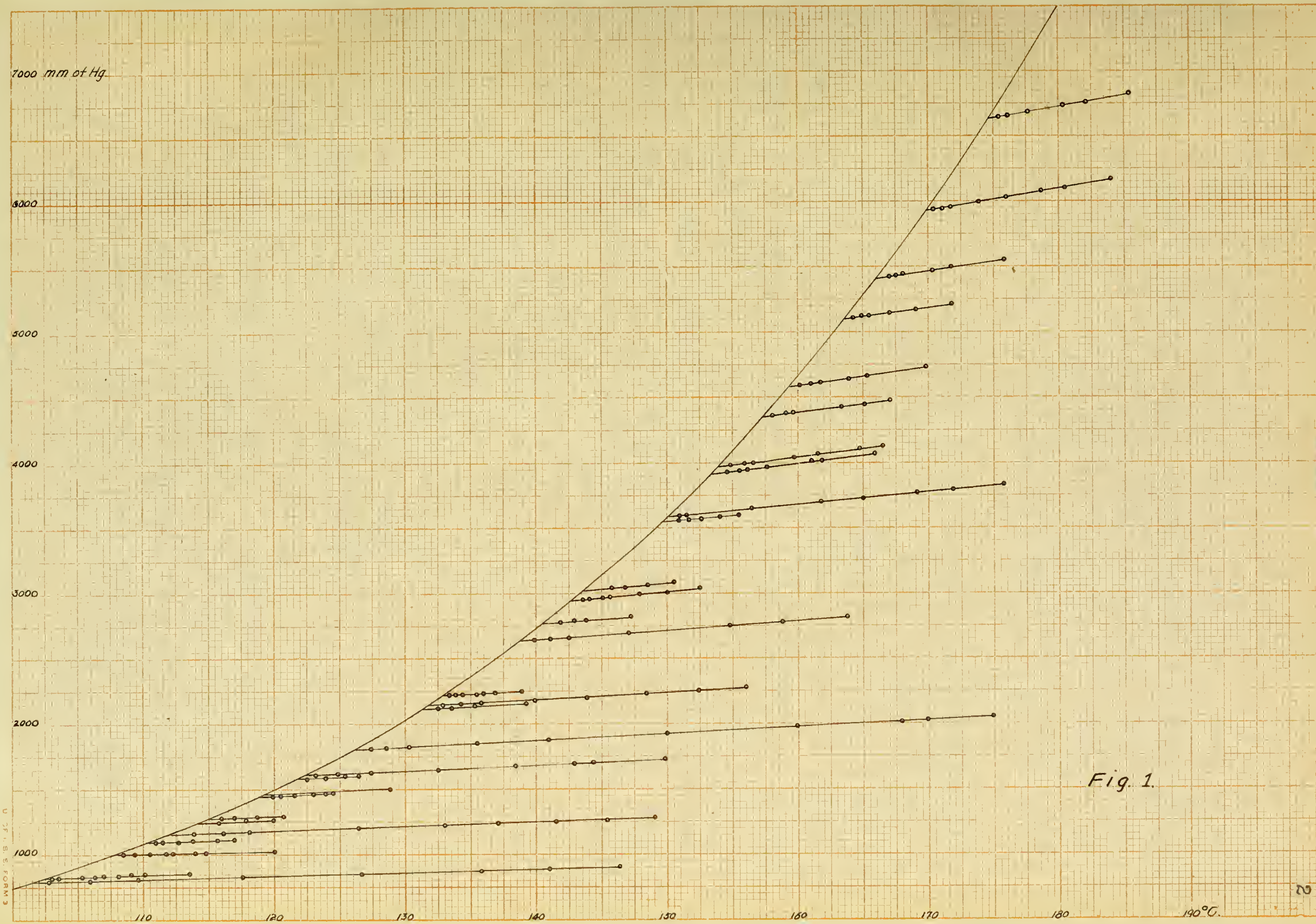

7000 mm of Hg
6000
5000
4000
3000
2000
1000
110
120
130
140
150
160
170
180
190°C.
U. S. G. S. FORM 3

Fig. 1.

small, so that several lines having different slopes may be made to represent substantially the conditions. As the comparison of the various values of the specific volumes will be referred to later it will not be necessary to make it at this time.

The PV - P diagram affords a good means of comparing experimental points and calculated points from any characteristic equation. Fig. 2 gives a comparison of the isothermals of Battelli, Regnault -Zeuner and the Munich experiments. The Regnault - Zeuner points were determined using $A = \frac{1}{424}$ instead of $A = \frac{1}{427}$ as used in the Munich experiments, so that the Regnault - Zeuner and Munich points lie much closer together than the figure would indicate. From this fact it is to be concluded, that the Munich experiments represent the true conditions very closely.

Another set of experiments bearing on a different phase of this subject, namely specific heats, was performed by Regnault.[5] From his early experiments on specific heats he concluded that the specific heat of superheated steam at atmospheric pressure was the constant value 0.48 for all temperatures.

The more recent experiments of Knoblauch and Jakob[2] and also of Knoblauch and Mollier,[3] at the Munich laboratory do not support Regnault's conclusion. From these experiments there is conclusive evidence that the specific heat C_p of superheated steam does depend upon the pressure as well as

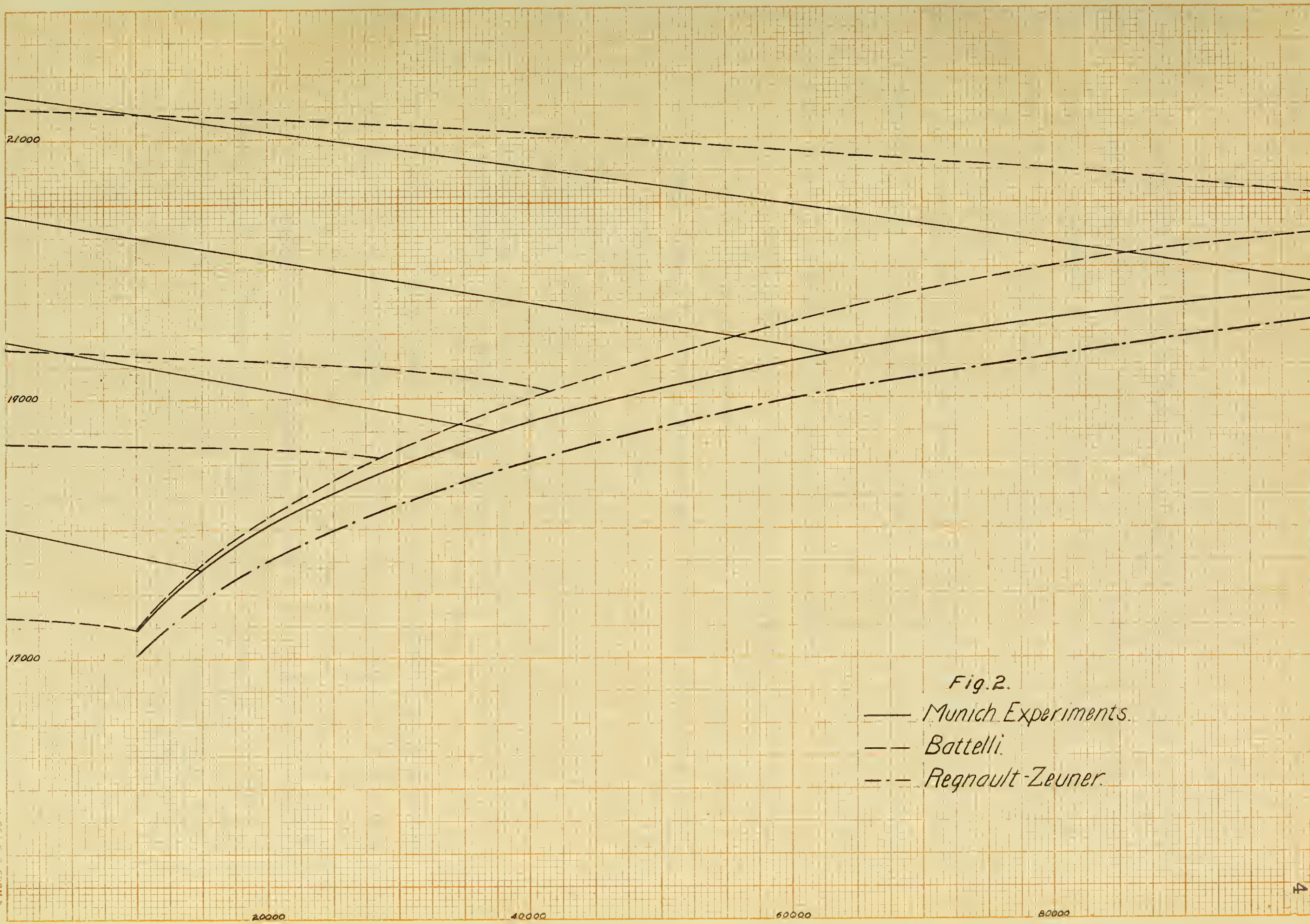


Fig.2.

U. OF I. S. S. FORM 3

the temperature. Examination of the specific heat curves for various pressures reveals the fact, that as the pressure and temperature become far removed from the saturation conditions, the specific heat approaches a common value for all pressures.

The experiments of Mallard and Le Chatelier[6] at about 3000°C., and of Langen[7] at about 1700°C., agree in making the specific heat a linear function of the temperature, the effect of pressure having become negligible.

Prof. C.C.Thomas[8] has concluded an extensive set of experiments on steam but the reliability of his methods is questioned. The following abstract is taken from an article by Prof. Thomas in the A.S.M.E. Trans. Vol. 29;

> "The whole operation of drying the steam preparatory to evaporating it, and of superheating it to some desired temperature above that of saturation is done in the one calorimeter. The apparatus thus consists essentially of one calorimeter, one thermometer, a source of steam and a source of heat in the form of electrical energy."

In the Munich experiments the drying and preliminary superheating was accomplished in a separate calorimeter from the one in which the final superheating was done.

Prof. Thomas further remarks, that the specific heats as determined by Knoblauch and Jakob, show a decrease with increasing temperatures until a minimum is reached for each pressure, after which, the specific heat increases with increase of temperature.

On this point Mr. J. A. Moyer[9] has shown by calculation, involving the impulse force of jets of superheated steam in nozzles and using the most recent and reliable data for the flow of superheated steam in nozzles, that the specific heat at constant pressure has a minimum value. This conforms with the observations of Knoblauch and Jakob[2] and of Knoblauch and Mollier.[3]

Prof. Heck[10] has effectively shown the variations of the Knoblauch and Jakob and Thomas curves of specific heats by means of the solid or three dimensioned diagram. Examining this figure it is seen that from 50 to 60 degrees of superheat out to the limit of the experiments the two sets of results agree very well, but that there is a marked difference near the saturation and the beginning of a wide divergence towards the region of high superheat. Near to the boundary line which separates the superheated from the saturation region, Prof. Heck says,

> "It appears that there are some residual molecular attractions to be overcome, and for this reason the specific heat is higher at and near this lower limit of superheat than it is farther out."

Knoblauch and Jakob[2] made a careful study of the flow of steam through their calorimeter and found experimental proof that water could be held in suspension in very highly superheated steam, and that for the purpose of evaporation, time and thorough mixing were essential as well as heat. In the Thomas experiments the steam passed through his cal-

orimeter at the rate of one and one half feet per second as being the lowest.

Prof. Heck's study of the Knoblauch and Jakob experiments tends to show agreement with Smith's[11] views regarding the latent heat of steam at 212°F. Smith found with quiescent evaporation that the latent heat of steam at 212°F., would be from three to four B.T.U. higher than is given by the Marks and Davis steam tables.

M. Armand Duchesne,[12] of the University of Liege, while calibrating thermometers unexpectedly discovered a discrepancy in the temperature readings which has caused considerable speculation among physicists.

Duchesne started out originally to study the variation of the temperature of the steam and the metal of the containing cylinder of a steam engine during the period of compression. During this period the steam becomes superheated and it was necessary to have a thermometer without calorific capacity. The result was the construction of the hyperthermometer, an electric thermocouple composed of numerous junctions of platinum and silver wire having a diameter of 1/100 of a millimeter (0.0004 of an inch). While calibrating his hyperthermometer with the ordinary mercury thermometer Duchesne discovered, that with saturated steam, the two temperature readings corresponded, but when using superheated steam there was a difference amounting in some

cases to as high as 80°C., above the mercury thermometer readings. By rearranging his mercury thermometer he succeeded in reducing these differences considerably, and he concludes that the hyperthermometer readings are correct.

Examining the specific heat curves of Duchesne, it is seen that the pressure variations cease at a temperature of 360°C. and the specific heat becomes a function of the temperature only. Duchesne calls attention to the divergence of his results with those of Knoblauch and Jakob, and explains this by the fact that Knoblauch and Jakob[2] used a mercury thermometer placed in the usual oil cup arrangement.

In general, Duchesne's experiments show a substantial agreement with the values as obtained for saturated steam using a mercury thermometer, but calls into question, all temperature, total heat, and specific heat values for superheated steam.

In this discussion no attempt will be made to incorporate the temperature measurements of Duchesne.

In the light of the preceding discussions the writer has come to the following preliminary conclusions regarding the properties of saturated and superheated steam. These the proposed theory will embody;

1. The experimental values of Knoblauch, Linde and Klebe as plotted on the PV-P plane, are reliable.

2. That the specific heat does attain a minimum value after which it rises with increase of temperature, and that the specific heat at constant pressure, is dependent upon that pressure.

3. That the experimental values found by Knoblauch and Jakob, and Knoblauch and Mollier, are to be accepted at the present time.

4. That the latent heat of evaporation at 212°F., should be higher than 970.4 B.T.U.

Part II

Linde's Characteristic Equation.

To represent the Munich experiments, Linde[11] proposed the following equation;

$$pv = BT - \left[C\left(\frac{373}{T}\right)^2 - D\right]\frac{1}{v}$$

but later changed this for convenience in calculating to

$$pv = BT - p(1 + ap)\left[C\left(\frac{373}{T}\right)^3 - D\right]$$

and in metric units B 47.1; a 0.000002; C 0.031; D 0.0052. The objection to this equation is as Linde has pointed out, that above 402°C. the correstion term changes sign, and the steam becomes a "more than perfect gas." To overcome this objection he suggests changing the exponent of T from 3 to 3.5 but this merely transfers the objection from 402°C. to 617°C. To overcome this objection entirely it is evident that the term D must be eliminated.

In general, the correction term should approach zero as a limit and the characteristic equation would become,

$$pv = BT$$

or the perfect gas equation, which would be the case if the pressure and temperature were far removed from the saturation conditions. From the standpoint of a perfect gas equation the value of B would equal the quotient of the universal gas constant R by the molecular weight of steam, or B should be 47.07 nearly.

The form of Linde's equation renders it somewhat inconvenient for purposes of computation. The essential feature

is the term (1 + ap) which gives the parabolic form to the isothermals when drawn on the PV - P plane. If this term be retained, the remaining constants may be changed without materially affecting the integrity of the equation. A further discussion will be found in part III.

As previously stated the calculated slopes affords a means of establishing the validity of the characteristic equation. From Linde's characteristic equation the following equation for the slopes is derived,

$$\left(\frac{dp}{dT}\right)_v = \frac{B + ncp(1 + ap)\frac{m}{T^{n+1}}}{\frac{BT}{p} + cap\frac{m}{T^n} - apD}$$

where n 3 and log m 7.715127.

From Goodenough's revised equation there results,

$$\left(\frac{dp}{dT}\right)_v = \frac{B + np(1 + 3ap^{\frac{1}{2}})\frac{M}{T^{n+1}}}{\frac{BT}{p} + \frac{3}{2}ap^{\frac{1}{2}}\frac{M}{T^n}}$$

Examining the following table it will be observed that the slopes obtained from Goodenough's revised equation are as a whole closer to the observed values of the Munich experiments than are Linde's values.

Sp.Vol. Cbm/kg.	Sat. Temp.°C	Sat.Pres. kg/sqm observed.	Calc.	$(dp/dT)_v$ Obs. KL&K.	Calc. Linde.	Calc. Rev.Eq.
1.598	101.4	10860	10860	30.4	30.4	30.8
1.122	112.3	15800	15842	44.3	43.9	44.4
.7405	126.5	24720	24690	68.0	67.4	68.6
.5204	139.2	35960	35980	99.3	97.9	99.3
.3897	150.3	48900	48930	134.0	132.9	134.8
.2809	163.2	69420	69280	188.6	188.9	192.3
.2428	170.0	80790	80780	225.0	221.7	223.8
.1910	180.6	103890	103890	293.0	287.5	289.8
.1817	183.0	109550	109570	313.0	303.7	306.6

Part III.

Goodenough's Earlier Equation.

To overcome the objection of Linde's equation Professor Goodenough[4] proposed in the first instance the following equation,

$$p(v + c) = BT - P(1 + ap)\frac{M}{T^n}$$

which is simpler in form and readily permits of further mathematical application. The values of the constants are in metric units, B 47.113; logM 11.19839; n 5; c 0.0055; and a 0.00000085.

Determining the values of $(dp/dT)_v$ from the above equation for any temperature T and corresponding pressure p, which gives the value of the slope at that point, it was found that the above constants gave the best agreement with the observed slopes. Since the "c" term does not appear in this slope equation, its value was determined from the PV-P diagram. Without this constant "c" the calculated isothermals would lie above the experimental isothermals, hence it was added to bring the two curves into coincidence.

Taking the second derivative of v with respect to T, holding p constant, and applying this derivative in the Clausius relation, there results for the specific heat, the following equation,

$$c_p = \phi(T) + \frac{AMn(n+1)}{T^{n+1}}p(1 + \frac{a}{2}p).$$

If now the values of c_p are reduced to zero pressures there

is a means of determining the function ϕT. Plotting the resulting values the function ϕT may be considered as a linear equation of the form,

$$A + BT.$$

Regarding the values of the specific heats thus obtained Dr. Davis[13], submits the following questions;

1. Does the characteristic equation predict the right variation of c_p with pressure?

2. Has the arbitrary function ϕT, been properly evaluated?

The easiest way to answer the first question is to reduce all the known measurements of c_p to zero pressure and plot the results against T. All points should lie on a smooth curve.

Dr. Davis found that the Munich experimental values satisfied this condition quite well, but Linde's equation gave values, which had a tendency to run high at high pressures. On the other hand Goodenough's equation gave satisfactory results throughout.

Regarding the second question, Dr. Davis says, that the straight line asymptote proposed by Goodenough is as good as any other. The difficulty lies in the fact that nothing is known regarding the slope of the curve below 100°C.

From the standpoint of total heats at saturation Dr. Davis says, that the proposed equation is satisfactory between temperatures of 175°F to 320°F, but beyond these limits the values of $i_{sat.}$ run high.

Prof. Heck[10] commenting on the preceding characteristic equation brought forth the argument that at high temperatures the PV-P curves would be too straight, because of the low value of "a", where as they should begin to show a marked tendency to curve downward toward the saturation curve. To obtain this condition a higher value for "a" must be used. The most serious objection raised by Prof. Heck, is the failure to satisfy the Clapeyron equation,

$$r = AuT\frac{dp}{dT}.$$

From 100°F. to 360°F. the differences between the values of latent heats as calculated by means of the Clapeyron equation and those obtained from the total heat equation are not large, but beyond 360°F. and below 100°F., the differences become large.

Since the Clapeyron equation is a rigorously exact relation it must be satisfied and such satisfaction may be considered as a criterion for the substantiation of the latent heat formula and incidentally of the characteristic equation itself.

Part IV.

Limitations of the Earlier Equation.

Various values were assigned to the constants in the earlier equation with the hopes of eliminating the objections cited. After numerous trials the best conditions were obtained with the following constants;

$\log M = 8.716000$; $B = 47.07$; $n = 4$; $c = 0$; $a = 0.00000171$;

The decrease in the value of "n" caused a better agreement with the specific heat curves of Knoblauch and Mollier[3]; the increase in "a" caused more curvature in the isothermals which gave better agreement with the experimental points; Although with the above constants the isothermals, specific heats and total heats at saturation were satisfactory there existed a discrepancy in the Clapeyron relation. The curves on the following page show the variations. Between temperatures of 32°F. and 400°F. the difference did not exceed two B.T.U., but beyond 400°F. the differences increased. It was found by trial that the term $(1 + ap)$ seemed to be the one that affected this difference the most. Since the pressure increases very rapidly with increase of temperature above 400°F., the quantity ap in the preceding expression became predominant, thus causing a too rapid decrease in the total heat values. Likewise the volumes v, in all probability, were too small.

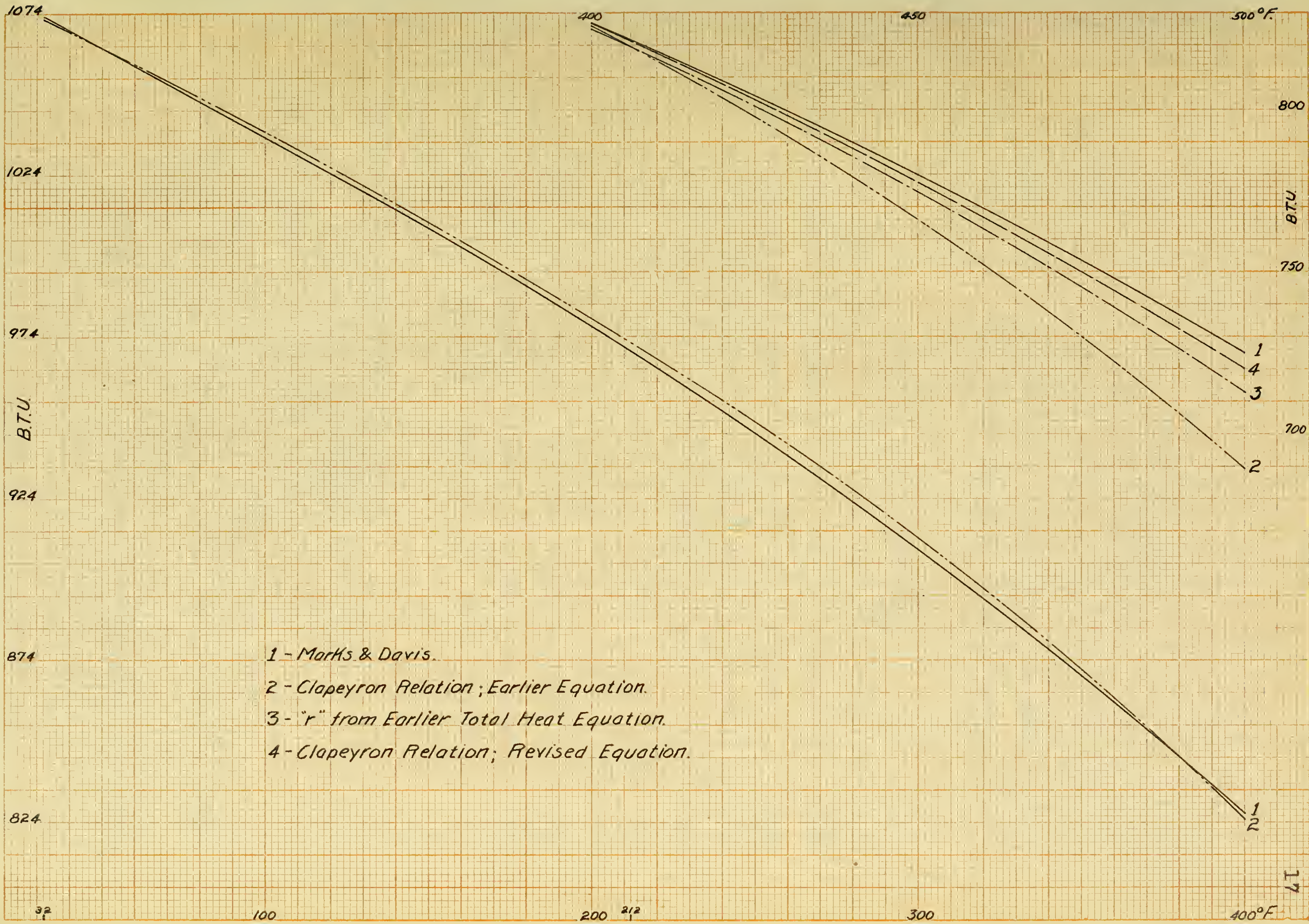
A further correction was found necessary when the specific heat values were determined near the saturation line.

They were found to be too low and in order to raise these values it was necessary to add a third term to the function ϕT, which then became,

$$\phi T = A + BT + \frac{C}{T^2}.$$

The values of the constants are, A=.301; B=.000252; C=7680. With these values when used in conjunction with the preceding values given for log M, B, n, and a, there existed a satisfactory agreement with the Knoblauch and Mollier[3] experimental points. When however, a comparison was made with the experiments of Langen[7] at high temperatures, the calculated specific heat curves were found to be too low.

After repeated attempts to correct these difficulties, it was decided, that a different form of the characteristic equation was needed. The results of the further investigation are given in the following section.


1074
1024
974
924
874
824
B.T.U.
32
100
200
212
300
400°F.
400
450
500°F.
800
750
700
B.T.U.
1
4
3
2
1
2
1 - Marks & Davis.
2 - Clapeyron Relation; Earlier Equation.
3 - "r" from Earlier Total Heat Equation.
4 - Clapeyron Relation; Revised Equation.

Part V.

The Revised Equation.

To meet the objections raised by Davis and Heck and also to embody the conclusions set forth at the beginning of this discussion, the characteristic equation has been given the form,

$$pv = BT - p(1 + 3ap^{\frac{1}{2}})\frac{M}{T^n}.$$

In metric units B=47.07; 3a=0.001131; log M=8.654292; n = 4. This equation is essentially the same as the previous equation with the exception of the "p" term within the parenthesis. The combined value of $3ap^{\frac{1}{2}}$ being materially greater than the single term ap of the former equation. Taking the square root of p instead of the first power has a very benificial effect upon all the values above 400°F. Comparing the latent heat values of the table on page 25 and the curves on the preceding page, it is seen very clearly, that the Clapeyron - Clausius relation has been satisfied to a marked degree.

The specific heat formula becomes,

$$c_p = A + BT + \frac{C}{T^2} + \frac{AMn(n+1)}{T^{n+1}}p(1 + 2ap^{\frac{1}{2}})$$

and the total heat formula becomes,

$$i_{sat.} = AT + \tfrac{1}{2}BT^2 - \frac{C}{T} - \frac{2AM(n+1)}{T^n}p(1 + 2ap^{\frac{1}{2}}) + i_o.$$

The values of the constants A, B and C are in metric units,

A = 0.290; B = 0.000261; C = 9700;

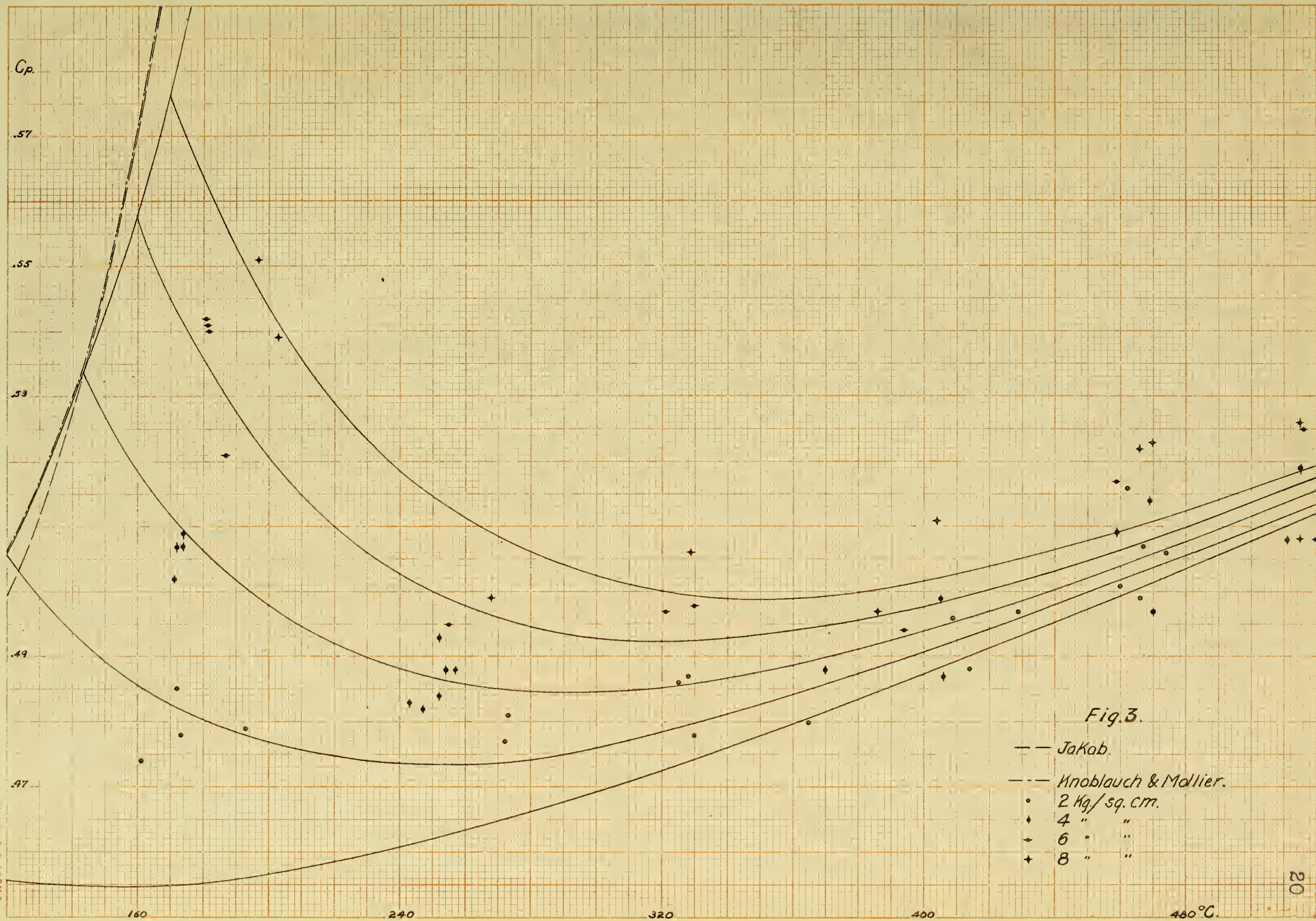
and in English units, A = 0.290; B = 0.000145; C = 31428.

With the new characteristic equation the maximum difference between the Clapeyron equation values for latent heats and those obtained by means of the total heat equation does not exceed 0.5 of a B.T.U. for the range from 32°F. to 550°F. Examination of the isothermals drawn from the calculated plotted points shows a remarkable degree of coincidence with the Munich experiments. Fig. 4.

Davis[13] has shown, in his paper on certain thermal properties of steam, that the value of c_p at saturation and 0°C. must be greater than 0.44. Testing the preceding equation of c_p for this condition it is found that the value is 0.492, thus satisfying the condition.

The addition of $\frac{C}{T^2}$ to the function ϕT, and the use of the one-half power instead of the first power of p, causes the specific heat curves to pass well within the region of Langen's experimental points for specific heats at very high temperatures.

On the whole, for saturated steam, the revised equation gives results that are entirely satisfactory.



Cp.
.57
.55
.53
.49
.47
160
240
320
400
480°C.
Fig.3.
Jakob.
Knoblauch & Mollier.
2 Kg/sq.cm.
4 " "
6 " "
8 " "

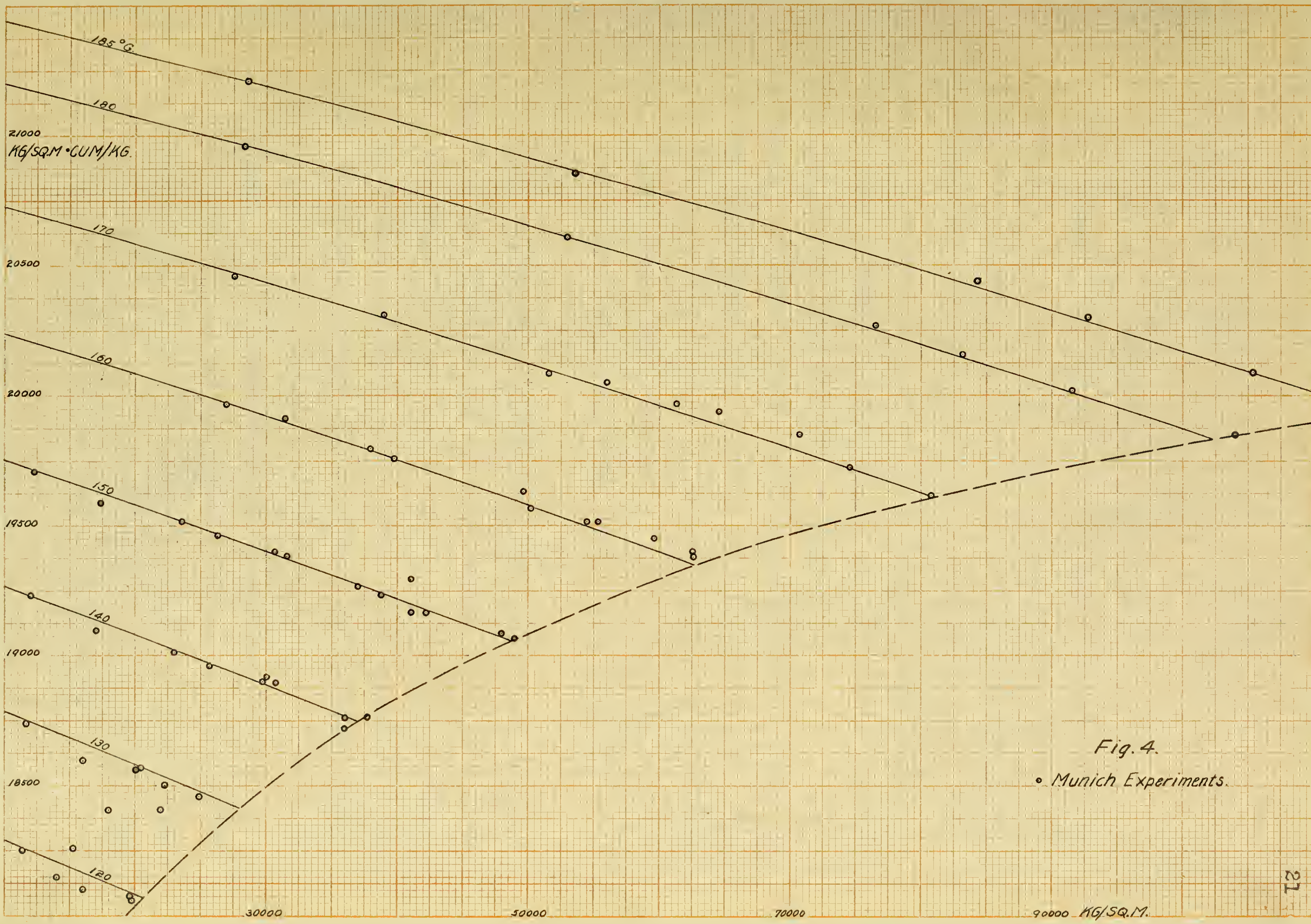


Fig. 4.

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Part VI.

Throttling Experiments.

So far only the conditions for saturated steam have been considered. Although the equations give satisfactory results for saturated steam, they give no proof of being satisfactory when superheated steam is considered. As a final test, comparison with the throttling experiments will be made, these being the only sources of information regarding superheated steam that are available.

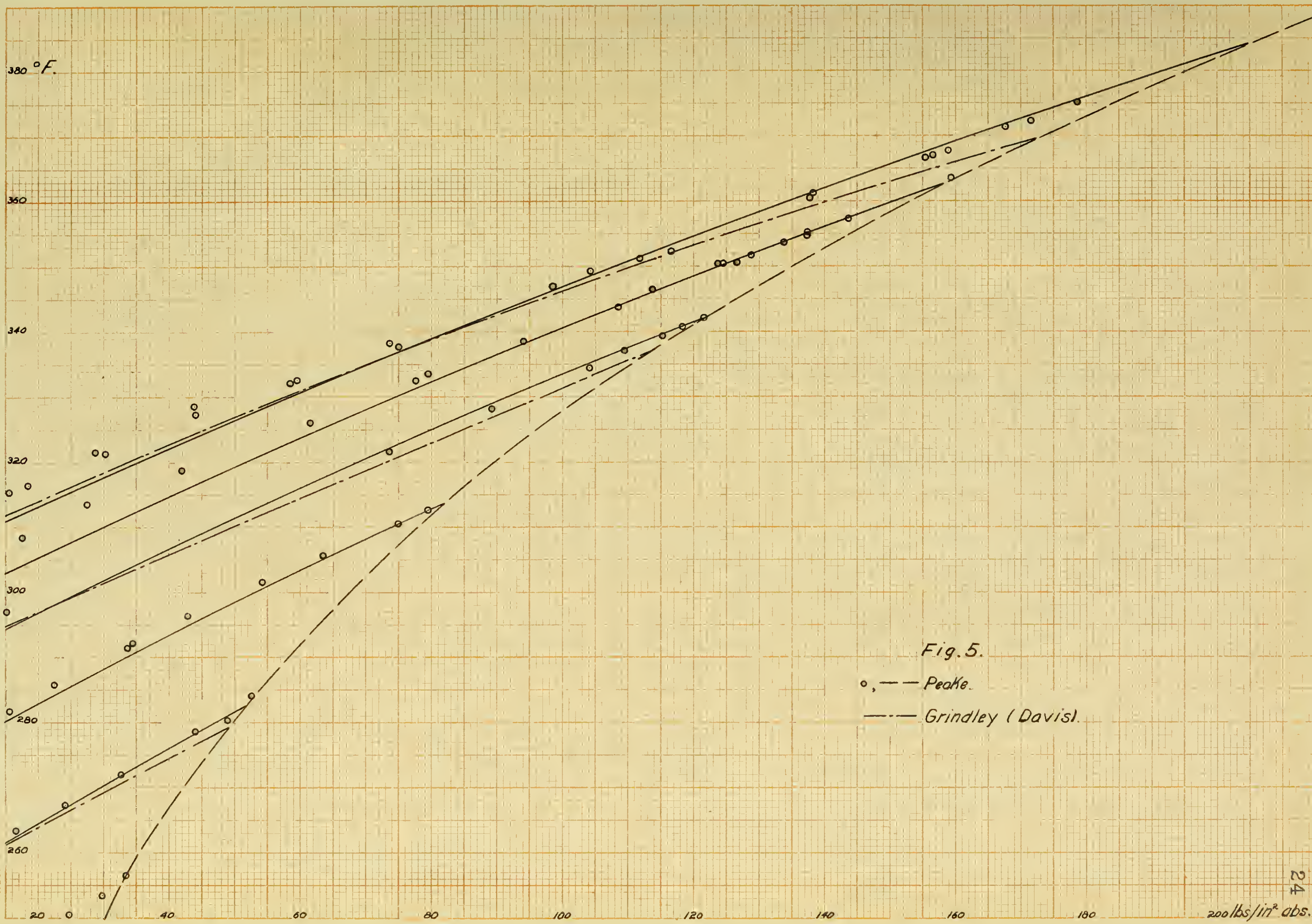
Although saturated steam is used in the initial state, it becomes superheated after passing through the plug or orifice and any desired degree of superheat can be maintained by regulating the back pressure. In this way the pressure and temperature may be measured both before and after expansion.

Messrs. Grindley[14] and Peake[15] have investigated the variation of the specific heat of superheated steam with pressure and temperature by means of the throttling calorimeter. The essential feature of the throttling calorimeter is, that the kinetic energy of the steam after passing through the orifice is transformed into heat which goes back into the steam. If the transformation is complete, the throttling calorimeter is equivalent to a porous plug. Peake interposed several pieces of wire gauze in the path of the steam to insure complete transformation of the kinetic energy, while Grindley took no precaution whatever.

Examination of Grindley's throttling curves as plotted shows, that in each case the steam drops several pounds in pressure before leaving the saturation line. He explains this by his so called "heat of gasification" theory. The explanation now given to this condition is, that wet steam instead of dry steam was used.

Peake's experiments were performed so as to avoid the apparent errors which appeared in Grindley's experiments, and an examination of his results and curves shows, that he succeeded.

These curves afford a means of determining the amount of superheat in steam at any given temperature and corresponding pressure, and also enables one to determine the validity of the total heat equation as deduced from the characteristic equation. At any point near the saturation curve on any particular throttling curve, the total heat may be calculated by means of the total heat formula; the values of p and T must be determined at this point from the throttling curve. The value of "i" being constant along this curve the value of p at any other point on the curve may be calculated by assuming a value for T. In other words a calculated throttling curve can be deduced and should it coincide with the experimental throttling curve, the validity of the total heat equation is established. Fig. 5 shows the agreement of the calculated throttling curves with the curves of Grindley and Peake.



380 °F.
360
340
320
300
280
260
20
40
60
80
100
120
140
160
180
200 lbs/in² abs.
○, — — Peake.
—·— Grindley (Davis).

Fig. 5.

Part VII.

Comparison of Values.

Volumes in Metric Units at Saturation.

Temps. °C	100	110	120	130	140	150	160	170	180
Pressure kg/sq m.	10333	14609	20243	27540	36839	48521	62990	80720	102160
Calculated	1.674	1.2105	.8921	.6687	.5090	.3929	.3072	.2429	.19420
K. L. & K.	1.674	1.2110	.8922	.6690	.5091	.3921	.3073	.2430	.19430

	Volumes.		Latent Heats.		
T°F	Calc.	M & D	Calc.	Clap.	M & D
32	3306	3294	1073.0	1072.8	1073.4
50	1708	1702	1063.7	1063.6	1063.3
100	351.7	350.8	1037.2	1037.3	1035.6
150	97.4	96.9	1009.3	1009.7	1007.4
200	33.72	33.60	979.7	980.1	977.8
250	13.84	13.82	947.3	947.8	945.3
300	6.47	6.46	911.7	911.8	909.5
350	3.345	3.342	872.0	871.9	870.1
400	1.868	1.872	827.4	827.4	827.2
450	1.105	1.11	777.1	777.0	780.0
500	0.682	0.66	719.8	719.9	725.0
550	0.433	0.42	654.7	654.0	658.0
600	0.279	0.27	579.0	575.0	572.0

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