NELSON

The Specific Heat of Superheated Steam

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THE SPECIFIC HEAT OF SUPERHEATED STEAM

BY

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THESIS

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IN

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Benjamin Nelson

ENTITLED The Specific Heat of Superheated Steam

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Mechanical Engineering

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APPROVED: G. A. Goodenough

Acting HEAD OF DEPARTMENT OF Mechanical Engineering

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THE SPECIFIC HEAT OF SUPERHEATED STEAM.

I.

INTRODUCTORY STATEMENT.

In 1910 Mr. A. S. Grossberg submitted as his thesis, a discussion on the specific heat of superheated steam together with charts of specific heat curves. This work was based on a theoretical development by Professor G. A. Goodenough. Since the completion of Mr. Grossberg's work it has appeared desirable to make changes in some of the constants involved in the discussion, necessitating a recalculation of the specific heats.

The recalculation of the specific heats using the new constants, is the object of this thesis. The historical sketch of the work on the determination has been omitted as it is given in Mr. Grossberg's thesis.

II.

THEORETICAL INVESTIGATION.

As early as 1867 Zeuner submitted a complete theory on the properties of superheated steam, based on the assumption of constant specific heat. Subsequent experimental data however, has proven that this assumption is erroneous and recent experiments at Munich, Germany, show conclusively that the characteristic equation derived in this theory is defective in form. Callendar has developed a general theory on the properties of steam, deriving equations for specific heat, entropy and energy, but again, the Munich experiments show that his fundemental equation is incorrect and that some of

his assumptions regarding C_p are invalid. Again Professor M Marks and Dr. Davis, as well as Professor Peabody have, without the aid of theory, constructed elaborate tables of the properties of superheated steam, getting the numerical results by graphic integration, having assumed specific heat curves to start with.

Professor Goodenough has modified somewhat, Linde's form of the characteristic equation and has developed from this equation, expressions for the specific heat, as well as for, heat content, total heat and intrinsic energy, which agree remarkably well, with the most recent experimental data.

The following discussion is condensed from Professor Goodenough's paper.

To derive this expression for specific heat, we have to start with the well known thermodynamic relation,

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -AT\frac{\partial^2 v}{\partial T^2} \qquad (1)$$

and the modified form of Linde's characteristic equation, $p(V+C) = BT-p(1+ap)\frac{m}{T^n}$. Placing this in the form, $(V+C) = \frac{BT}{p} -(1+ap)\frac{m}{T^n}$, we obtain by successive differentiation $\frac{\partial V}{\partial T} = \frac{B}{p} - \frac{mn}{T^{n+1}}(1+ap)$

$$\frac{\partial^2 v}{\partial T^2} = -\frac{mn(n+1)}{T^{n+2}}(1+ap) \qquad (2)$$

Substituting (2) in (1) we obtain

$$\left(\frac{\partial C_p}{\partial p}\right)_T = \frac{Amn(n+1)}{T^{n+1}}(1+ap) \qquad (3)$$

Taking T as a constant and integrating (3) with respect to p, there results

$$C_p = \frac{Amn(n+1)}{T^{n+1}} p(1+\frac{a}{2}p) \text{ plus constant of integration.}$$

We must necessarily assume that, since T was held constant during the integration that the constant of integration will be a function of T. Hence:-

$$C_p = \phi(T) + \frac{Amn(n+1)}{T^{n+1}} p(1+\frac{a}{2}p) \quad (4)$$

or $$C_p = \phi(T) + f(p_1T_1) \quad (4')$$

Assuming that the characteristic equation is correct, then the expression for C_p given by (4) must be of the right form and it is readily seen that if the function, $\phi(T)$ can be determined, there results an explicit expression for C_p, in terms of p and T.

To determine now, the proper form of this function of T, $\phi(T)$, is the all important element of this investigation. If p is made equal to zero, equation (4) becomes $C_p = \phi(T)$. Callendar holds that at zero pressure C_p should have a constant value, but Knoblauch and Jakob, from their direct determinations by experiment, show that C_{p_o} cannot be a constant.

Professor Goodenough has established the form of this function by quite a different line of reasoning. An inspection of equation (4) shows, that the term $f(p_1T)$, having the term T^{n+1} in the denominator, grows smaller as the temperature increases. At moderately low temperatures ($T = 100°F - 1000°F$), this term has an appreciable value but as the temperature increases to say 2000°F, this term becomes negligible and there results, for all pressures

$$C_p = \phi(T) \quad (5)$$

If we plot curves showing the relation between C_p and T,

at constant pressures, for several pressures, we obtain a series of curves, all of the same general slope, fairly wide apart near saturation but continually approaching one another as the temperature increases, finally merging at high temperatures. $C_p = \emptyset(T)$, is an asymotote to each one of these curves.

It is necessary then, in the determination of $\emptyset(T)$, to determine the relation between C_p and T at high temperatures, where the influence of the pressure is negligible. The data obtained, from the explosion experiments of Mallard and La Chatelier at high temperatures, those of Langen and the two sets of calorimeter experiments by Holborn and Henning, was investigated. Values of C_p were calculated from equations for C_p, obtained from each of the above mentioned experiments and curves were plotted with these values. These curves agreed as far as general form is concerned, but were far from being coincident. A curve was then constructed which agreed fairly well with the curve of Mallard and La Chatelier at high temperatures and which was made to agree fairly well with the curves determined for lower temperatures by the experiments of Holborn and Henning. The curve chosen to represent $\emptyset(T)$ coincided at high temperatures with this mean curve mentioned above, but at lower temperatures fell below the mean curve, due to the introduction of the $f(p_1T)$ term, which becomes appreciable for temperatures moderately near the saturation point. This curve has an equation of the third or fourth degree.

as $\emptyset(T) = a + bT + cT^2$

or $\emptyset(T) = a + bT + cT^2 + dT^3$

This equation gives a curve of parabolic form but for technical appliance we are concerned only with a relatively small range, about 300° - 600°F and for this range, we can replace the curve by a straight line having approximately the same slope. We can assume then, for our work the $\phi(T)$ expressed by the linear equation,

$$\phi(T) = \alpha + \beta T \qquad (6)$$

Equation (4) then becomes

$$C_p = \alpha + \beta T + \frac{Amn(n+1)}{T^{n+1}} p(1+ \frac{a}{2} p) \qquad (7)$$

Since the constant a, and m, are known there remains to be determined α and β. These are determined by means of the experiments of Knoblauch and Jakob. From these experiments curves of specific heat against temperatures were plotted for pressures of 2, 4, 6, and 8 Kg. Then since a, and m, are known, values of α, and β, were assumed so that the equation (7) fitted these experimental curves.

The values decided on were for the Centigrade scale

$\alpha = 0.367$ $\qquad\qquad$ $\beta = 0.00018$

Then $$\phi(T) = 0.367 + 0.00018T \qquad (8)$$

For the Farenheit Scale.

$\alpha = 0.367$ $\qquad\qquad$ $\beta = 0.0001$

$$\phi(T) = 0.367 + 0.0001\ T \qquad (9)$$

With these values of the constants α and β, the calculated curves agree with the experimental curves except at 350°C, and this is due probably to an experimental error. The C_p at saturation can be calculated by means of the formula

$$C_{p\ \text{Sat.}} = \frac{dH}{dT} - \frac{r}{T} - AT\frac{dp}{dT}\left(\frac{\partial V}{\partial T}\right)_p \qquad (10)$$

Where H denotes the total heat of saturated steam and r, the latent heat of vaporization, $\frac{dp}{dT}$ is derived from the relation $p = f(T)$ that applies to saturated steam, and the derivative $\left(\frac{\partial V}{\partial T}\right)_p$ can be found by means of the characteristic equation of superheated steam.

A table has been prepared showing the differences in the specific heats, as taken from the curves and as calculated at saturation and the values from 15 pounds per square inch to 300 pounds per square inch are here tabulated, for comparison.

Pressure lb. per sq. inch	Values of (C_p) Sat.				
	from 10	from 7	Marks and Davis	Diff.	Percent Diff.
15	0.4995	0.4775	0.472	-4.4	-5.4
50	0.5157	0.5228	0.508	-1.4	-1.5
100	0.5609	0.5609	0.565	-0.0	-0.7
150	0.5917	0.5876	0.630	-0.7	-6.5
200	0.6143	0.6097	0.705	-0.8	-15.0
300	0.6565	0.6454	0.898	-1.6	-36.0

From this discussion it seems safe to assume that formula (10) can be adopted for finding values of C_p for the range commonly used in technical practice.

III.

SPECIFIC HEAT CURVES.

Taking a range of pressure from 0# to 300# absolute and degrees of superheat from 0° to 600°, values of the specific heat at constant pressure were calculated and a series of curves were plotted as shown on page (17). Then another series of curves were drawn showing the relation between C_p

and temperatures as shown on page (18).

While these curves are of value as representing theoretical conclusions, they are not of much practical or direct value, since what we are concerned with is, the mean specific heat between saturation and the known degree of superheat. Curves therefore, of mean C_p were calculated by integrating the area bounded by every 100° of superheat, the X axis and the curve. From this area the mean height above the X axis was found, or in other words the mean C_p. These curves are found on pages (19) and (20). For purpose of checking, the mean C_p at 300° and 600° superheat were calculated for each pressure, by means of formula.

$$C_{p_m} = \alpha + \frac{\beta}{2}(T + T_s) + \frac{Amn(n+1)p(1+\frac{a}{2}p)(\frac{1}{T_s^5} - \frac{1}{T^5})}{T - T_s} \qquad (11)$$

Tables giving values of C_p and mean C_p are found under headings, Table I and Table II, respectively.

The derivation of the equation for mean specific heat is as follows:-

$$\text{Mean } C_p = \frac{\int_{T_s}^{T} C_p \, dT}{T - T_s} \qquad (12)$$

which becomes by substitution,

$$\text{Mean } C_p = \frac{1}{T - T_s} \int_{T_s}^{T} \left[\alpha + \beta T + \frac{Amn(n+1)}{T^{n+1}} p(1+\frac{a}{2}p)\right] dT =$$

$$\alpha + \frac{\beta}{2}(T + T_s) + \frac{Amn(n+1)p(1+\frac{a}{2}p)(\frac{1}{T^5} - \frac{1}{T^5})}{T - T_s} \qquad (13)$$

IV.

SAMPLE CALCULATIONS.

Calculations for C_p at 50 pounds per square inch pressure and 100° superheat.

$$C_p = \alpha + \beta T + \frac{Amn(n+1)p(1+\frac{a}{2}p)}{T^{n+1}}$$

$p = 50.00$

$T = 840.58$

$= 0.367$

$= 0.0001$

$a = 0.0006$

$T = 0.084058$

$\log 144\ Amn(n+1) = 14.425053$

$\log T^{n+1} = 17.54747$

$(1+ap) = 1.0150$

$\log (1-ap) = 0.00454$

$$\log \frac{144\ Amn(n+1)p(1+\frac{a}{2}p)}{T^{n+1}} = \bar{2}.58109$$

$$\text{"} = 0.038114$$

$C_p = .367 + .084058 + .038114 = .48917$

SAMPLE CALCULATIONS (CONT.)

Calculations for C_{pm} at 250 pounds per square inch pressure and 300° Superheat.

$$C_{pm} = \alpha + \frac{\beta}{2}(T + T_s) + \frac{Amn(n+1)p(1+\frac{a}{2}p)(\frac{1}{T_s^5} - \frac{1}{T^5})}{T - T_s}$$

$T_s = 860.7$

$T = \underline{1160.7}$

$T + T_s = 2021.4$

$(1+ap) = 1.075$

$p(1+ap) = 268.75$

$1/T_s^5 = 2.117 \times 10^{-15}$

$1/T^5 = \underline{.47468 \times 10^{-15}}$

$(\frac{1}{T_s^5} - \frac{1}{T^5}) = 1.64242 \times 10^{-15}$

$\log T_s = 2.934852$

$\underline{\qquad 5}$

$\log T_s^5 = 14.674260$

$\log T = 3.064720$

$\underline{\qquad 5}$

$\log T^5 = 15.323600$

$\log 1/T_s^5 = \bar{15}.325740$

$\log 1/T^5 = \bar{16}.676400$

$\log(\frac{1}{T_s^5} - \frac{1}{T^5}) = \bar{15}.315480$

$\log 268.25 = 2.429348$

$\log m = \underline{13.725080}$

$\log \text{sum} = 1.369908$

Number whose log = 1.369908 = 23.437

$\frac{23.437}{300} = .0781$

$C_{pm} = .0781 + .367 + .10107 = .54617$

TABLE I.

V.

Calculated Values of Specific Heat.

Absolute Pressure (p)	1	2	3	5	10
Saturation Temp. (ts)	101.83		141.5	162.3	193.2
C_p at Saturation	.43165	.43891	.44404	.45295	.46590
Degrees Superheat 20	.43204	.43800	.44301	.45150	.46300
40	.43278	.43850	.44261	.44900	.46037
60	.43379	.43892	.44269	.44845	.45859
80	.43499	.43969	.44313	.44833	.45750
100	.43635	.44069	.44387	.44860	.45694
120	.43783	.44188	.44481	.44918	.45681
140	.43941	.44322	.44596	.45200	.45704
160	.44106	.44467	.44725	.45102	.45755
180	.44278	.44621	.44806	.45220	.45830
200	.44456	.44784	.45016	.45351	.45924
250	.44911	.45216	.45425	.45722	.46224
300	.45383	.45667	.45864	.46136	.46588
350	.45865	.46137	.46323	.46577	.46994
400	.46352	.46615	.46794	.47036	.47428
450	.46843	.47101	.47274	.47507	.47880
500	.47337	.47590	.47760	.47985	.48346
550	.47832		.48249	.48470	.48820
600	.48329	.48576	.48744	.48959	.49301

TABLE I (CONT.)

Abs. P. (p)	15	20	25	30	40	50.
Sat.Temp.(ts)	213.0	228.0	240.1	250.3	267.3	281.0
Cp at Sat.	.47757	.48628	.49398	.50090	.51267	.52256
Degrees Sup.20		.48031	.48708	.49312	.50358	.51250
40		.47577	.48179	.48718	.49656	.50500
60	.46620	.47237	.47776	.48259	.49099	.49817
80	.46433	.46989	.47475	.47909	.48666	.49310
100	.46312	.46816	.47256	.47649	.48335	.48917
120	.46268	.46704	.47104	.47461	.48086	.48616
140	.46220	.46645	.47009	.47334	.47906	.48389
160	.45898	.46620	.46957	.47257	.47780	.48226
180	.46269	.46632	.46943	.47220	.47704	.48115
200	.46334	.46672	.46961	.47391	.47667	.48047
250	.46576	.46866	.47112	.47330	.47640	.48029
300	.46899	.47156	.47356	.47560	.47889	.48165
350	.47276	.47507	.47701	.47870	.48162	.48405
400	.47689	.47903	.48079	.48233	.48498	.48716
450	.48126	.48326	.48491	.48633	.48877	.49078
500	.48582	.48770	.48924	.49061	.49288	.49475
550	.49046	.49229		.49504	.49721	.49897
600	.49520	.49697	.49840	.49962	.50170	.50337

TABLE I (CONT.)

Abs. P. (p)	60	80	100	125	150	200
Sat. Temp.(t_s)	292.7	312.0	327.8	344.4	358.5	381.9
C_p at Sat.	.53210	.54476	.56076	.57202	.58796	.61005
Degrees Sup. 20	.52063	.53246		.55947	.57120	.59116
40	.51178	.52247		.54664	.55731	.57541
60	.50468	.51438	.52578	.53617	.54582	.56226
80	.49903	.50786	.51806	.52756	.53740	.55130
100	.49455	.50262	.51187	.52052	.52900	.54234
120	.49106	.49848	.50685	.51475	.52250	.53456
140	.48839	.49520	.50282	.50997	.51740	.52826
160	.48639	.49268	.49965	.50633	.51290	.52306
180	.48496	.49080	.49718	.50336	.50900	.51888
200	.48401	.48944	.49532	.50105	.50627	.51535
250	.48326	.48788	.49278	.49755	.50190	.50951
300	.48421	.48823	.49232	.49646	.50016	.50365
350	.48631	.48987	.49340	.49702	.50023	.50586
400	.48920	.49241	.49552	.49875	.50158	.50656
450	.49264	.49560	.49807	.50130	.50384	.50831
500	.49647	.49923	.50176	.50445	.50694	.51083
550	.50059	.50319	.50553	.50803	.51017	.51342
600	.50498	.50739	.50958	.51194	.51394	.51906

TABLE I. (CONT.)

Absolute Pressure (p)		250	300
Saturation Temp. (t_s)		401.1	417.5
C_p at Saturation.		.62853	.64586
Degrees Superheat.	20	.60595	.62367
	40	.59070	.60498
	60	.57622	.58922
	80	.56405	.57592
	100	.55424	.56471
	120	.54529	.55326
	140	.53816	.54709
	160	.53220	.54384
	180	.52727	.53777
	200	.52321	.53265
	250	.51724	.52349
	300	.51229	.51814
	350	.51093	.51544
	400	.51089	.51474
	450	.51185	.51538
	500	.51462	.51704
	550	.51656	.51945
	600	.52046	.52242

TABLE II. - Mean Specific Heat.

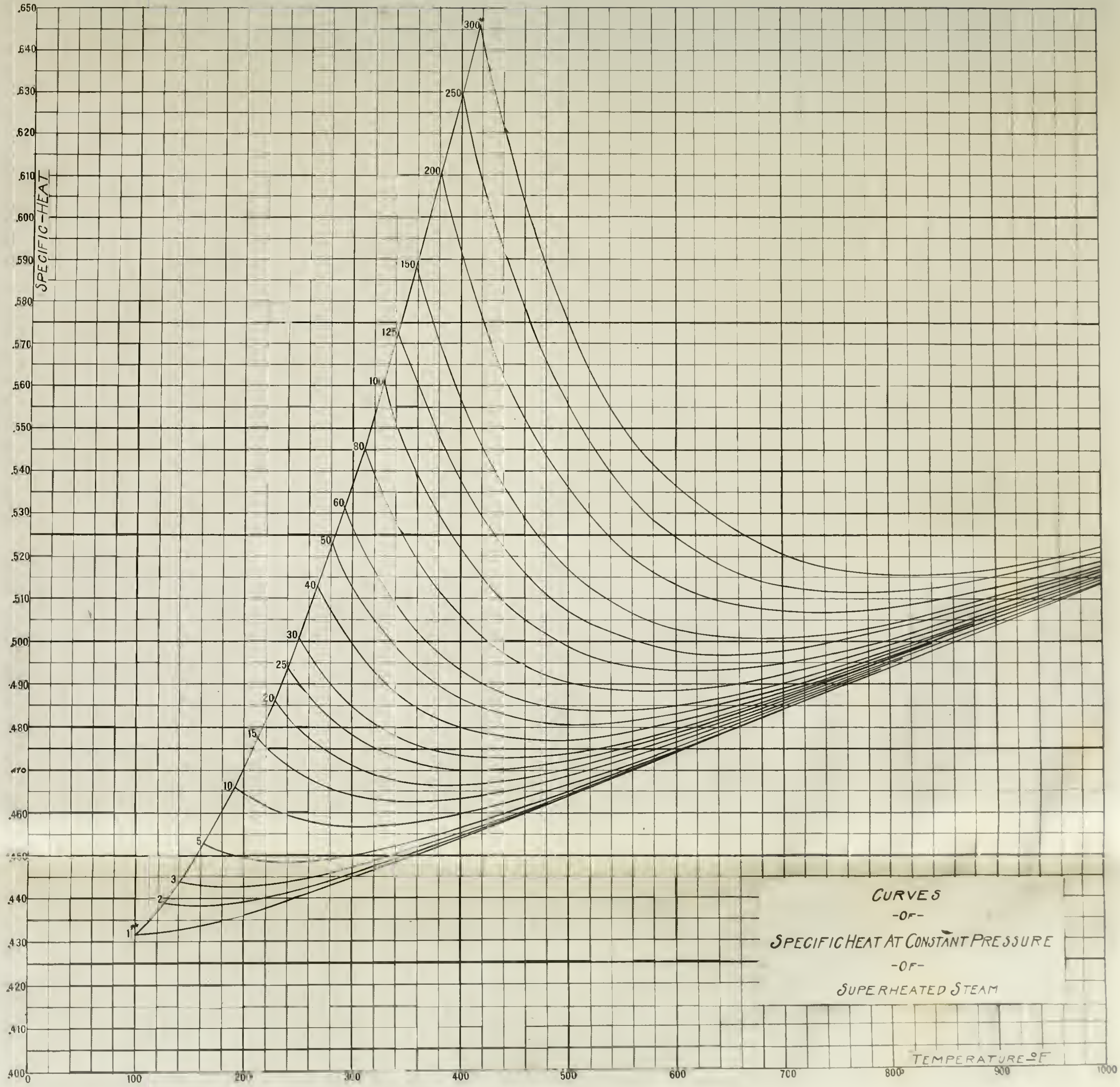
Absolute Pressure (p)	1#	2#	3#	5#	10#	15#
C_p at Saturation.	.4316	.4389	.4440	.4529	.4659	.4775
Degrees Superheat 20	.4320	.4381	.4437	.4518	.4641	.4748
40	.4324	.4380	.4435	.4509	.4626	.4727
60	.4329	.4382	.4433	.4504	.4617	.4710
80	.4335	.4385	.4433	.4495	.4605	.4694
100	.4340	.4388	.4435	.4424	.4595	.4685
120	.4342	.4390	.4436	.4493	.4592	.4674
140	.4347	.4397	.4137	.4494	.4589	.4667
160	.4358	.4405	.4440	.4495	.4588	.4660
180	.4362	.4411	.4442	.4497	.4588	.4657
200	.4372	.4415	.4445	.4499	.4590	.4653
250	.4386	.4430	.4460	.4510	.4592	.4653
300	.4411	.4450	.4477	.4524	.4602	.4657
350	.4430	.4467	.4495	.4547	.4615	.4664
400	.4457	.4490	.4517	.4555	.4624	.4673
450	.4477	.4517	.4536	.4575	.4637	.4680
500	.4500	.4535	.4561	.4595	.4659	.4695
550	.4523	.4560	.4577	.4625	.4675	.4717
600	.4543	.4580	.4606	.4650	.4699	.4732

TABLE II. (CONT.)

Abs. Pr. (p)		20#	25#	30#	40#	50#	60#	80#
C_p at Sat.		.4863	.4939	.5009	.5126	.5225	.5321	.5447
Deg. Sup.	20	.4826	.4905	.4960	.5070	.5165	.5250	.5385
	40	.4800	.4877	.4930	.5035	.5123	.5200	.5336
	60	.4780	.4853	.4900	.5000	.5082	.5160	.5285
	80	.4765	.4835	.4880	.4975	.5054	.5130	.5240
	100	.4750	.4817	.4858	.4950	.5034	.5095	.5200
	120	.4741	.4800	.4842	.4936	.5004	.5073	.5165
	140	.4734	.4786	.4832	.4916	.4985	.5044	.5140
	160	.4723	.4774	.4816	.4895	.4961	.5027	.5110
	180	.4718	.4762	.4804	.4880	.4946	.5007	.5090
	200	.4708	.4755	.4793	.4869	.4936	.4910	.5074
	250	.4700	.4744	.4782	.4850	.4903	.4956	.5036
	300	.4700	.4741	.4777	.4840	.4890	.4938	.5018
	350	.4705	.4742	.4775	.4836	.4885	.4925	.5000
	400	.4710	.4747	.4779	.4837	.4876	.4920	.4986
	450	.4720	.4759	.4784	.4838	.4874	.4918	.4980
	500	.4736	.4765	.4795	.4840	.4875	.4920	.4980
	550	.4750	.4770	.4804	.4850	.4880	.4925	.4984
	600	.4766	.4792	.4820	.4860	.4888	.4935	.4987

TABLE II. (CONT.)

Absolute Pressure (p)		100#	125#	150#	200#	250#	300#
C_p at Saturation.		.5607	.5720	.5879	.6100	.6285	.6458
Degrees Superheat.	20	.5520	.5645	.5790	.5978	.6175	.6340
	40	.5460	.5584	.5715	.5899	.6075	.6242
	60	.5404	.5525	.5645	.5820	.5990	.6146
	80	.5356	.5475	.5587	.5755	.5910	.6056
	100	.5312	.5430	.5538	.5700	.5850	.5989
	120	.5277	.5390	.5488	.5650	.5792	.5915
	140	.5245	.5350	.5445	.5602	.5740	.5856
	160	.5217	.5315	.5406	.5560	.5692	.5801
	180	.5191	.5290	.5370	.5523	.5646	.5758
	200	.5120	.5260	.5341	.5420	.5606	.5714
	250	.5120	.5200	.5279	.5410	.5525	.5674
	300	.5085	.5160	.5238	.5350	.5458	.5550
	350	.5060	.5138	.5201	.5313	.5408	.5496
	400	.5045	.5119	.5180	.5286	.5370	.5458
	450	.5040	.5105	.5165	.5260	.5340	.5425
	500	.5038	.5096	.5151	.5245	.5320	.5395
	550	.4038	.5092	.5145	.5235	.5302	.5375
	600	.4038	.5090	.5146	.5224	.5292	.5358



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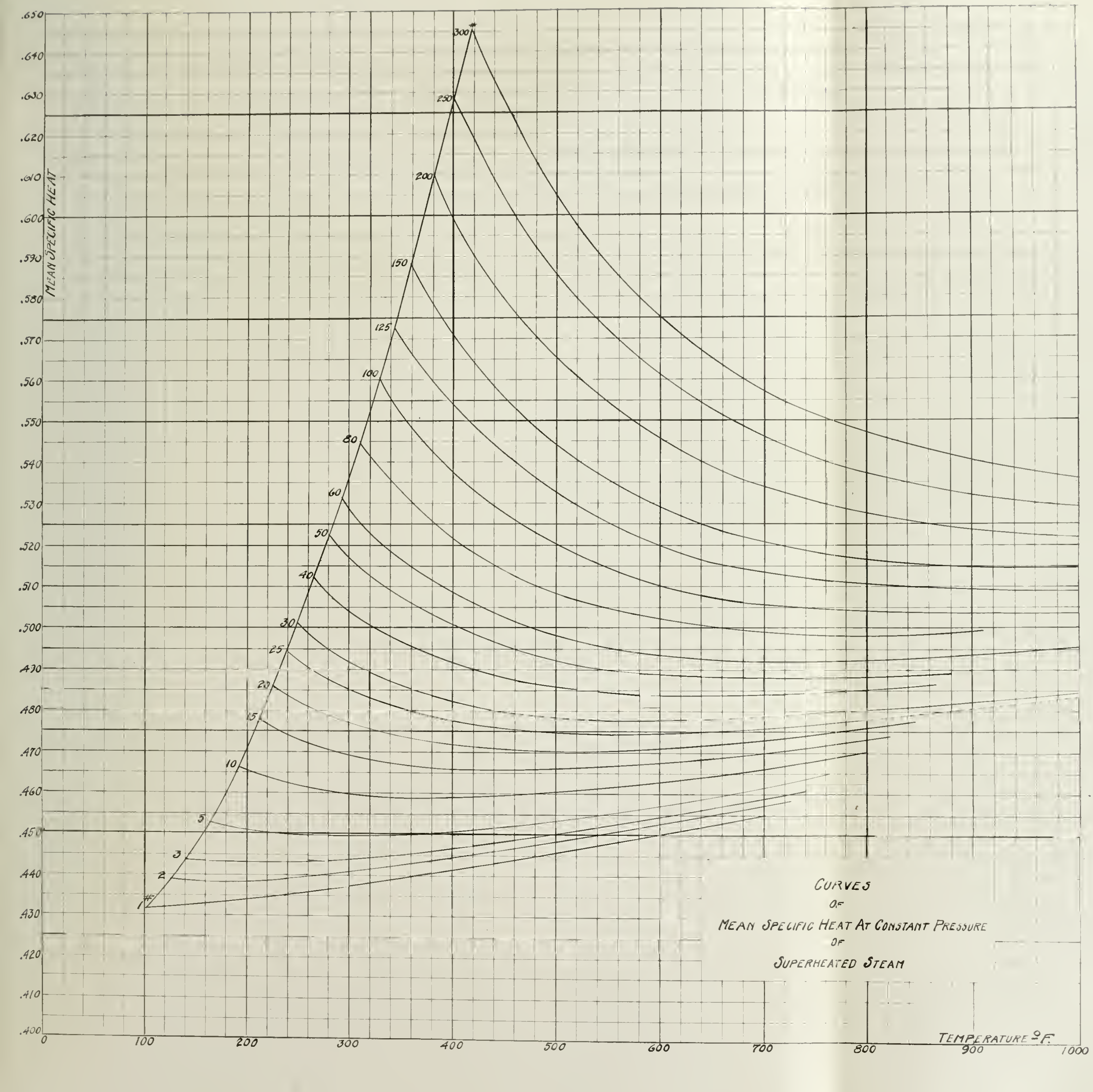

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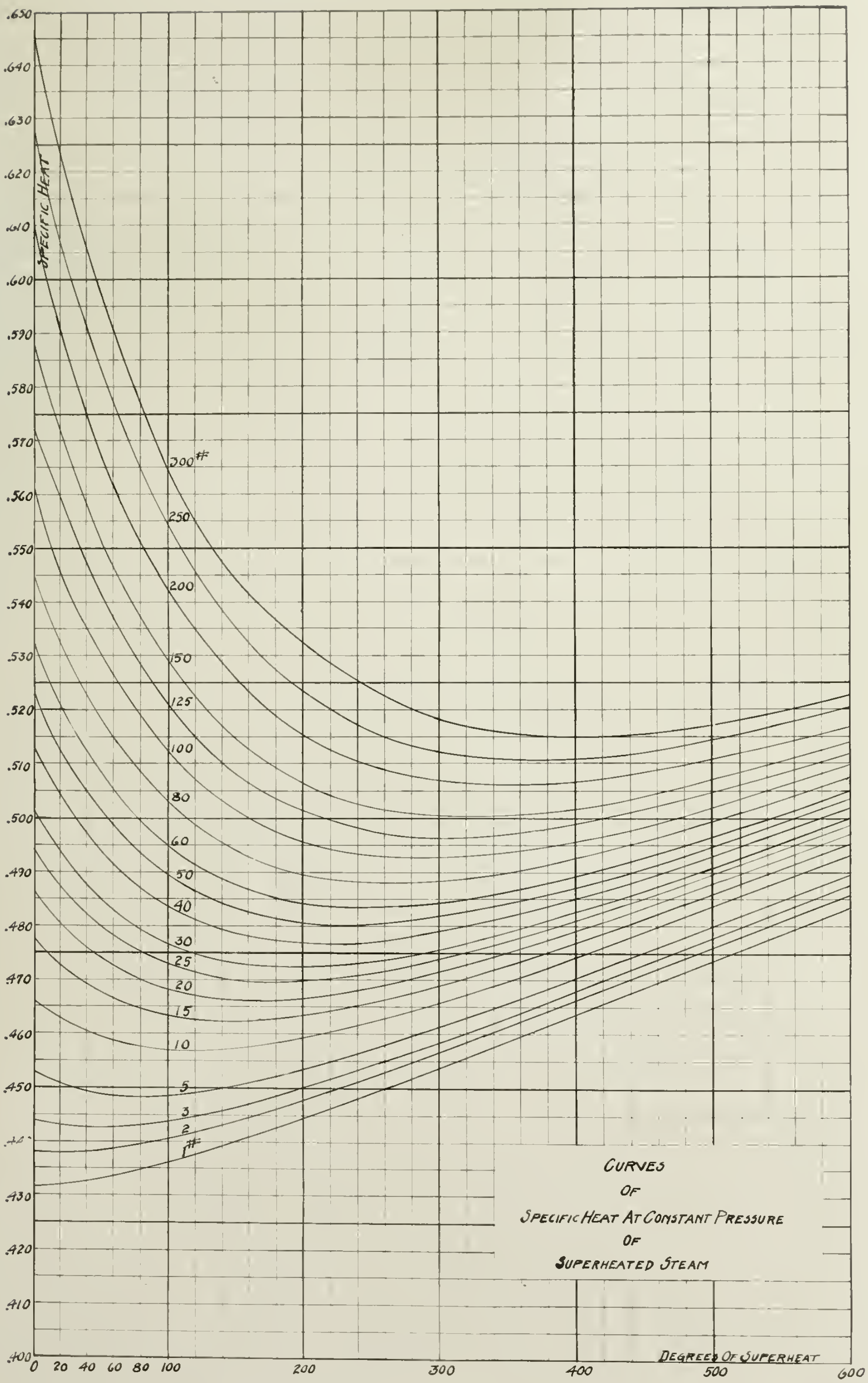

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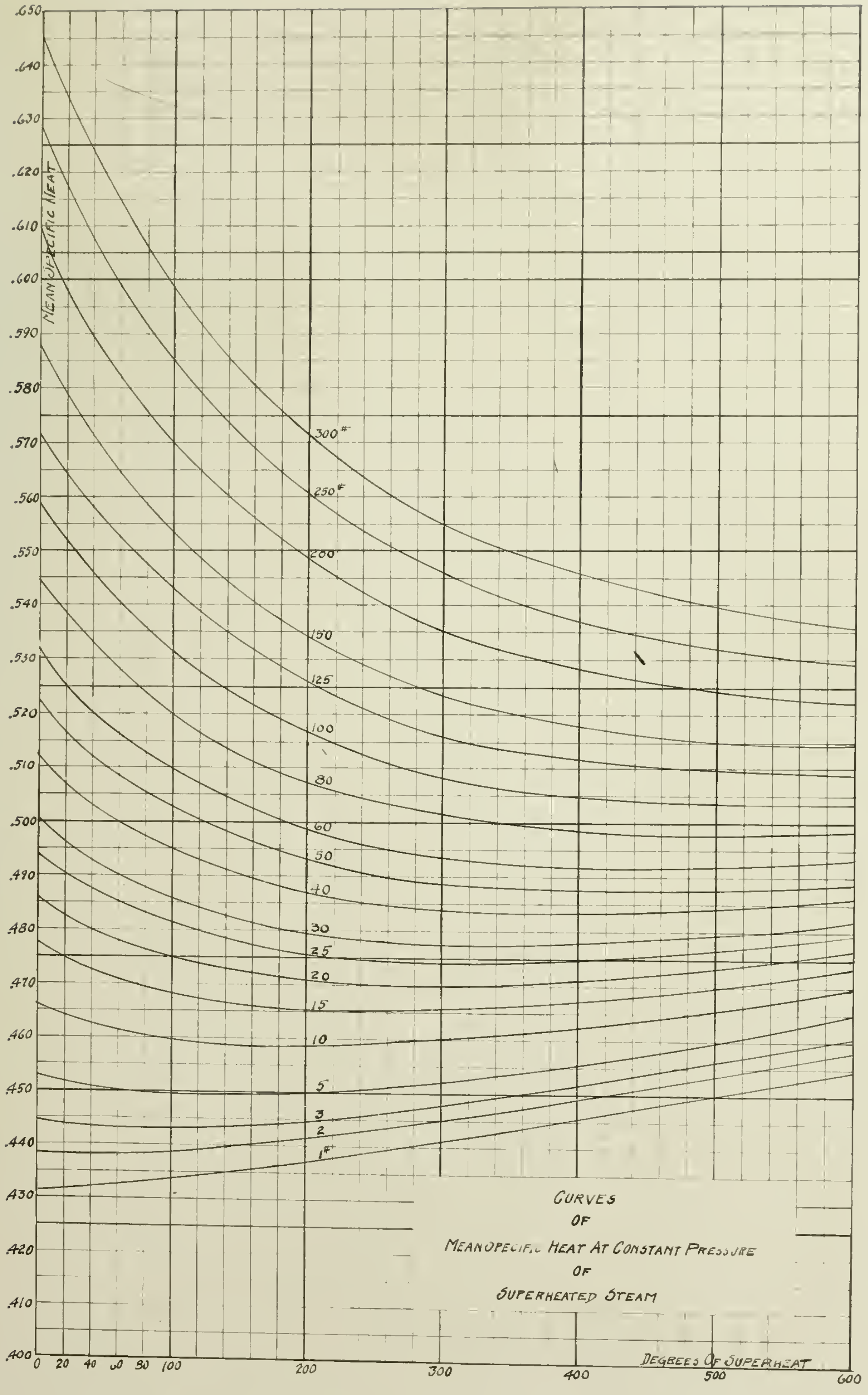

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