

ROYAL AIRCRAFT ESTABLISHMENT
BEDFORD

R. & M. No. 3158
(20,618)
A.R.C. Technical Report



MINISTRY OF AVIATION

AERONAUTICAL RESEARCH COUNCIL
REPORTS AND MEMORANDA

Thermodynamic Charts for the Decomposition
Products of 80, 85 and 90 per cent
w/w Hydrogen Peroxide (H.T.P.)

By ENID CARTER

LONDON: HER MAJESTY'S STATIONERY OFFICE

1960

SEVEN SHILLINGS NET

R. & M. No. 3158

Thermodynamic Charts for the Decomposition Products of 80, 85 and 90 per cent w/w Hydrogen Peroxide (H.T.P.)

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COMMUNICATED BY THE DEPUTY CONTROLLER AIRCRAFT (RESEARCH AND DEVELOPMENT)
MINISTRY OF SUPPLY

*Reports and Memoranda No. 3158**
April, 1958

Summary. Thermodynamic charts showing enthalpy, entropy and specific volume for a range of pressures and temperatures have been constructed for the decomposition products of 80, 85 and 90 per cent w/w hydrogen peroxide (H.T.P.) for regions above and below the saturation line. Examples are given to show how gas velocity, venturi nozzle throat and exit areas, exit pressure, specific heat at constant pressure, γ , characteristic velocity and thrust coefficient can be deduced from the charts and the rider scale which is also enclosed with this paper.

1. *Introduction.* Subsequent to the publication of thermodynamic charts for the decomposition products of 80 per cent w/w hydrogen peroxide (H.T.P.)¹ a need developed for similar charts for the decomposition products of 85 per cent and 90 per cent w/w H.T.P. which would also show values of properties over a wider range of pressures. The charts described and presented in this note are intended to satisfy this need.

The data are presented in the form of enthalpy-log specific volume ($i - \log v$) charts for 80, 85, and 90 per cent H.T.P. and a Mollier diagram for a smaller range of 80 per cent H.T.P. It has been found that the type of information required for calculation of the flow of gas through a nozzle is more readily available from the ($i - \log v$) chart than from the Mollier diagram. Presentation of data in the form of a ($i - \log v$) chart was first suggested by Spalding² and first presented, together with a rider scale, by Williams³.

2. *Use of Charts and Examples.* Five properties of state: pressure, temperature and specific volume, entropy and enthalpy, are plotted in the charts. Provided the values of two of these properties are known, the values of the three corresponding properties can be found directly from the chart.

* R.A.E. Tech. Note RPD 164, received 15th December, 1958.

Other data which can be obtained are:

(i) Specific heat at constant pressure, c_p .

If a mean value of c_p is required over a known temperature range this can be obtained from the chart by means of the relationship

$$c_p = \frac{\Delta i}{(\Delta T)_{p = \text{const}}}$$

Example: c_p is required for $p = 20$ kg/sq cm between $t = 300$ deg C and $t = 400$ deg C for 80 per cent w/w H.T.P.

i at 300 deg C and 20 kg/sq cm = 478 kcal/kg,

i at 400 deg C and 20 kg/sq cm = 519 kcal/kg;

therefore

$$c_p = \frac{41}{100} = 0.41 \frac{\text{kcal}}{\text{kg deg K}}$$

(ii) Ratio of specific heats, $\gamma = c_p/c_v$.

Values of γ can be obtained in two ways:

(a) γ defined as

$$\frac{c_p}{c_v} = \frac{c_p}{c_p - \frac{R}{M}},$$

where $R = 1.98584$ kcal/kg mole deg K, can be calculated from c_p .

(b) γ defined by the adiabatic relationship

$$\left(\frac{p_1}{p_2}\right)^{(\gamma-1)/\gamma} = \frac{T_1}{T_2}$$

can be obtained from the chart.

Example: γ is required between temperatures of 300 deg C = 573.16 deg K and 400 deg C = 673.16 deg K for an adiabatic expansion from $p = 20$ kg/sq cm for 80 per cent w/w H.T.P.

Find the entropy line which passes through $p = 20$ kg/sq cm and $t = 300$ deg C and read off the pressure; $p = 10$ kg/sq cm.

Therefore

$$\frac{\gamma - 1}{\gamma} = \frac{\log \frac{673.16}{573.16}}{\log \frac{20}{10}} = 0.2318,$$

$$\gamma = 1.30.$$

The following data can be read off the ($i - \log v$) charts only:

(iii) Exit area and velocity knowing exit pressure and combustion chamber pressure, or exit pressure and velocity knowing exit area and combustion chamber pressure.

(a) To obtain the exit area per unit flow rate it is necessary to use the rider scale, the construction of which is described in the Appendix. Determine the entropy line which passes through the intersection of the combustion-chamber pressure line and the relevant initial enthalpy line.

Superimpose the horizontal line of the rider scale on the initial-enthalpy line (*Note:* The temperatures of the initial enthalpy lines correspond to the initial temperature of the liquid H.T.P.). Slide the rider scale horizontally until the velocity scale passes through the intersection of the exit pressure line and the above mentioned isentrope. The exit velocity is given by the point of intersection; the arrow on the rider scale then points to the required area.

Example: Given a combustion-chamber pressure of 20 kg/sq cm, an exit pressure of 1 kg/sq cm and an initial temperature of 20 deg C for 80 per cent w/w H.T.P., the entropy corresponding to these conditions is found to be 1.114 kcal/kg deg C. Moving the rider till the velocity scale passes through the intersection of this isentrope with the exit pressure line of 1 kg/sq cm, the velocity is found to be 1120 m/sec; the corresponding area per unit flow rate as shown by the arrow on the rider scale is found to be 12.8 sq cm sec/kg.

(b) To obtain the exit pressure knowing the exit area, the same procedure as above is followed, but the rider scale is moved horizontally until the arrow points to the known area. The required pressure is then given by the point at which the velocity curve cuts the isentrope.

Example: Given a combustion-chamber pressure of 20 kg/sq cm, an exit area of 10 sq cm sec/kg, and an initial temperature of 20 deg C for 80 per cent w/w H.T.P., the corresponding entropy, as before, is 1.114 kcal/kg deg C. The velocity curve is found to be cut by this isentrope at a value of 1066 m/sec and the corresponding exit pressure is 1.50 kg/sq cm.

(iv) Throat area.

To obtain the throat area per unit flow rate find, as in the case of exit areas, the entropy line which passes through the point of intersection of the initial pressure line and the initial enthalpy line. Place the rider scale so that the horizontal line lies on the initial enthalpy line and move the scale horizontally until the velocity curve is tangential to the entropy line. The arrow then points to the throat area per unit flow rate.

Example: Given a combustion chamber pressure of 20 kg/sq cm, and an initial temperature of 20 deg C for 80 per cent w/w H.T.P., the corresponding entropy is seen from the chart to be 1.114 kcal/kg deg C. When the rider scale is located so that the horizontal line lies on the initial enthalpy line, and the velocity curve is tangential to the entropy line of 1.114 kcal/kg, the arrow is found to point to the value of 4.05 sq cm sec/kg for the throat area per unit flow rate.

(v) Characteristic velocity, C^* .

The characteristic velocity C^* is defined as

$$p \frac{A_t}{Q} g.$$

A_t/Q is obtained as in (iv) above, and is then multiplied by the combustion pressure p and gravitational acceleration g to give C^* .

(vi) Thrust coefficient, C_F .

The thrust coefficient C_F is defined as

$$\frac{\text{exit velocity}}{C^*}.$$

The exit velocity is obtained as in (iii) above and C^* as in (v) above.

LIST OF SYMBOLS AND REFERENCE POINTS

A	Area (sq cm)
A_t	Throat area (sq cm)
C^*	Characteristic velocity (m/sec)
C_F	Thrust coefficient
c_p	Specific heat at constant pressure (kcal/kg deg K)
c_v	Specific heat at constant volume (kcal/kg deg K)
g	Gravitational acceleration (m/sec ²)
i	Specific enthalpy of mixture (kcal/kg)
i_0	Specific enthalpy of oxygen (kcal/kg)
i_s	Specific enthalpy of steam (kcal/kg)
i_w	Specific enthalpy of water (kcal/kg)
J	Mechanical equivalent of heat (m kg/kcal)
M	Molecular weight of mixture
M_0	Molecular weight of oxygen
M_s	Molecular weight of steam
	} $0 = 16.00$
p	Total pressure of mixture of steam and oxygen (kg/sq cm)
p_0	Partial pressure of oxygen (kg/sq cm)
p_s	Partial pressure of steam (kg/sq cm)
p_w	Reference partial pressure of oxygen (kg/sq cm)
Q	Mass flow rate (kg/sec)
R	Universal gas constant (<i>see</i> Appendix)
S	Specific entropy of mixture (kcal/kg deg K)
S_0	Specific entropy of oxygen (kcal/kg deg K)
S_s	Specific entropy of steam (kcal/kg deg K)
S_w	Specific entropy of water (kcal/kg deg K)
t	Temperature of mixture (deg C)
t_0	Temperature of oxygen (deg C)
t_s	Temperature of steam (deg C)
T_0	Temperature of oxygen (deg K)
u	Velocity (m/sec)
v	Specific volume of mixture (cu m/kg)
v_0	Specific volume of oxygen (cu m/kg)
v_s	Specific volume of steam (cu m/kg)
w_0	Weight of oxygen in 1 kg of decomposition products (kg)
w_s	Weight of H ₂ O remaining as steam in 1 kg of decomposition products (kg)
x	Percentage of hydrogen peroxide in H.T.P.
γ	Defined in Section 2

REFERENCES

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1	E. Carter	Thermodynamic charts for the decomposition products of 80 per cent hydrogen peroxide. A.R.C. 16,502. October, 1953.
2	D. B. Spalding	A mechanical method of determining nozzle characteristics as applied to the decomposition products of concentrated hydrogen peroxide solution. (Unpublished.)
3	W. H. Williams	Thermodynamic charts for the combustion products of nitric acid and kerosene. R. & M. 2982. July, 1950.

APPENDIX

Sources of Data and Method of Constructing the Charts

1. *Sources.* It was assumed that oxygen obeys the perfect-gas laws within the ranges of temperature and pressure covered by these charts. The validity of this assumption was checked by comparing the values of the properties of state obtained by using perfect-gas laws with the corresponding values obtained from the general-limit method of deriving equations of state, postulated by Beattie¹, and also with values obtained from a chart of the properties of oxygen published by the Institut International du Froid, Laboratoire Kamerlingh Onnes, Leyden, 1942. There was a discrepancy of less than 3 per cent in pressure and 1 per cent in enthalpy. These errors reduce to less than 1 per cent and 0.3 per cent in the charts as presented with this note and apply only to a small region of high pressure and low temperature. Values of enthalpy and entropy were obtained from the tables of properties of gases by Keenan and Kaye². The values of enthalpy were adjusted to make the enthalpy zero at 0 deg C for both the ($i - \log v$) charts and the Mollier diagram. For the ($i - \log v$) charts the values of entropy were adjusted to make the entropy zero at 0 deg C and 1 lb/sq in. For the Mollier diagram it was assumed that the entropy given in the oxygen tables is for a pressure of 0.1 kg/sq cm.

Steam does not obey the perfect-gas laws in the regions covered in this paper, but there are accurate tables³ giving values for p_s , i_s , t_s , S_s and v_s . These tables, however, do not give values for temperatures above 550 deg C. For temperatures above 550 deg C, the equations of state given by Koch³ were used to extend the range to 760 deg C. The values of the enthalpy of the perfect-gas state were taken from the figures given by Keenan and Kaye⁴ for the perfect gas.

2. *Construction of the ($i - \log v$) Charts.* 2.1. *Above the Saturation Line.* It is assumed that hydrogen peroxide decomposes completely according to the equation



For hydrogen peroxide of x per cent w/w concentration we have then

$$1 \text{ kg of H.T.P.} \rightarrow \left(\frac{18 \cdot 016}{34 \cdot 016} \frac{x}{100} + \frac{100 - x}{100} \right) \text{ kg of H}_2\text{O} + \left(\frac{16 \cdot 000}{34 \cdot 016} \frac{x}{100} \right) \text{ kg of O}_2. \quad (2)$$

As oxygen obeys the perfect-gas laws within the range of the charts

$$p_0 v_0 = R \frac{T_0}{M_0}, \quad (3)$$

where

$$R = 0.08478 \frac{\text{kg}}{\text{cm}^2} \frac{\text{m}^3}{\text{kg mol deg K}};$$

and also

$$(S_0)_{p_0} = (S_0)_{p_x} - \frac{R}{M_0} \log_e \left(\frac{p_0}{p_x} \right), \quad (4)$$

where

$$R = 1.98584 \frac{\text{kcal}}{\text{kg mol deg K}}.$$

Also

$$v = \left(\frac{18.016}{34.016} \frac{x}{100} + \frac{100-x}{100} \right) v_s = \left(\frac{16.000}{18.016} \frac{x}{100} \right) v_0, \quad (5)$$

which follows from equation (2), since each gas is assumed to occupy the same total volume as the mixture.

Further

$$t = t_s = t_0, \quad (6)$$

$$p = p_s + p_0. \quad (7)$$

From equation (2) we have

$$i = \left(\frac{18.016}{34.016} \frac{x}{100} + \frac{100-x}{100} \right) i_s + \left(\frac{16.000}{34.016} \frac{x}{100} \right) i_0, \quad (8)$$

$$S = \left(\frac{18.016}{34.016} \frac{x}{100} + \frac{100-x}{100} \right) S_s + \left(\frac{16.000}{34.016} \frac{x}{100} \right) S_0. \quad (9)$$

The following procedure was used to obtain the values for the mixture:

- (1) Select p_s and t ($= t_s = t_0$)
- (2) Read off i_s , S_s and v_s from steam tables or calculate them from the appropriate equations
- (3) Find v_0 from equation (5)
- (4) Find p_0 from equation (3)
- (5) Read off i_0 and $(S_0)_{p_x}$ from oxygen tables and adjust these values to our reference points
- (6) Find $(S_0)_{p_0}$ from equation (4)
- (7) Combine these results to give v , p , i and S using equations (5), (7), (8) and (9).

When constructing the $(i - \log v)$ charts, pv was plotted against p for constant temperature lines, and S was plotted against v for constant temperature. Hence values of v were obtained for selected values of p and S at known temperatures.

2.2. The Saturation Line and Points Below It. The saturation line was determined by reading off the appropriate values of p_s , i_s , t_s , S_s and v_s for saturated steam from the steam tables. The corresponding values of v_0 , t_0 , i_0 and S_0 were obtained and values for the mixture were then calculated.

The lines of constant humidity on the charts indicate various ratios of water to total products expressed as percentage w/w. Thus the line 4 per cent w/w corresponds to the condition that in each kilogram of total products there is 0.04 kg of water. The weights of water corresponding to the selected percentages were subtracted from the weight of H₂O in 1 kg of mixed products and these values of w_s were used in the relationship

$$v_0 = \frac{w_s}{w_0} v_s, \quad (10)$$

p_0 , i_0 , and S_0 for oxygen being calculated as before using the appropriate values of i_s , t_s , S_s and v_s for saturated steam. The volume occupied by the water was so small that it was neglected.

These results were combined using equations (6) and (7) and the three following equations:

$$i = \left(\frac{18.016}{34.016} \frac{x}{100} + \frac{100-x}{100} - w_w \right) i_s + \left(\frac{16.000}{34.016} \frac{x}{100} \right) i_0 + w_w i_w,$$

$$S = \left(\frac{18.016}{34.016} \frac{x}{100} + \frac{100-x}{100} - w_w \right) S_s + \left(\frac{16.000}{34.016} \frac{x}{100} \right) S_0 + w_w S_w,$$

$$v = \left(\frac{16.000}{34.016} \frac{x}{100} \right) v_s.$$

p vs v was plotted against v and v was plotted against S for lines of constant humidity. Values of v were then read off for selected values of p and S .

3. *Construction of the Mollier Diagram.* When constructing the i - S chart, p and v were plotted against S for constant temperature lines for points above the saturation line and values of S were found for selected values of p and v . On and below the saturation line p and v were plotted against S for lines of constant humidity and values of S were found for selected values of p and v .

It will be noticed that values of S in the Mollier diagram are different from the values of S given in the $(i - \log v)$ chart by a value of 0.577 kcal/kg deg K. This is because of the different reference points for the entropy of oxygen already referred to. It makes no difference to the use of the charts as the zero for entropy is arbitrary and entropy differences only are required.

4. *Construction of Rider Scale.* The relationship existing when enthalpy is transformed into kinetic energy is

$$u = \sqrt{(2g \int \Delta i)}.$$

Velocity is plotted horizontally using the same scale as is used in the charts for specific volume and i is plotted vertically downwards using the same scale as is used in the charts for enthalpy. Now $A/Q = v/u$ and therefore

$$\log \frac{A}{Q} = \log v - \log u.$$

Hence if the velocities on the rider scale and the areas and volumes on the chart are all plotted to the same logarithmic scale, the principle for finding the area per unit flow rate is the same as that on which a slide rule is based: the log velocity length is subtracted from the log volume length giving the area on a log scale. The arrow on the velocity scale is located so that it points to the correct value of A/Q given by the relationship $A/Q = v/u$ for values of $v = 1$ cu m/kg and $u = 1000$ m/sec, i.e.,

$$\frac{A}{Q} = 10 \text{ sq cm sec/kg.}$$

5. *Initial Enthalpy Lines.* The heats of formation and dilution for various percentage concentrations of H.T.P. and the heats of formation for water are given in tables published by the U.S. National Bureau of Standards⁵ for 25 deg C. The initial enthalpy of the mixture at 25 deg C is then given by the equation

$$i = \left(\frac{18 \cdot 016}{34 \cdot 016} \frac{x}{100} + \frac{100 - x}{100} \right) i_{\text{H}_2\text{O}} + \left(\frac{16 \cdot 000}{34 \cdot 016} \frac{x}{100} \right) i_{\text{O}_2} + \frac{x}{100} (\Delta H_{\text{H}_2\text{O}_2}^F - \Delta H_{\text{H}_2\text{O}}^F),$$

in which $i_{\text{H}_2\text{O}}$ and i_{O_2} (the enthalpies of water and oxygen), and $\Delta H_{\text{H}_2\text{O}_2}^F$ and $\Delta H_{\text{H}_2\text{O}}^F$ (the heat of formation and dilution of H_2O_2 and the heat of formation of H_2O) are taken at 25 deg C. These values were then adjusted to give the initial enthalpies for the required temperatures by means of the relationship

$$i_t = i_{25^\circ\text{C}} + (t - 25)c_{p, \text{H.T.P.}}$$

Values of the specific heat of H.T.P. of various concentrations are given in tables of calorimetric properties of the system $\text{H}_2\text{O} - \text{H}_2\text{O}_2$ by Giguère *et al*⁶.

LIST OF REFERENCES TO APPENDIX

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4	J. H. Keenan and J. Kaye ..	<i>loc. cit.</i> , Table 15.
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6	P. A. Giguère <i>et al.</i>	Hydrogen peroxide and its analogues VII calorimetric properties of the systems $\text{H}_2\text{O} - \text{H}_2\text{O}_2$ and $\text{D}_2\text{O} - \text{D}_2\text{O}_2$. <i>Can. J. Chem.</i> 33 . 804, 1955.

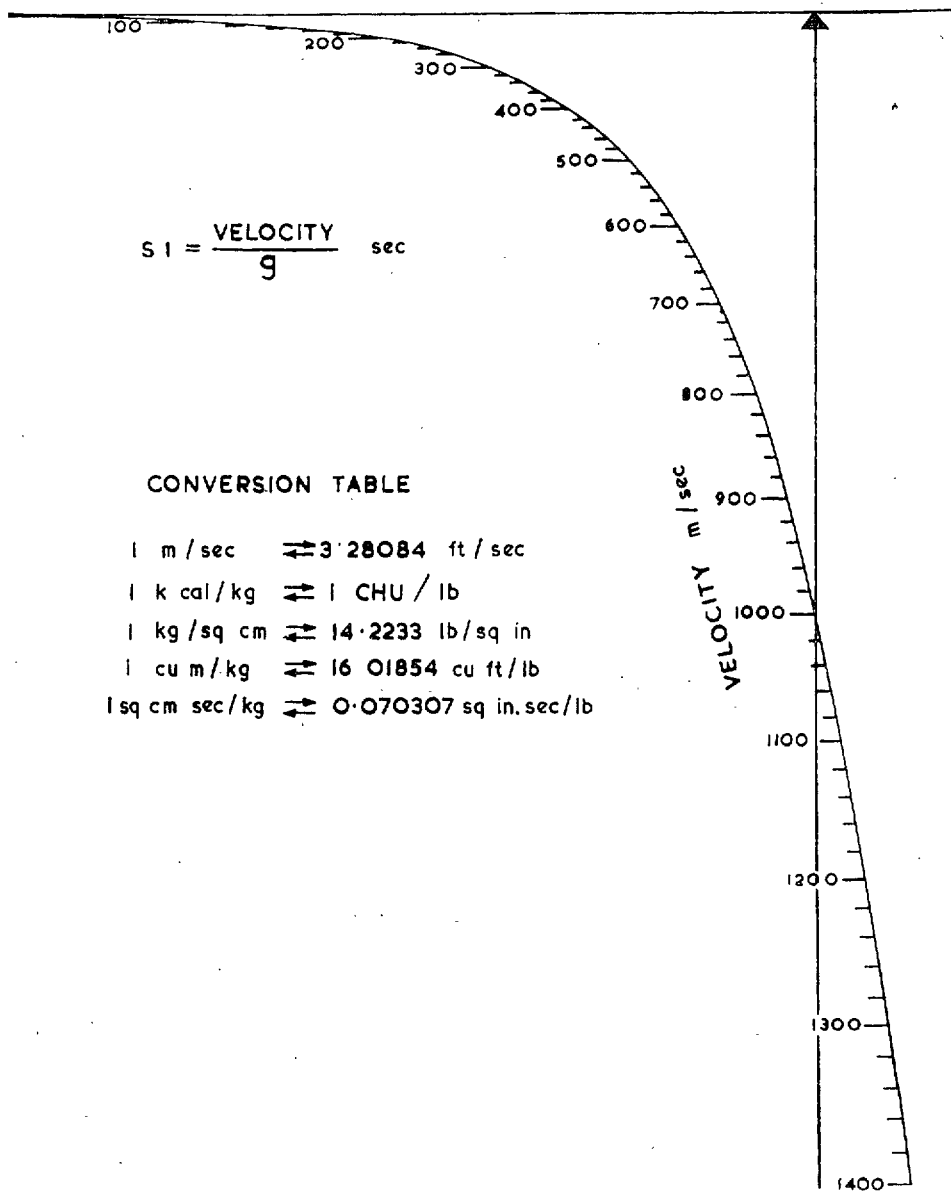


FIG. 4

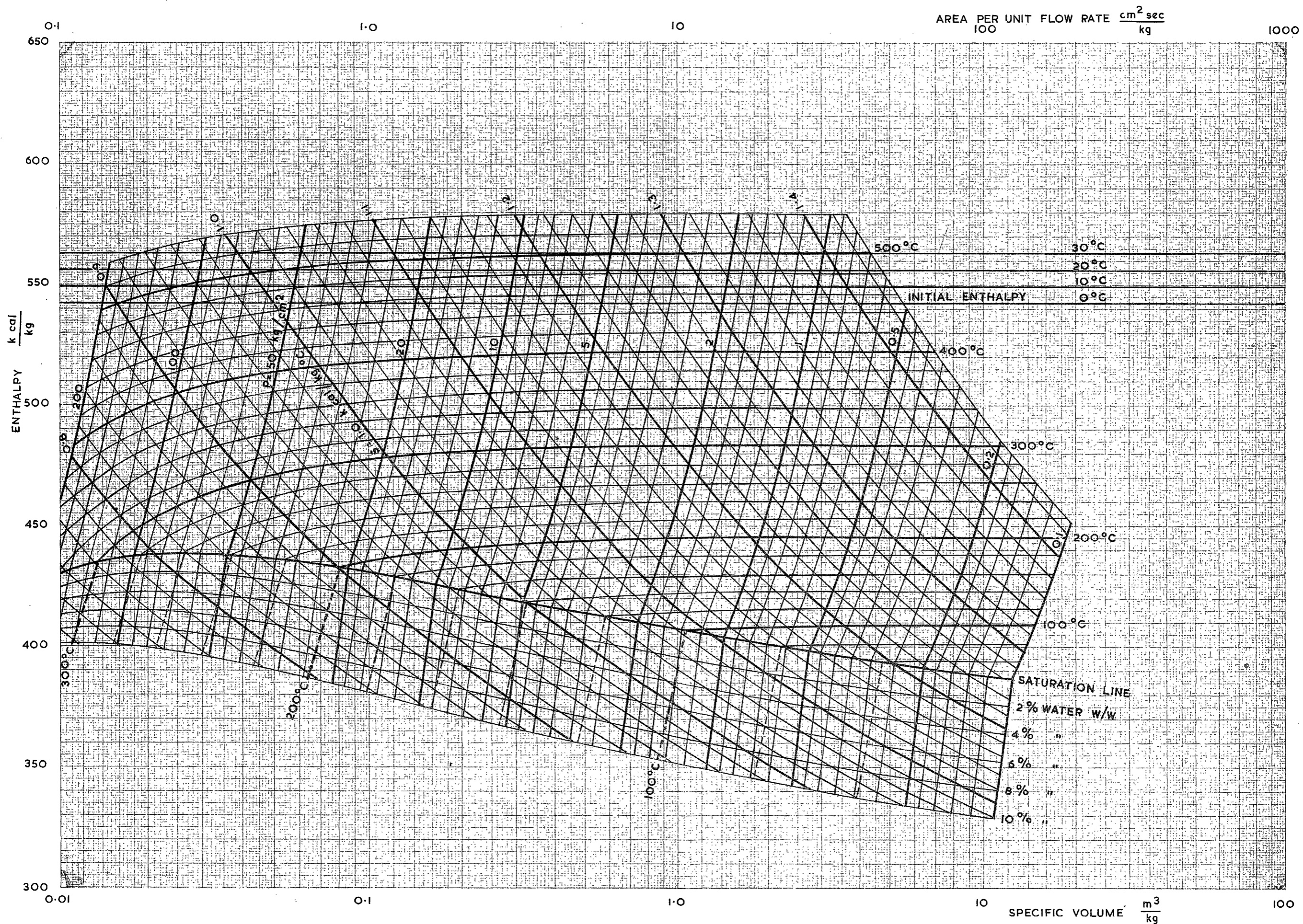


FIG. 1. Enthalpy—log specific volume
($I-\log v$) chart for the decomposition products of 80 per cent. H.T.P.

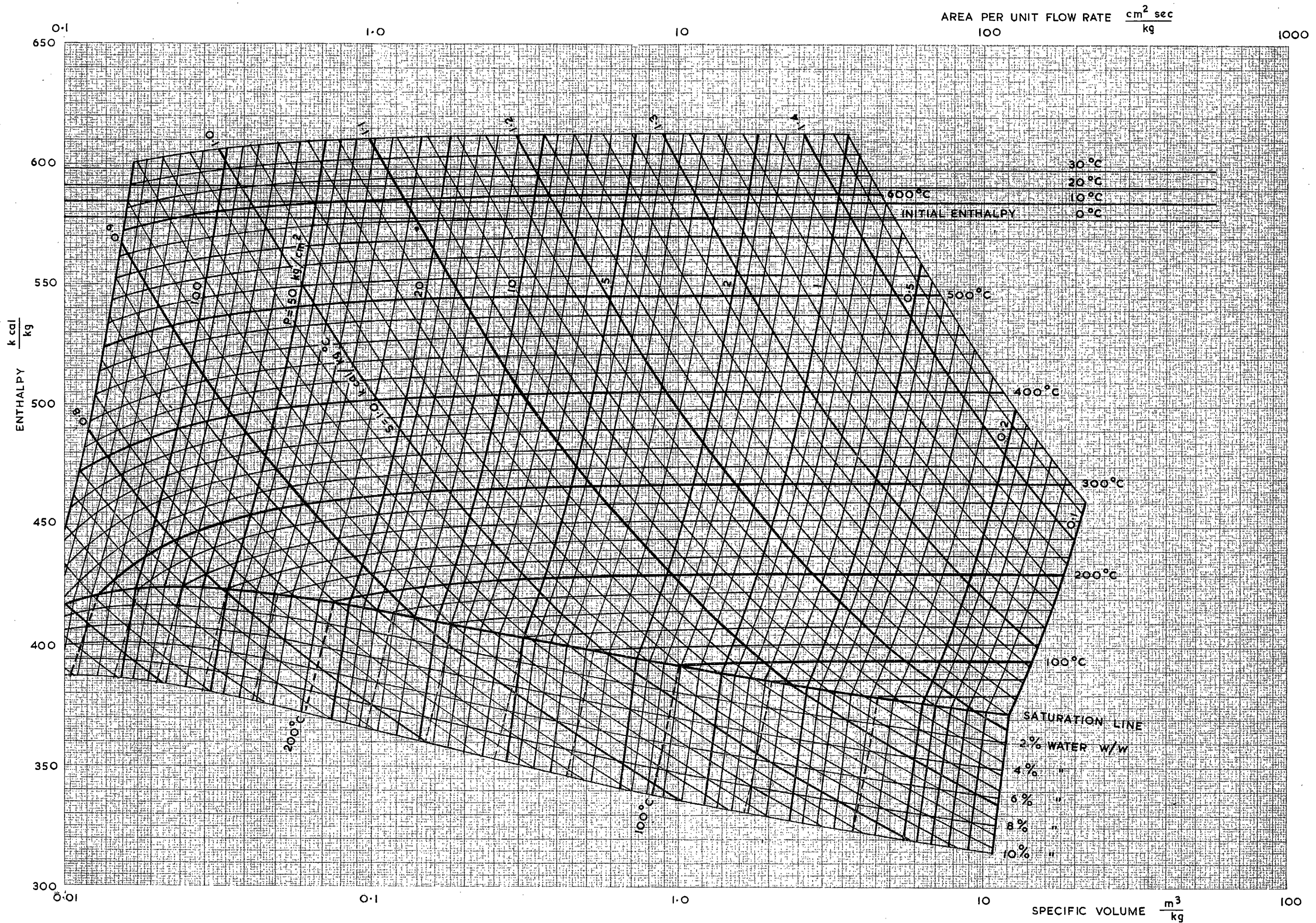


FIG. 2. Enthalpy—log specific volume
(1-log v) chart for the decomposition products of 85 per cent. H.T.P.

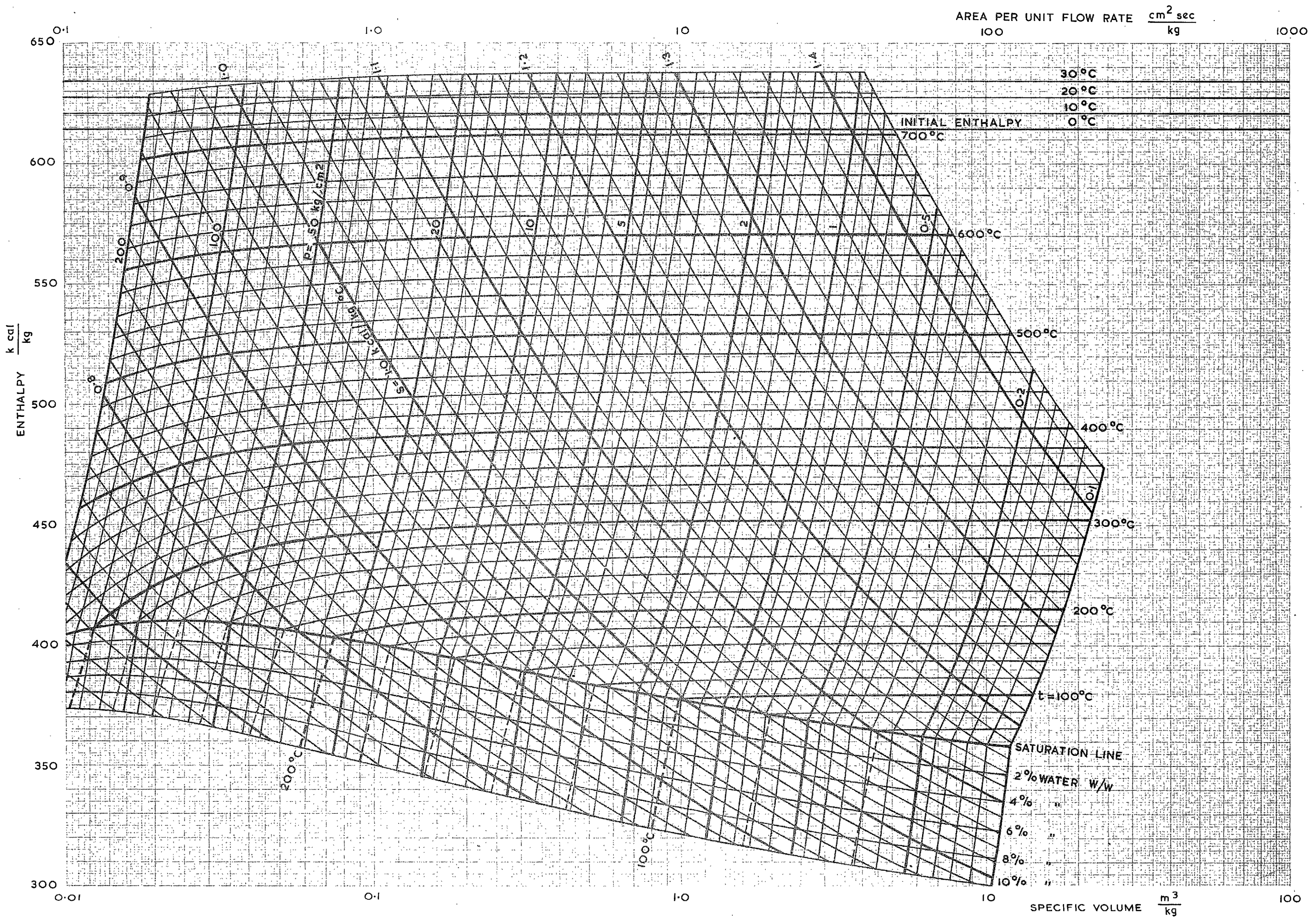
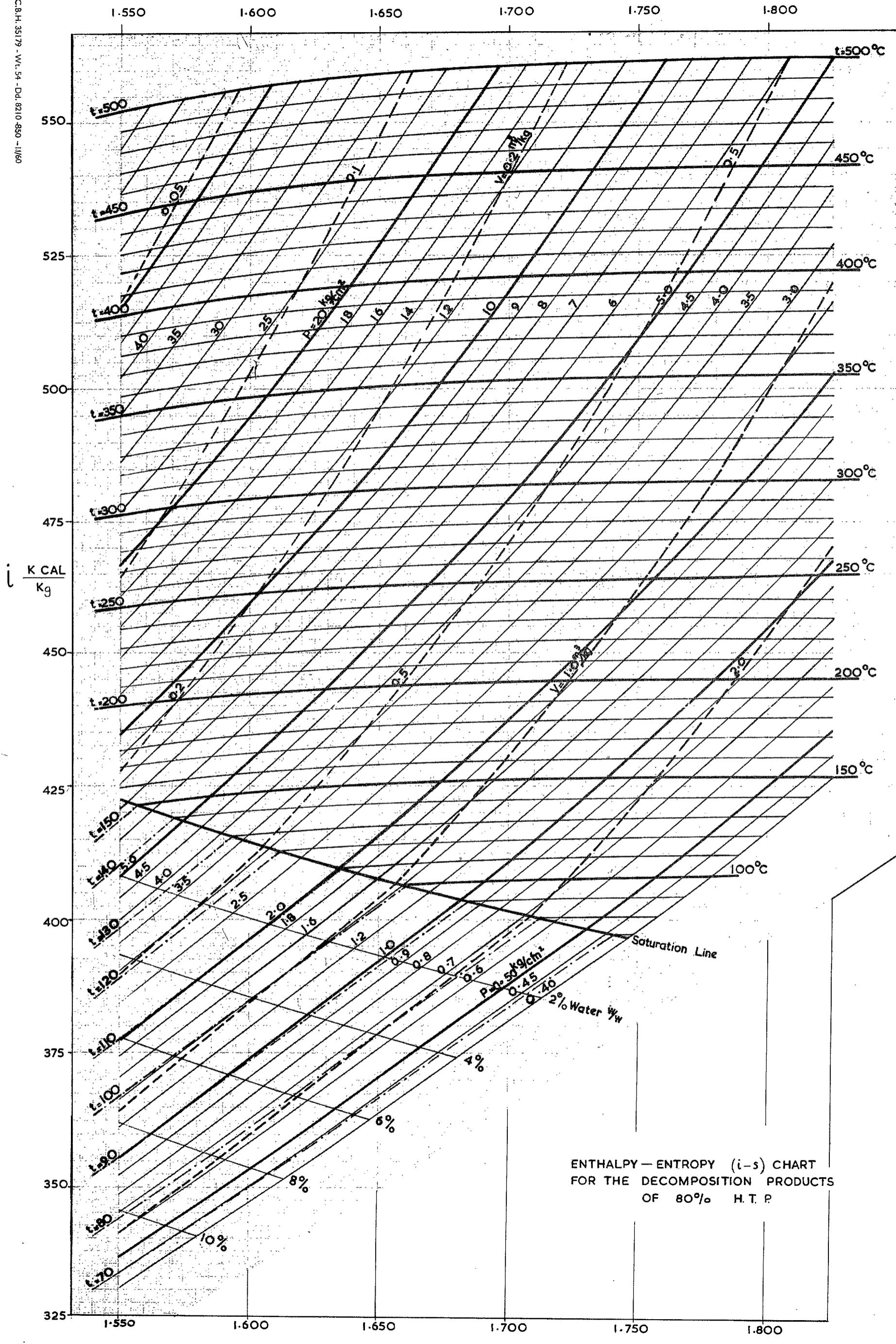


FIG. 3. Enthalpy—log specific volume ($h-\log v$) chart for the decomposition products of 90 per cent. H.T.P.



ENTHALPY - ENTROPY (i-s) CHART FOR THE DECOMPOSITION PRODUCTS OF 80% H.T.P.

FIG.5. ENTHALPY - ENTROPY (i-s) CHART

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