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Enthalpy Charts: For Dissociating Gas
Mixtures in the Temperature Range
600 deg to 4000 deg K

By

H. REICHERT, Dr. Ing.

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Enthalpy Charts: For Dissociating Gas Mixtures in the Temperature Range 600 deg to 4000 deg K

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H. REICHERT, Dr. Ing.

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Summary.—Enthalpy charts have been constructed to facilitate dealing with the thermodynamic problems of combustion and flow of dissociating gases within the temperature range of 600 deg to 4,000 deg K.

By means of a quantity called 'reaction enthalpy' (which is defined in this note), it is possible without previous knowledge of the composition of the mixture of gases to work out dissociation processes occurring at equilibrium. Also, if required, the composition of the mixture can be obtained from the charts. The charts are confined to the C,H,O-system, but their extension to include N in the system is quite simple. 28‡ charts with the total pressure p and the molar ratio n_O/n_H as parameters have been constructed in the first place for the four pressures $p = 0.1, 1.0, 10.0$ and 100.0 kg/sq cm, and for the seven molar ratios $n_O/n_H = 0, 0.2, 0.4, 0.6, 0.8, 1.0$ and ∞ . The four charts (reduced in scale) for the molar ratio $n_O/n_H = 0.4$ are attached as examples. Full scale charts will be supplied on request.

The present note describes work that had to be laid aside in 1947, and has now been resumed. The work done up to that date has been already described by Lutz.

1. *Introduction.*—The thermodynamic treatment of combustion and flow problems, which is of particular significance in contemporary rocket engineering, is made difficult by the immense amount of time required for exact calculation. Realizing that the knowledge of the mixture composition is an important basis for all thermodynamic calculations, Lutz¹ has put forward details of a method by which the composition of a mixture of dissociating gases can be estimated relatively quickly. For engineering purposes, however, it is often desirable to avoid estimating the gas composition and to be able to work directly with state diagrams, such as the Mollier diagram. Enthalpy-entropy diagrams for dissociating gases, however, can only be constructed for one specified reacting mixture, and hence cannot be used to represent general conditions.

The accompanying enthalpy charts have been constructed on the basis of the reaction enthalpy as defined by Lutz, and with the use of a reasonable number of charts, they facilitate the treatment of thermodynamic problems of combustion reactions over a technically useful range of temperatures of up to 4,000 deg K in a simple and straightforward manner.

First a general indication of the Lutz system of reaction thermodynamics will be given, followed by the development of data for the construction of the charts; finally the method of use is described. Four tables are given to show the thermal data and the values of the equilibrium constants, which have been summarized from the work published by Lutz² up to 1947. The appendix consists of a sample set of enthalpy charts.

†R.A.E. Tech. Note R.P.D. 35, received 29th January, 1954.

‡Only twenty charts were completed finally: for the four specified pressures $p = 0.1, 1.0, 10.0$ and 100.0 kg/sq cm, and for the five molar ratios $n_O/n_H = 0, 0.2, 0.4, 0.6$ and 0.8 . This range will be found to cover most requirements.

2. *Thermodynamic Relationships.*—2.1. *The Equation of State.*—The dissociating gases chiefly of interest in engineering (O_2 , H_2 , H_2O , CO , CO_2 , N_2) are, in the temperature range under consideration, sufficiently removed from their critical points or the liquid state for the state equation of a perfect gas to be assumed valid for an individual gas component i ; that is:

$$p_i v_i = R_i T, \quad \dots \dots \dots \quad (1)$$

or
$$p_i V = G_i R_i T \quad \dots \dots \dots \quad (1a)$$

in which V is the total volume of the mixture, and G_i the partial weight of the individual gas component i .

The total pressure p of the mixture is the sum of the partial pressures:

$$p = \Sigma p_i \quad \dots \dots \dots \quad (2)$$

and the gas constant³ of an individual gas component is:

$$R_i = \frac{R}{M_i} = \frac{1.98718}{M_i} \text{ cal/g}^\circ\text{K} \quad \dots \dots \dots \quad (3)$$

where M_i = molecular weight;

hence
$$p_i V = RT \frac{G_i}{M_i} \quad \dots \dots \dots \quad (1b)$$

or
$$p_i M_i V = RT G_i,$$

that is, for the entire mixture,

$$V \Sigma p_i M_i = RT \Sigma G_i = RTG,$$

or
$$v \Sigma p_i M_i = RT. \quad \dots \dots \dots \quad (4)$$

2.2. *Definition of Reaction Enthalpy.*—The first law of thermodynamics for 1 kg of the mixture can be written in terms of the enthalpy i as:

$$dq = d \Sigma g_i i - v dp, \quad \dots \dots \dots \quad (5)$$

where g_i is the proportion by weight of an individual gas, and $\Sigma g_i = 1$.

Then from equation (1b):

$$g_i = \frac{G_i}{G} = \frac{p_i M_i}{\Sigma p_i M_i}, \quad \dots \dots \dots \quad (6)$$

and it follows from equations (4) and (5) that:

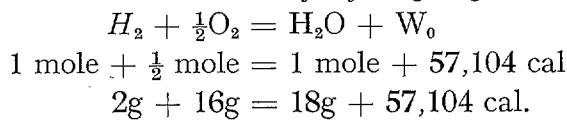
$$dq' = d \frac{\Sigma p_i I_i}{\Sigma p_i M_i} - \frac{RT}{\Sigma p_i M_i} dp, \quad \dots \dots \dots \quad (5a)$$

where I_i is the molar enthalpy.

This form of the first law allows the changes of state of mixtures of dissociating gases to be dealt with, if the individual partial pressures p_i are known.

The equation (5a) is, however, not in a suitable form, as in general a change of internal heat energy is associated with any change of state, so that dq' indicates the sum of the internal energy change on dissociation or recombination and of the external heat change. However, by using a suitable definition of enthalpy the separation of internal and external energy can be effected quite simply.

We will take the oxy-hydrogen gas reaction as an example:



If we consider 1 mole H_2 and $\frac{1}{2}$ mole O_2 to be mixed at absolute zero and the reaction to go to completion, then 57,104 cal are released; the heat content of the mole of H_2O formed and cooled again to 0 deg K is 57,104 cal less than the heat content of the original mixture. If the enthalpies of the original gases H_2 and O_2 are chosen arbitrarily to be zero at 0 deg K, 1 mole of H_2O relative to the reaction has a 'reaction enthalpy' at 0 deg K of $-57,104$ cal. As technical problems are always only concerned with differences of enthalpies and never absolute enthalpies the zero of enthalpy can be chosen at will, and not necessarily at 0 deg K. (In steam tables, for example, the zero of enthalpy for water is at 0 deg C = 273.16 deg K.)

It therefore seems advantageous to standardize the 'reaction enthalpy' system to correspond with the normal definition of the enthalpy of formation as follows:

At 25 deg C = 298.16 deg K (and 1 Atm = 1.033227 kg/sq cm) the reaction enthalpies of elements in their standard states (that is O_2 , H_2 , N_2 gaseous, C solid as graphite) will be assigned zero values, so that at standard temperature the reaction enthalpy is equal to the enthalpy of formation.

Therefore the enthalpy of reaction is defined thus:

The reaction enthalpy of a mixture at T deg K indicates the difference between the enthalpy of the mixture at T deg K and the enthalpy of the original elements in their standard state at 298.16 deg K.

Or alternatively:

The reaction enthalpy gives the quantity of heat that must be added to the original elements to bring them from their normal state at 298.16 deg K to their state at T deg K after reaction of the mixture.

Table 1 shows the absolute enthalpies of the most important technical gases² (including solid carbon and gaseous carbon), and the energy changes of the corresponding reactions at absolute zero² are shown below:

Energy change in cal at absolute zero and at 298.16 deg K at 1 Atm

Reaction	0 deg K	298.16 deg K
C (graphite) + $O_2 \rightleftharpoons CO_2$	-93,969†	-94,052
C (graphite) + $\frac{1}{2}O_2 \rightleftharpoons CO$	-27,202†	-26,416
$CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$	-66,767	-67,636
C (graphite) $\rightleftharpoons C$ (diamond)	+577†	+453
$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$ (gas)	-57,104†	-57,798
$\frac{1}{2}H_2 + OH \rightleftharpoons H_2O$ (gas)	-66,900‡	-67,653
$\frac{1}{2}H_2 \rightleftharpoons H$	+51,240††	+51,709
$\frac{1}{2}O_2 \rightleftharpoons O$	+58,530‡‡	+59,103
$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftharpoons NO$	+21,500‡‡	+21,622
H_2O (liquid) $\rightleftharpoons H_2O$ (gas)		+10,520†
C (graphite) $\rightleftharpoons C$ (gas)	+125,000§	+126,229
$2C$ (gas) $\rightleftharpoons C_2$ (gas)	-83,000§	-83,922

†NBS/RP 1634. ‡Dwyer. J. Chem. Phys. 12. p. 351. 1944. ††Beutler, for 3/4 ortho—and 1/4 para— H_2 .

‡‡J. D'Ans and E. Lax. Taschenbuch fuer Chemiker & Physiker. Berlin, 1943.

§ Information supplied by Prof. Eucken, Göttingen.

For the example of the oxy-hydrogen gas reaction, as already stated :

$$W_0 = 57,104 \text{ cal,}$$

and the following enthalpy values for 298·16 deg K are extracted from Table 1 :

$$I_{\text{H}_2} = 2,024 \text{ cal}$$

$$I_{\text{O}_2} = 2,070 \text{ cal}$$

$$I_{\text{H}_2\text{O}} = 2,365 \text{ cal.}$$

If the reaction enthalpies (indicated by an asterisk) are standardized in accordance with the definition given above, we get for the elements O₂ and H₂ the following values :

$$\left. \begin{array}{l} I_{\text{H}_2}^* = 0 \text{ cal} \\ I_{\text{O}_2}^* = 0 \text{ cal} \end{array} \right\} \text{ at } 298 \cdot 16 \text{ deg K}$$

$$\left. \begin{array}{l} I_{\text{H}_2}^* = - 2,024 \text{ cal} \\ I_{\text{O}_2}^* = - 2,070 \text{ cal} \end{array} \right\} \text{ at } 0 \text{ deg K}$$

and for $I_{\text{H}_2\text{O}}^*$ at 0 deg K we have :

$$I_{\text{H}_2\text{O}}^* = - 57,104 - 2,024 - \frac{1}{2}(2,070) = - 60,163 \text{ cal}$$

and at 298·16 deg K :

$$I_{\text{H}_2\text{O}}^* = - 60,163 + 2,365 = - 57,798 \text{ cal.}$$

This value also indicates the enthalpy of formation of gaseous H₂O.

Table 2 shows the values obtained in this way for the reaction enthalpies I^* up to 4,000 deg K. For example it can be seen that for CO the reaction enthalpy changes its sign between 3,400 deg K and 3,500 deg K, that is, it passes through zero. If we consider the reaction of 1 mole C (graphite) with $\frac{1}{2}$ mole O₂ at 25 deg C at constant pressure, a temperature between 3,400 deg K and 3,500 deg K (3,454 deg K to be accurate) is developed, when there is complete conversion to CO alone. Combustion temperatures, therefore, can be estimated quite simply by means of reaction enthalpies.

The advantage of the particular standardization chosen now becomes clear. As the formation enthalpies of technically important substances are known and in consequence their reaction enthalpies, all thermodynamic calculations can be carried out by means of a clear and straight forward method.

If the reaction enthalpy I^* cal/mole or i^* cal/g is used the first law of thermodynamics takes the usual form :

$$dq = di^* - v dp \text{ cal/g,} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (5b)$$

where
$$i^* = \frac{\sum p_i I_i^*}{\sum p_i M_i} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (7)$$

$$v = \frac{RT}{\sum p_i M_i}, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (4a)$$

and p_i indicates the partial pressure of an individual component of the mixture, M_i the molecular weight, v the specific volume in cu m/kg and R the universal gas constant. If we know the partial pressure p_i of the mixture, all the state values can be calculated very easily by means of equations (5b), (7) and (4a) and the enthalpy values I^* of Table 2. It is, however, important to remember that dq in equation (5b) means only the *external* heat supplied to the system, as in the usual method of stating the first law of thermodynamics for individual gases, and that the *internal* heat changes occurring during dissociation or recombination are indicated by i^* .

This result has more than a formal significance ; it means that henceforth all changes of state can be followed by a well known and elementary method and that errors due to the difference between calorific value and chemical energy are obviated, and what is most important isentropic lines can be represented simply.

2.3. *Reaction Equilibria.*—If we introduce the entropy s in equation (5b), we have for a reversible change of state :

$$T ds = di^* - v dp \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (8)$$

and for reactions at constant temperature and pressure we get :

$$di^* - T ds = 0$$

$$\text{or} \quad d(i^* - Ts) = 0, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (9)$$

where s is the absolute entropy which can be split up as follows :

$$s = s^0 - \frac{R}{M} \ln \frac{p}{p_0}, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (10)$$

where the temperature dependent portion at p_0 is s^0 and the pressure dependent portion is $(R/M) \ln (p/p_0)$. The mole-entropies S^0 , which for convenience in technical calculations refer to 1 at = 1 kg/sq cm (*not* 1 Atm), are shown in Table 3.

If n_i = number of moles of component i of the mixture then :

$$i^* = \frac{\sum n_i I_i^*}{\sum n_i M_i} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (11)$$

$$\text{and} \quad s = \frac{\sum n_i S_i}{\sum n_i M_i}, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (12)$$

and it follows from equations (9) and (10) that :

$$\Delta \Sigma R \ln \left(\frac{p_i}{p_0} \right)^{n_i} = \Delta \Sigma n_i \left(S_i^0 - \frac{I_i^*}{T} \right), \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (13)$$

where p_i/p_0 is the partial pressure p_i of component i measured in units of the reference pressure p_0 related to S_0 and, therefore, expressed in *at* units ; p_i/p_0 can then be replaced by p_i (*at*), although the equilibrium constants from the left side of equation (13) are no longer dimensionless as required in a logarithmic treatment.

In the oxy-hydrogen gas reaction 1 mole H_2 and $\frac{1}{2}$ mole O_2 are replaced by 1 mole H_2O ; hence from equation (13) it follows that :

$$R \ln \frac{p_{H_2O}}{p_{H_2} \sqrt{p_{O_2}}} = R \ln K_{H_2O} = \left(S^0 - \frac{I^*}{T} \right)_{H_2O} - \left(S^0 - \frac{I^*}{T} \right)_{H_2} - \frac{1}{2} \left(S^0 - \frac{I^*}{T} \right)_{O_2} \quad \dots \quad (13a)$$

From Tables 2 and 3 we obtain for 2,000 deg K :

$$\left(S_0 - \frac{I^*}{T} \right)_{H_2O} = 63.325 + \frac{40,403}{2,000} = 83.527$$

$$\left(S_0 - \frac{I^*}{T} \right)_{H_2} = 45.070 - \frac{12,648}{2,000} = 38.746$$

$$\left(S_0 - \frac{I^*}{T} \right)_{O_2} = 64.277 - \frac{14,140}{2,000} = 57.202,$$

and hence :

$$R \ln \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} \sqrt{p_{\text{O}_2}}} = 83.527 - 38.746 - \frac{1}{2}(57.502) = 16.180.$$

Converting to base 10 logarithms we get :

$$\log \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} \sqrt{p_{\text{O}_2}}} = \log K_{\text{H}_2\text{O}} = \frac{16.180}{2.302585 \times 1.9872} = 3.5361$$

$$K_{\text{H}_2\text{O}}^{2000^\circ} = 0.3436 \times 10^4.$$

The equilibrium constants K from equations (13) and (13a) have been calculated and are shown in Table 4 in the form :

$$K = \frac{p_{\text{gas}}}{\prod (p_{\text{element}})^{n_i}} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (14)$$

(The numerator refers to gas component produced, and the denominator to the reacting elements).

Thus

$$\left. \begin{aligned} K_{\text{H}_2\text{O}} &= \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} \sqrt{p_{\text{O}_2}}} \\ K_{\text{OH}} &= \frac{p_{\text{OH}}}{\sqrt{p_{\text{H}_2}} \sqrt{p_{\text{O}_2}}} \\ K_{\text{O}} &= \frac{p_{\text{O}}}{\sqrt{p_{\text{O}_2}}} \\ K_{\text{H}} &= \frac{p_{\text{H}}}{\sqrt{p_{\text{H}_2}}} \\ K_{\text{NO}} &= \frac{p_{\text{NO}}}{\sqrt{p_{\text{N}_2}} \sqrt{p_{\text{O}_2}}} \end{aligned} \right\} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \quad (15)$$

In heterogeneous reactions, as for instance $\text{C (graphite)} + \text{O}_2 = \text{CO}_2$, it is clear from expression (13) that the solid carbon, C, appears on the right-hand side, but makes no contribution to the gas-pressure term on the left-hand side.

Therefore

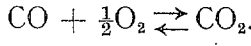
$$\left. \begin{aligned} K_{\text{CO}_2} &= \frac{p_{\text{CO}_2}}{p_{\text{O}_2}} \\ K_{\text{CO}} &= \frac{p_{\text{CO}}}{\sqrt{p_{\text{O}_2}}} \end{aligned} \right\} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \quad (15a)$$

and

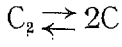
If there is no carbon, C, present in the solid state the two constants (15a) must be replaced by :

$$K_{\text{CO}_2}^{\text{CO}} = \frac{p_{\text{CO}_2}}{p_{\text{CO}} \sqrt{p_{\text{O}_2}}} = \frac{K_{\text{CO}_2}}{K_{\text{CO}}}, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (15b)$$

corresponding to the reaction :



For gaseous carbon two further equilibrium constants are taken into account ; for the reaction :



In the choice of the method of presentation particular stress has been laid on the attempt to secure the greatest possible accuracy of interpolation with a relatively small number of graphs. To this end the total pressure p and the ratio $n_{\text{C}}/n_{\text{H}}$ have been chosen as parameters and the reaction enthalpy i^* has been plotted against a 'reaction ratio'. The oxygen ratio $n_{\text{O}}/n_{\text{H}}$ is not a suitable parameter for this method of presentation, as the carbon component is not taken into account, and hence difficulties occur with mixtures of low hydrogen content. The oxygen ratio can, however, be standardized quite simply by defining a reaction ratio Γ in a similar way to a mixture ratio, such that when $\Gamma = 0$ there is only fuel, when $\Gamma = 1$ there is only oxygen and when $\Gamma = 0.5$ the mixture is stoichiometric. From this definition we have :

$$\Gamma = \frac{n_{\text{O}}}{2n_{\text{C}} + \frac{1}{2}n_{\text{H}} + n_{\text{O}}} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (21)$$

The following relation holds between Γ and the usual oxygen ratio λ_0 :

$$\Gamma = \frac{\lambda_0}{1 + \lambda_0}$$

The Γ presentation has the advantage of showing a numerical symmetry for 'weak' and 'rich' mixtures, which is desirable in any graphical presentation, whereas in the λ_0 presentation the fuel excess region is compressed from 0 to 1, and the less important oxygen excess region occupies the range from 1 to ∞ .

Fig. 1 shows schematically the construction of an enthalpy chart ; the abscissa represents Γ and the ordinate the reaction enthalpies i^* for different temperatures ; the parameters are the total pressure p and the ratio $n_{\text{C}}/n_{\text{H}}$. Lines of constant entropy and lines of constant molecular weights are also shown on the chart. As a preliminary measure 28 graphs† have been prepared for 4 values of the total pressures, $p = 0.1, 1.0, 10$ and 100 kg/sq cm and for the 7 values $n_{\text{C}}/n_{\text{H}} = 0, 0.2, 0.4, 0.6, 0.8, 1.0$ and ∞ over the temperature range 600 deg K to 4,000 deg K. The temperature lines have been entered at intervals of 50 deg, 100 deg or 200 deg dependent on good pictorial representation. As an example 4 charts for the ratio $n_{\text{C}}/n_{\text{H}} = 0.4$ and the 4 total pressures $p = 0.1, 1.0, 10$ and 100 kg/sq cm are included in the appendix. Curves for the three key values p_{H_2} , p_{O_2} and n_{O} for different temperatures are shown in the lower part of each chart and from these the gas composition can be determined if required. This will be discussed in more detail in a later section.

3.2. *Fundamentals for Calculating Individual Points on a Chart.*—The method of construction of the charts is best explained by indicating how to calculate individual points. For each point the equilibrium mixture composition for a given temperature must be first calculated. Equations (15) to (15d) for the equilibrium constants are used for this purpose as well as relations (16) to (21). For one individual chart, p and $n_{\text{C}}/n_{\text{H}}$ are assumed. If values of p_{H_2} or p_{O_2} are selected, the remaining partial pressures and finally the value of Γ can be calculated. Whether it is more advantageous to begin with a given value of p_{H_2} or of p_{O_2} depends in which Γ -section points are desired. Basically the Γ -range can be divided as shown in Fig. 1 into three sections: excess oxygen section, $\Gamma > 0.5$ to 1, fuel excess section up to the solid carbon boundary $\Gamma < 0.5$, and a section with solid carbon from the solid boundary to $\Gamma = 0$. Fig 2 shows schematically the basic change of p_{H_2} and p_{O_2} relative to Γ and it can be seen that for calculating points in section $\Gamma > 0.5$ it is better to start with p_{O_2} and in the $\Gamma < 0.5$ section with p_{H_2} . Finally by means of the values for p_{C}^{v} and $p_{\text{C}_2}^{\text{v}}$ (Table 4) it can be determined whether p_{C} and p_{C_2} can be neglected. The calculations then proceed as follows :

† See footnote to Summary (page 1).

(a) p_C^V negligibly small ; outside solid carbon boundary.

We have

$$n_C = p_{CO_2} + p_{CO} \quad \dots \quad (16a)$$

and from equation (20) :

$$\begin{aligned} p &= n_C + n_H - p_{H_2O} - p_{H_2} + p_{O_2} + p_O \\ &= (1 + 2n_C/n_H)(p_{H_2O} + p_{H_2}) + (1 + n_C/n_H)(p_{OH} + p_H) + p_{O_2} + p_O \end{aligned}$$

or

$$\begin{aligned} p &= (1 + 2n_C/n_H) \{K_{H_2O} p_{H_2} \sqrt{(p_{O_2})} + p_{H_2}\} \\ &\quad + (1 + n_C/n_H) \{K_{OH} \sqrt{(p_{H_2})} \sqrt{(p_{O_2})} + K_H \sqrt{(p_{H_2})}\} + p_{O_2} + K_O \sqrt{(p_{O_2})}. \end{aligned} \quad (22)$$

Rearranging the terms we obtain for p_{O_2} :

$$\begin{aligned} p_{O_2} + \sqrt{(p_{O_2})} [K_O + (1 + n_C/n_H)K_{OH} \sqrt{(p_{H_2})} + (1 + 2n_C/n_H)K_{H_2O} p_{H_2}] \\ = p - (1 + n_C/n_H)K_H \sqrt{(p_{H_2})} - (1 + 2n_C/n_H)p_{H_2}, \end{aligned}$$

which can now be expressed in the form :

$$p_{O_2} + 2a \sqrt{(p_{O_2})} = b \quad \dots \quad (23)$$

where

$$2a = K_O + (1 + n_C/n_H) K_{OH} \sqrt{(p_{H_2})} + (1 + 2n_C/n_H)K_{H_2O} p_{H_2}$$

and

$$b = p - (1 + n_C/n_H)K_H \sqrt{(p_{H_2})} - (1 + 2n_C/n_H)p_{H_2}.$$

The solution is

$$\sqrt{(p_{O_2})} = \sqrt{(a^2 + b)} - a. \quad \dots \quad (24)$$

In a similar way arranging the term we obtain for p_{H_2} :

$$p_{H_2} + \sqrt{(p_{H_2})} \frac{(1 + n_C/n_H)(K_{OH} \times \sqrt{(p_{O_2})} + K_H)}{(1 + 2n_C/n_H)(K_{H_2O} \times \sqrt{(p_{O_2})} + 1)} = \frac{p - p_{O_2} - K_O \sqrt{(p_{O_2})}}{(1 + 2n_C/n_H)(K_{H_2O} \sqrt{(p_{O_2})} + 1)}$$

which can be expressed in the form :

$$p_{H_2} + 2a \sqrt{(p_{H_2})} = b \quad \dots \quad (23a)$$

with a corresponding solution. The values of p_{CO_2} and p_{CO} can be derived from equations (15b) and (16a).

(b) p_C^V negligibly small ; solid carbon boundary.—Equations (15a) are also valid in this case. Thus

$$\begin{aligned} p &= K_{CO_2} p_{O_2} + K_{CO} \sqrt{(p_{O_2})} + K_{H_2O} p_{H_2} \sqrt{(p_{O_2})} + p_{H_2} + K_{OH} \sqrt{(p_{H_2})} \sqrt{(p_{O_2})} \\ &\quad + K_H \sqrt{(p_{H_2})} + p_{O_2} + K_O \sqrt{(p_{O_2})}, \end{aligned}$$

that is :

$$p_{O_2} + \sqrt{(p_{O_2})} \frac{K_{CO} + K_{H_2O} p_{H_2} + K_{OH} \sqrt{(p_{H_2})} + K_O}{1 + K_{CO_2}} = \frac{p - p_{H_2} - K_H \sqrt{(p_{H_2})}}{1 + K_{CO_2}}$$

and can be expressed in the form $p_{O_2} + 2a \sqrt{(p_{O_2})} = b$, with a corresponding solution. At the solid carbon boundary n_C^L there is only one correct value for p_{O_2} or p_{H_2} for a given ratio n_C^L/n_H . We must assume a value for p_{H_2} and calculate p_{O_2} by means of the last equation to get n_C^L/n_H ; p_{H_2} must then be amended until n_C^L/n_H reaches the desired value.

(c) p_C^V negligibly small ; solid carbon region.—We have

$$n_C = (p_{CO_2} + p_{CO}) + n_C^S = n_C^L + n_C^S.$$

The values of p_{O_2} and p_{H_2} can be calculated as in para. (b), then the value n_C/n_H for the charts is :

$$\frac{n_C}{n_H} = \frac{n_C^L}{n_H} + \frac{n_C^S}{n_H}$$

(d) p_C and p_{C_2} not negligible ; gas region.—We have

$$n_C = p_{CO_2} + p_{CO} + p_C + p_{C_2}$$

Equation (22), therefore, becomes :

$$p + p_{C_2} = (1 + 2n_C/n_H)(K_{H_2O}p_{H_2} \sqrt{(p_{O_2}) + p_{H_2}}) + (1 + n_C/n_H)\{K_{OH} \sqrt{(p_{H_2})} \sqrt{(p_{O_2}) + K_H \sqrt{(p_{H_2})}\} + p_{O_2} + K_O \sqrt{(p_{O_2})}. \quad (25)$$

To obtain the solution, we first proceed as in para. (a) neglecting p_{C_2} , then calculate p_{C_2} by means of equations (15c) and (15d) ; using this value we recalculate equation (25) and repeat the process until the values of p_{C_2} agree. It should be noted that $p_C < p_C^V$ and $p_{C_2} < p_{C_2}^V$.

(e) *Sublimation boundary*.—At the sublimation boundary :

$$p_C = p_C^V \text{ and } p_{C_2} = p_{C_2}^V$$

and equations (15a) are also valid.

The solution is obtained as in para. (b) and it should also be noted that :

$$n_C^V = K_{CO_2}p_{O_2} + K_{CO} \sqrt{(p_{O_2}) + p_C^V + 2p_{C_2}^V}$$

or $n_C^V = n_C^L + p_C^V + 2p_{C_2}^V$,

that is $\frac{n_C^V}{n_H} = \frac{n_C^L}{n_H} + \frac{p_C^V + 2p_{C_2}^V}{n_H}$

(f) *Sublimation region*.—The solution is obtained as in para. (c) and it should be noted that :

$$\frac{n_C}{n_H} = \frac{n_C^V}{n_H} + \frac{n_C^S}{n_H}$$

(g) *Region in which the effects of dissociation can be neglected*.—Dissociation has practically no effect at temperatures below 1,400 deg K. By omitting the atomic partial pressures p_H , p_O , etc, the computation equations can be used for this region in a considerably simplified form.

(h) *Determination of the values of the state functions*.—After calculating the mixture compositions for individual points as described above, the desired values of the state functions, e.g., reaction enthalpy, molecular weight and entropy, can be calculated from the equations :

$$i^* = \frac{\sum p_i I_i^*}{\sum p_i M_i} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (7)$$

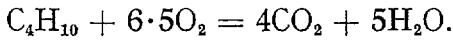
$$M = \frac{\sum p_i M_i}{\sum p_i} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (26)$$

$$s = \frac{\sum p_i S_i^0 - R \sum p_i \ln p_i}{\sum p_i M_i} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (10a)$$

The values used for I^* , M and S^0 are shown in Tables 2 and 3.

4. *Use of the Charts.*—4.1. *Determination of State of the Gas.*—The combustion of butane C_4H_{10} and oxygen will be considered as an example to illustrate the method of using the charts since the n_C/n_H ratio = 0.4 for this mixture is exactly that for which the attached charts are drawn and consequently no interpolation is required for n_C/n_H . For other problems the values of the state functions have to be interpolated from the charts by taking the values of n_C/n_H nearest to those required.

For the stoichiometric combustion of butane and oxygen we have :



If combustion takes place with a 20 per cent deficiency of oxygen, only 5.2 moles O_2 are available and therefore as $n_C/n_H = 0.4$

and
$$n_O/n_H = \frac{2 \times 5.2}{10} = 1.04$$

hence
$$\Gamma = \frac{n_O/n_H}{2n_C/n_H + n_O/n_H + \frac{1}{2}} = 0.4444.$$

For $\Gamma = 0.4444$ and the two temperatures 2,000 deg K and 3,000 deg K the following values can be read off the charts :

p	T	i^*	M	S
0.1	2000	-1522	25.0	2.85
	3000	+ 831	18.1	3.72
1.0	2000	-1518	25.0	2.67
	3000	- 416	22.2	3.09
10.0	2000	-1516	25.0	2.48
	3000	- 862	24.2	2.74
100.0	2000	-1516	25.0	2.30
	3000	- 992	24.8	2.51

The state functions for any desired pressure between 0.1 and 100 kg/sq cm can finally be estimated by graphical interpolation.

4.2. *Determination of Mixture Composition.*—By means of the i^* , Γ -charts it is possible to obtain the values of the state functions of mixtures of dissociating gases without any knowledge of the composition. To assist, however, in those cases where the gas composition is itself of interest, the three key values p_{H_2} , p_{O_2} and n_O can be read off the lower part of the charts. The remaining partial pressures can then be obtained from equations (15) to (15d).

From the key value n_O , if Γ is given one obtains :

$$n_H = \frac{n_O/\Gamma - n_O}{2n_C/n_H + \frac{1}{2}}$$

and
$$n_C = n_H \times n_C/n_H.$$

For the example which is being considered, *i.e.*, the combustion of butane and oxygen ($\Gamma = 0.4444$, $n_C/n_H = 0.4$) the following values for n_O and hence for n_H and n_C are obtained from the charts :

p	T	n_O	n_H	n_C	p_{H_2}	p_{O_2}
0.1	2000	0.1158	0.1115	0.0446	0.0083	$\rightarrow 0$
	3000	0.0840	0.0808	0.0323	0.0104	0.0055
1.0	2000	1.16	1.115	0.446	0.084	$\rightarrow 0$
	3000	1.03	0.992	0.397	0.089	0.033
10.0	2000	11.6	11.15	4.46	0.84	$\rightarrow 0$
	3000	11.18	10.75	4.30	0.72	0.09
100.0	2000	116.0	111.5	44.6	8.4	$\rightarrow 0$
	3000	114.8	110.4	44.2	6.7	$\rightarrow 0$

At points where p_{O_2} or $p_{H_2} \rightarrow 0$, we first estimate p_{H_2O} from the simplified relationship $n_H = 2p_{H_2O} + 2p_{H_2}$. The order of magnitude of p_{O_2} and p_{H_2} can then be determined from the equilibrium condition for H_2O .

4.3. *Use of the Charts for Mixtures Containing Nitrogen.*—The i^* , Γ -charts can be extended to cover mixtures containing nitrogen. Each point is valid for a given mixture of C, H and O, whose components are indicated as usual by n_C , n_H and n_O . For any point, therefore, the basic relations :

$$n_C = p_{CO_2} + p_{CO} \quad \dots \quad (16a)$$

$$n_H = 2p_{H_2O} + 2p_{H_2} + p_{OH} + p_H \quad \dots \quad (17)$$

$$n_O = 2p_{CO_2} + p_{CO} + p_{H_2O} + 2p_{O_2} + p_{OH} + p_O \quad \dots \quad (18)$$

and
$$p = \Sigma p_i \quad \dots \quad (20)$$

are exact.

If a N-component is added to this mixture, then n_C and n_H are unaffected, but n_O and p are changed as follows :

$$n_O^N = n_O + p_{NO} \quad \dots \quad (27)$$

$$p^N = p_{\text{chart}} + p_{N_2} + p_{NO} \quad \dots \quad (28)$$

In addition the following relations must be fulfilled :

$$n_N = 2p_{N_2} + p_{NO} \quad \dots \quad (19)$$

and
$$K_{NO} = \frac{p_{NO}}{\sqrt{(p_{N_2})} \sqrt{(p_{O_2})}} \quad \dots \quad (15)$$

As p_{NO} is usually small compared with p_{N_2} we obtain from equation (19) the following value for p_{N_2} as a first approximation :

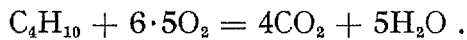
$$p_{N_2} = \frac{1}{2} n_O \frac{n_N}{n_O},$$

where the difference between n_O and n_O^N is neglected. The value of p_{NO} is then obtained from equation (15). If p_{NO} is not negligibly small, a smaller value of the reaction ratio Γ must be taken

4.4. *Reaction Temperatures.*—By definition the reaction enthalpy is the quantity of heat that must be given to the initial components before combustion to bring them to the reaction state of the mixture. If no heat is added from outside, then the enthalpy remains the same; the temperature of combustion is, therefore, characterized by the same reaction enthalpy as that of the propellants entering the combustion chamber.

It can be seen on the charts that the minimum of the reaction enthalpy deviates slightly from the stoichiometric point $F = 0.5$ as the temperature rises, *i.e.*, as the effect of dissociation becomes more pronounced. This is in agreement with the well known fact that without dissociation the highest reaction temperature is given by a stoichiometric mixture, whereas with dissociating mixtures the highest reaction temperature shifts away from the stoichiometric point. It has been assumed frequently in the past that mixtures with 10 to 20 per cent fuel excess are most favourable if dissociation takes place. A glance at all the available enthalpy charts shows that the processes are not uniform and are more complex than this. The high heat of dissociation of hydrogen shifts the most favourable point in the reverse direction, so that for mixtures with a high content of hydrogen the reaction conditions are more favourable when there is an excess of oxygen. Up to the present it has been hopeless to attempt a general view of these processes by dealing with individual cases. Hence the enthalpy charts afford a unique and comprehensive explanation of such problems. The calculation of mixture composition which often requires a day's work is now unnecessary, since the enthalpy of the mixture can be read off directly, and similarly the gas composition can be obtained if it is of interest.

The combustion of butane with oxygen will be used again as an example :



It is assumed that butane will be liquid and oxygen gaseous at 0 deg C when introduced into the reaction chamber. The initial enthalpies must first be calculated.

For the fuel :

$$I_{\text{O}_F}^* = H_u + n_{\text{C}}I_{\text{CO}_2}^* + \frac{1}{2}n_{\text{H}}I_{\text{H}_2\text{O}}^* , \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (32)$$

where n_{C} and n_{H} are molar ratios of the fuel, and H_u is the lower calorific value of the fuel. For butane :

$$n_{\text{C}} = 4, \quad n_{\text{H}} = 10$$

and $H_u = 634,120$ cal/mole⁵.

Hence the initial enthalpy at 0 deg C :

$$I_{\text{O}_F}^* = 634,120 - 4 \times 94,260 - 5 \times 57,999 = - 32,915 \text{ cal/mole}.$$

To this amount must be added the initial enthalpy (heat of formation) of the oxidant. Here the initial enthalpy of gaseous oxygen at 0 deg C is by definition the same as the reaction enthalpy.

The method of calculation is shown in the following table, which gives the calculations for combustion with 6 moles O₂ (fuel excess) and with 7 moles O₂ (oxygen excess) in addition to

those for the stoichiometric reaction :

Oxygen molecular ratio		+6.0	+6.5	+7.0	
Γ		+0.48	+0.5	+0.5185	
$I_{O_F}^*$		-32915	-32915	-32915	
$n_o \times I_{O_2}^*$		-1050	-1137.5	-1225	
I_o^*		-33965	-34052.5	-34140	
$\sum n_i M_i$		+250.08	+266.08	+282.08	
i_o^*		-135.8	-128.0	-121.0	
$T^\circ K$	p	0.1	+2809	+2803	+2796
		1.0	3090	3083	3075
		10.0	3411	3400	3386
		100.0	+3767	+3750	+3733

At the end of the table the reaction temperatures T , as read off the charts, are tabulated for $p = 0.1, 1.0, 10.0$ and 100.0 kg/sq cm.

4.5. *Exhaust Velocities.*—In jet or rocket propulsion the thrust produced is equal to the impulse of the exhausted combustion products, that is to the product of the mass of combustion products exhausted per second and multiplied by the exhaust velocity from the nozzle. Thus determination of exhaust velocity is one of the main thermodynamic problems. High reaction temperatures are not the only criterion for the best fuel mixture, as a high exhaust velocity from the nozzle is also of importance. The exhaust velocity depends mainly on combustion chamber temperature, but also on the thermal properties of the mixture and the combination processes during expansion.

For the theoretical exhaust velocity we have :

$$W_{th} = 91.5 \sqrt{(\Delta i_{ad}^*)} \text{m/sec.}$$

The adiabatic enthalpy difference Δi_{ad}^* can be determined by means of the i^* ; Γ -charts, since the isentropes, $s = \text{constant}$, have been drawn on the charts for this purpose. It would take only a short time to obtain the values of the thermodynamic functions from the enthalpy charts and draw a Mollier diagram for a special mixture. In this way it is possible to work out the equilibrium processes rapidly, whereas in the past we have assumed that the mixture composition remains constant during the expansion process, and have regarded it as being 'frozen'.

5. *Conclusions.*—The use of the accompanying enthalpy charts has been explained by means of a few examples, merely to give an indication of their possible applications without making the note too lengthy. Questions of the most suitable fuel mixtures or the choice of fuel mixtures, the effect of combustion-chamber pressure, etc., can also be dealt with quite simply. The new

charts throw a clear light for the first time on the solution of many dissociation problems. Finally it may be concluded that the construction of further charts for special pressures or special molar ratios n_C/n_H would be a worthwhile proposition.

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TABLE 1 — Absolute Enthalpies I cal/mole

T deg K	O ₂	H ₂	H ₂ O	N ₂	C (solid)		CO	CO ₂	NO	OH	H	O	C	C ₂
					(graphite)	(diamond)								
273·16	1895	1852	2164	1898	202	115	1899	2030	2019	1929	1357	1475	1357	1901
298·16	2070	2024	2365	2072	252	128	2073	2238	2193	2106	1481	1608	1481	2040
300	2083	2037	2380	2085	255	131	2085	2255	2207	2119	1490	1617	1490	2088
400	2792	2731	3190	2782	503	325	2784	3195	2920	2829	1987	2135	1987	2795
500	3524	3430	4020	3485	821	602	3490	4223	3643	3536	2484	2646	2484	3520
600	4279	4129	4873	4198	1198	950	4210	5322	4380	4241	2981	3152	2981	4267
700	5057	4832	5755	4925	1622	1355	4946	6481	5134	4948	3478	3655	3478	5035
800	5854	5537	6666	5669	2082	1804	5700	7689	5908	5661	3974	4157	3974	5823
900	6670	6248	7607	6428	2569	2284	6471	8940	6700	6380	4471	4658	4471	6627
1000	7497	6966	8580	7203	3075	2782	7257	10222	7508	7107	4968	5159	4968	7444
1100	8335	7692	9580	7992	3596	3289	8056	11536	8327	7844	5465	5658	5465	8271
1200	9184	8428	10613	8793	4130	3802	8868	12872	9157	8593	5962	6157	5962	9108
1300	10041	9173	11675	9605	4680		9690	14234	9995	9354	6458	6656	6458	9953
1400	10905	9929	12762	10425	5242		10521	15611	10841	10127	6955	7155	6955	10803
1500	11776	10694	13876	11254	5814		11359	17004	11693	10910	7452	7653	7452	11659
1600	12653	11470	15014	12090	6394		12203	18411	12551	11703	7949	8151	7949	12519
1700	13536	12256	16173	12933	6981		13054	19829	13415	12505	8446	8649	8446	13382
1800	14425	13052	17351	13783	7577		13910	21257	14283	13316	8942	9147	8942	14249
1900	15319	13858	18547	14639	8180		14771	22696	15155	14135	9439	9645	9439	15118
2000	16219	14672	19760	15499	8791		15636	24144	16030	14962	9936	10143	9936	15990
2100	17125	15493	20992	16362	9408		16505	25600	16908	15796	10433	10641	10433	16863
2200	18036	16322	22238	17228	10032		17377	27062	17790	16637	10929	11139	10929	17739
2300	18952	17158	23497	18096	10663		18251	28530	18674	17484	11426	11637	11426	18616
2400	19873	18001	24769	18966	11300		19128	30003	19561	18337	11923	12135	11923	19494
2500	20799	18851	26053	19839	11943		20007	31480	20450	19195	12420	12633	12420	20373
2600	21730	19707	27347	20715	12592		20889	32962	21340	20057	12917	13132	12917	21254
2700	22666	20569	28650	21593	13245		21773	34450	22232	20924	13413	13631	13413	22136
2800	23606	21436	29962	22474	13904		22659	35944	23126	21796	13910	14130	13910	23018
2900	24551	22308	31281	23358	14568		23546	37444	24022	22673	14407	14629	14407	23701
3000	25500	23186	32607	24245	15237		24434	38950	24918	23555	14904	15129	14904	24785
3100	26453	24068	33940	25133	15910		25324	40460	25816	24442	15401	15630	15401	25670
3200	27410	24954	35278	26022	16587		26215	41972	26716	25333	15897	16132	15897	26555
3300	28372	25845	36621	26912	17268		27108	43486	27618	26228	16394	16635	16394	27440
3400	29338	26739	37969	27803	17954		28003	45002	28521	27126	16891	17140	16891	28327
3500	30308	27637	39321	28695	18643		28900	46520	29425	28027	17388	17646	17388	29214
3600	31282	28538	40676	29589	19335		29798	48041	30331	28931	17885	18152	17885	30101
3700	32260	29442	42035	30485	20032		30697	49565	31238	29838	18381	18658	18381	30988
3800	33241	30348	43397	31382	20731		31596	51093	32146	30748	18878	19164	18878	31876
3900	34226	31257	44762	32280	21434		32495	52624	33056	31661	19375	19670	19375	32764
4000	35215	32168	46129	33178	22140		33395	54159	33967	32576	19872	20176	19872	33652

TABLE 2 — Reaction Enthalpies I^* cal/mole and Molecular Weights M g/mole

T deg K	O ₂	H ₂	H ₂ O	N ₂	CO	CO ₂	NO	OH	H	O	C (solid)		C ₁	C ₂
											(graphite)	(diamond)		
0	-2070	-2024	-60163	-2072	-28489	-96290	+19429	+7749	+50228	+57495	-252	+325	+124748	+166946
273·16	-175	-172	-57999	-174	-26590	-94260	21448	9678	51585	58970	-50	440	126105	168397
298·16	+0	+0	-57798	+0	-26416	-94052	21622	9855	51709	59103	+0	453	126229	168536
300	13	13	-57783	13	-26404	-94035	21636	9868	51718	59112	3	456	126238	168584
400	722	707	-56973	710	-25705	-93095	22349	10578	52215	59630	251	650	126735	169291
500	1454	1406	-56143	1413	-24999	-92067	23072	11285	52712	60141	569	927	127232	170016
600	2209	2105	-55290	2126	-24279	-90968	23809	11990	53209	60647	946	1275	127729	170763
700	2987	2808	-54408	2853	-23543	-89809	24563	12697	53706	61150	1370	1680	128226	171531
800	3784	3513	-53497	3597	-22789	-88601	25337	13410	54202	61652	1830	2129	128722	172319
900	4600	4224	-52556	4356	-22018	-87350	26129	14129	54699	62153	2317	2609	129219	173123
1000	5427	4942	-51583	5131	-21232	-86068	26937	14856	55196	62654	2823	3107	129716	173940
1100	6265	5668	-50583	5920	-20433	-84754	27756	15593	55693	63153	3344	3614	130213	174768
1200	7114	6404	-49550	6721	-19621	-83418	28586	16342	56190	63652	3878	4127	130710	175604
1300	7971	7149	-48488	7533	-18799	-82056	29424	17103	56686	64151	4428		131206	176449
1400	8835	7905	-47401	8353	-17968	-80679	30270	17876	57183	64650	4990		131703	177299
1500	9706	8670	-46287	9182	-17130	-79286	31122	18659	57680	65148	5562		132200	178155
1600	10583	9446	-45149	10018	-16286	-77879	31980	19452	58177	65646	6142		132697	179015
1700	11466	10232	-43990	10861	-15435	-76461	32844	20254	58674	66144	6729		133194	179878
1800	12355	11028	-42812	11711	-14579	-75033	33712	21065	59170	66642	7325		133690	180745
1900	13249	11834	-41616	12567	-13718	-73594	34584	21884	59667	67140	7928		134187	181614
2000	14149	12648	-40403	13427	-12853	-72146	35459	22711	60164	67638	8539		134684	182486
2100	15055	13469	-39171	14290	-11984	-70690	36337	23545	60661	68136	9156		135181	183359
2200	15966	14298	-37925	15156	-11112	-69228	37219	24386	61157	68634	9780		135677	184235
2300	16882	15134	-36666	16024	-10238	-67760	38103	25233	61654	69132	10411		136174	185112
2400	17803	15977	-35394	16894	-9361	-66287	38990	26086	62151	69630	11048		136671	185990
2500	18729	16827	-34110	17767	-8482	-64810	39879	26944	62648	70128	11691		137168	186869
2600	19660	17683	-32816	18643	-7600	-63328	40769	27806	63145	70627	12340		137665	187750
2700	20596	18545	-31513	19521	-6716	-61840	41661	28673	63641	71126	12993		138161	188632
2800	21536	19412	-30201	20402	-5830	-60346	42555	29545	64138	71625	13652		138658	189514
2900	22481	20284	-28882	21286	-4943	-58846	43451	30422	64635	72124	14316		139155	190397
3000	23430	21162	-27556	22173	-4055	-57340	44347	31304	65132	72624	14985		139652	191281
3100	24383	22044	-26223	23061	-3165	-55830	45245	32191	65629	73125	15658		140149	192166
3200	25340	22930	-24885	23950	-2274	-54318	46145	33082	66125	73627	16335		140645	193051
3300	26302	23821	-23542	24840	-1381	-52804	47047	33977	66622	74130	17016		141142	193936
3400	27268	24715	-22194	25731	-486	-51288	47950	34875	67119	74635	17702		141639	194823
3500	28238	25613	-20842	26623	+411	-49770	48854	35776	67616	75141	18391		142136	195710
3600	29212	26514	-19487	27517	1309	-48249	49760	36680	68113	75647	19083		142633	196597
3700	30190	27418	-18128	28413	2208	-46725	50667	37587	68609	76153	19780		143129	197484
3800	31171	28324	-16766	29310	3107	-45197	51575	38497	69106	76659	20479		143626	198372
3900	32156	29233	-15401	30208	4006	-43666	52485	39410	69603	77165	21182		144123	199260
4000	33145	30144	-14034	31106	4906	-42131	53396	40325	70100	77671	21888		144620	200148

TABLE 3 — Entropy Values S° cal/mole $^{\circ}\text{C}$ for 1 kg/cm²

T deg K	O ₂	H ₂	H ₂ O	N ₂	CO	CO ₂	NO	OH	H	O	C (solid)		C	C ₂
											(graphite)	(diamond)		
298.16	49.068	31.276	45.171	45.832	47.366	51.126	50.400	43.951	27.456	38.528	1.3609	0.5829	37.910	49.265
300	49.113	31.318	45.219	45.874	47.407	51.181	50.542	43.994	27.486	38.562	1.3737	0.5918	37.940	49.577
400	51.158	33.315	47.548	47.883	49.417	53.880	52.496	46.041	28.915	40.051	2.081	1.14	39.369	51.488
500	52.788	34.874	49.399	49.450	50.992	56.178	54.109	47.616	30.024	41.191	2.788	1.76	40.478	53.225
600	54.165	36.149	50.955	50.750	52.303	58.174	55.454	48.902	30.929	42.115	3.474	2.39	41.383	54.587
700	55.361	37.232	52.313	51.870	53.438	59.960	56.617	49.989	31.694	42.891	4.127	3.01	42.148	55.771
800	56.427	38.173	53.529	52.862	54.444	61.572	57.651	50.939	32.357	43.561	4.740	3.61	42.811	56.822
900	57.387	39.011	54.637	53.757	55.352	63.045	58.584	51.786	32.943	44.151	5.314	4.18	43.397	57.769
1000	58.259	39.769	55.663	54.574	56.181	64.396	59.433	52.552	33.466	44.677	5.846	4.70	43.920	58.630
1100	59.057	40.460	56.616	55.324	56.943	65.648	60.213	53.254	33.939	45.152	6.342	5.18	44.393	59.419
1220	59.795	41.100	57.514	56.020	57.651	66.811	60.934	53.906	34.371	45.586	6.807	5.63	44.825	60.147
1300	60.484	41.697	58.364	56.671	58.308	67.901	61.604	54.514	34.768	45.985	7.247		45.222	60.823
1400	61.126	42.255	59.170	57.280	58.925	68.922	62.232	55.087	35.136	46.355	7.663		45.590	61.453
1500	61.724	42.785	59.938	57.851	59.501	69.882	62.819	55.628	35.479	46.699	8.057		45.933	62.043
1600	62.289	43.285	60.673	58.391	60.064	70.788	63.373	56.140	35.800	47.020	8.431		46.254	62.598
1700	62.824	43.761	61.377	58.903	60.562	71.647	63.896	56.626	36.101	47.322	8.787		46.555	63.121
1800	63.332	44.216	62.052	59.389	61.052	72.463	64.392	57.089	36.385	47.607	9.1275		46.839	63.617
1900	63.815	44.652	62.700	59.852	61.518	73.241	64.864	57.531	36.654	47.876	9.4535		47.108	64.087
2000	64.277	45.070	63.325	60.293	61.961	73.985	65.313	57.954	36.909	48.131	9.7665		47.363	64.534
2100	64.719	45.470	63.927	60.714	62.384	74.695	65.741	58.361	37.151	48.374	10.068		47.605	64.960
2200	65.143	45.856	64.507	61.116	62.789	75.375	66.151	58.752	37.382	48.605	10.3585		47.836	65.367
2300	65.548	46.227	65.068	61.502	63.178	76.027	66.544	59.128	37.603	48.826	10.639		48.057	65.757
2400	65.939	46.586	65.610	61.872	63.551	76.654	66.922	59.491	37.814	49.038	10.9105		48.268	66.131
2500	66.315	46.933	66.135	62.228	63.910	77.256	67.285	59.841	38.017	49.242	11.173		48.471	66.490
2600	66.680	47.269	66.642	62.572	64.256	77.838	67.634	60.180	38.212	49.438	11.427		48.666	66.835
2700	67.034	47.595	67.134	62.904	64.590	78.400	67.971	60.508	38.400	49.626	11.6735		48.854	67.168
2800	67.377	47.911	67.611	63.224	64.912	78.944	68.296	60.825	38.581	49.808	11.913		49.035	67.489
2900	67.709	48.216	68.072	63.534	65.223	79.471	68.611	61.134	38.755	49.983	12.146		49.209	67.799
3000	68.033	48.513	68.521	63.835	65.524	79.982	68.915	61.434	38.923	50.152	12.373		49.377	68.099
3100	68.345	48.801	68.958	64.126	65.816	80.477	69.210	61.724	39.086	50.316	12.594		49.540	68.389
3200	68.648	49.082	69.383	64.408	66.099	80.958	69.495	62.007	39.244	50.475	12.809		49.698	68.670
3300	68.944	49.356	69.796	64.682	66.373	81.425	69.772	62.282	39.397	50.629	13.0185		49.851	68.942
3400	69.232	49.623	70.198	64.948	66.640	81.878	70.041	62.550	39.545	50.780	13.223		49.999	69.207
3500	69.523	49.883	70.590	65.206	66.900	82.319	70.303	62.811	39.689	50.926	13.4225		50.143	69.464
3600	69.796	50.138	70.972	65.458	67.153	82.748	70.558	63.066	39.829	51.069	13.6175		50.283	69.714
3700	70.063	50.386	71.346	65.703	67.399	83.166	70.808	63.315	39.965	51.208	13.8085		50.419	69.957
3800	70.323	50.628	71.710	65.942	67.639	83.574	71.051	63.558	40.097	51.343	13.9955		50.551	70.194
3900	70.578	50.864	72.065	66.175	67.873	83.972	71.288	63.796	40.226	51.475	14.1785		50.680	70.424
4000	70.827	51.095	72.412	66.403	68.102	84.361	71.519	64.028	40.352	51.603	14.3575		50.806	70.649

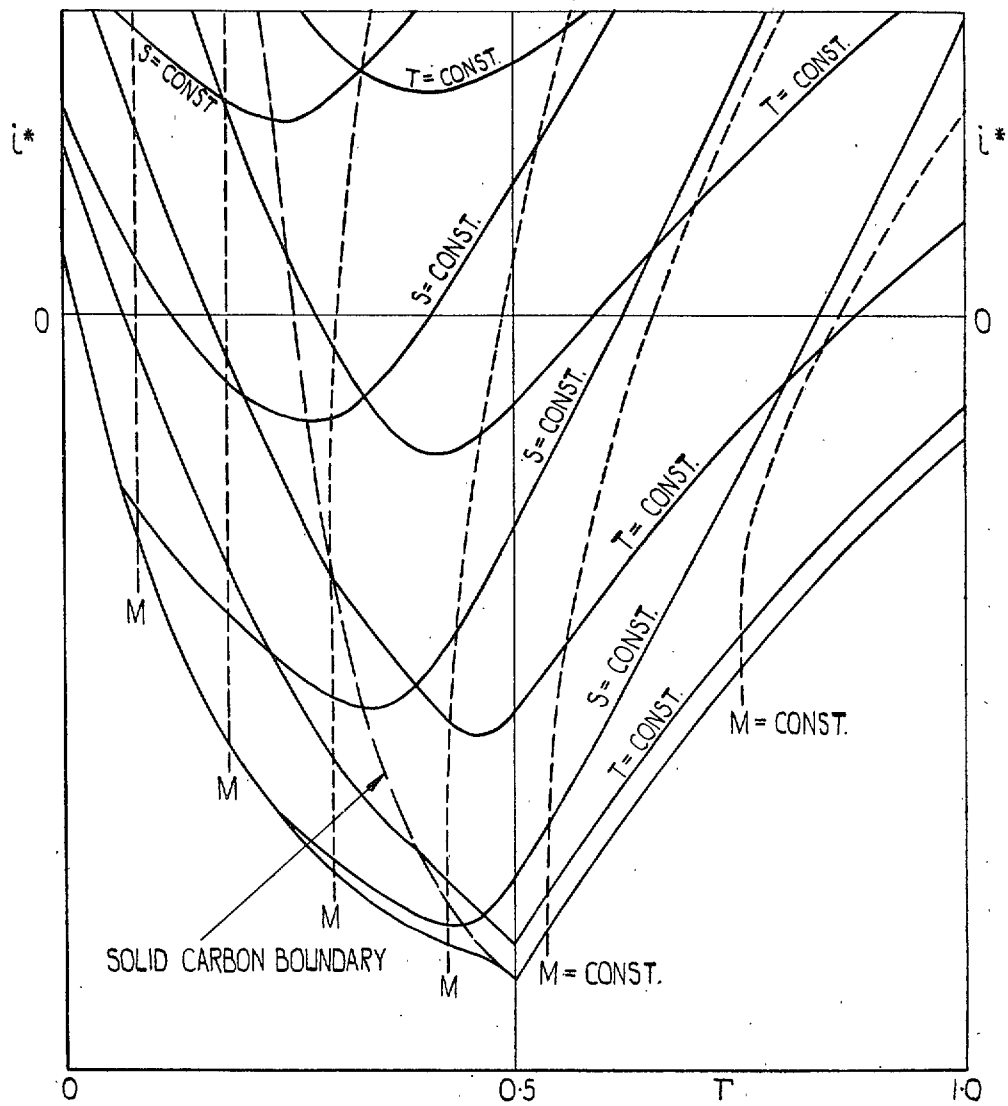


FIG. 1. Enthalpy Chart.

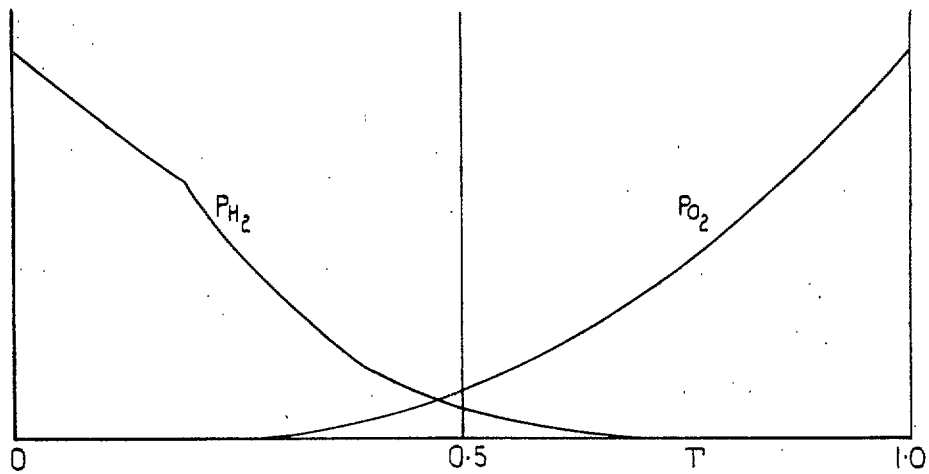
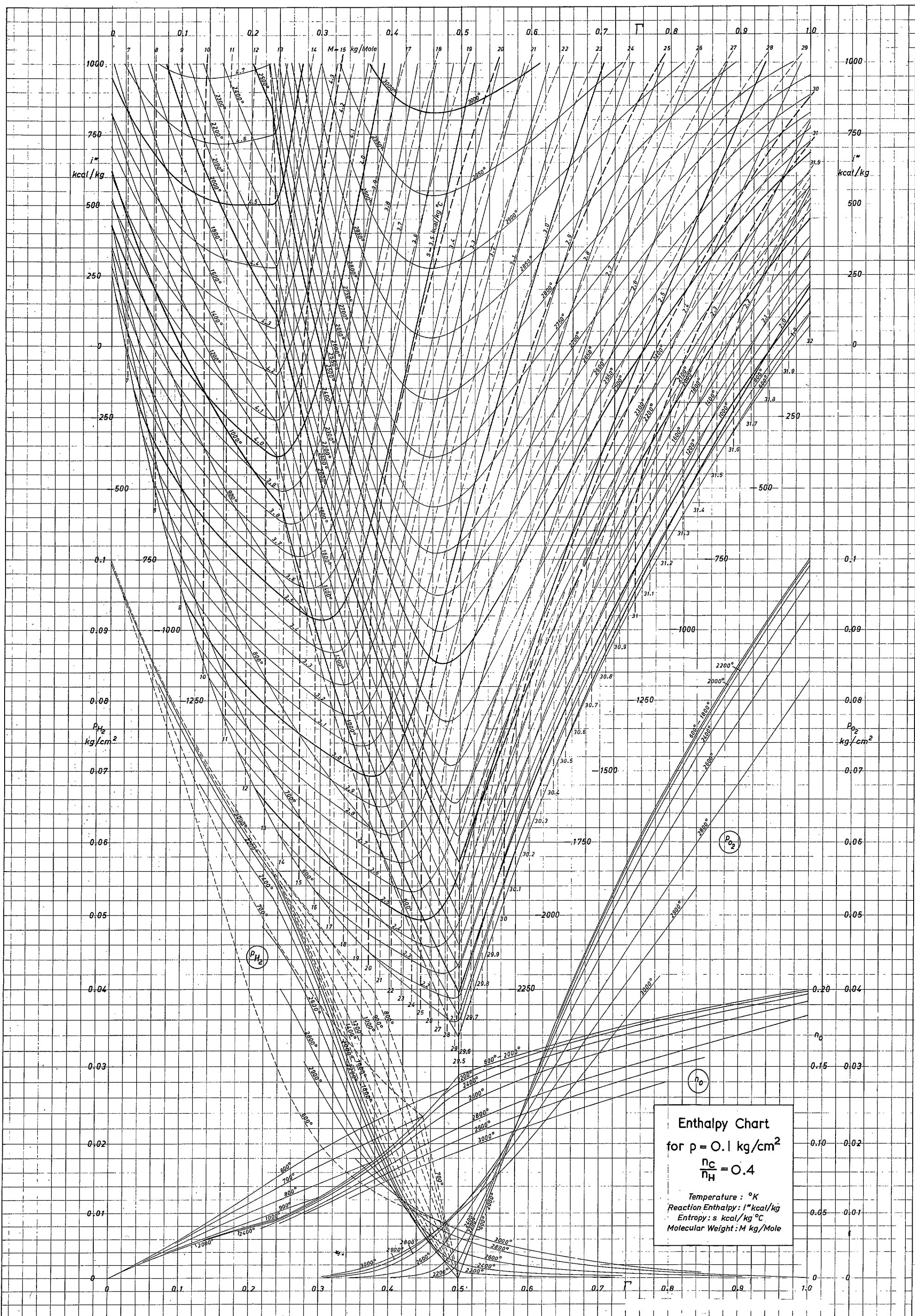


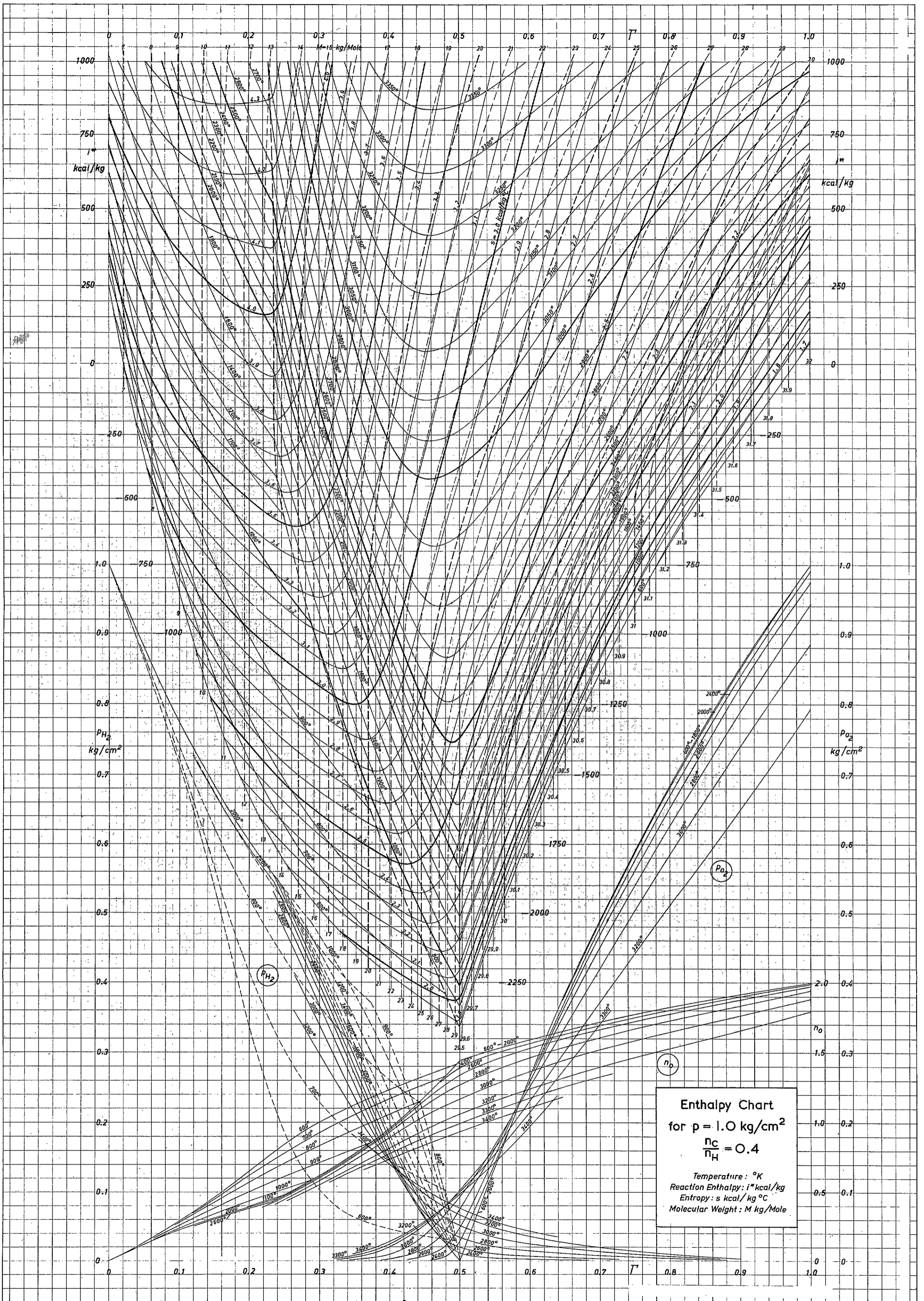
FIG. 2. Variation of p_{H_2} and p_{O_2}

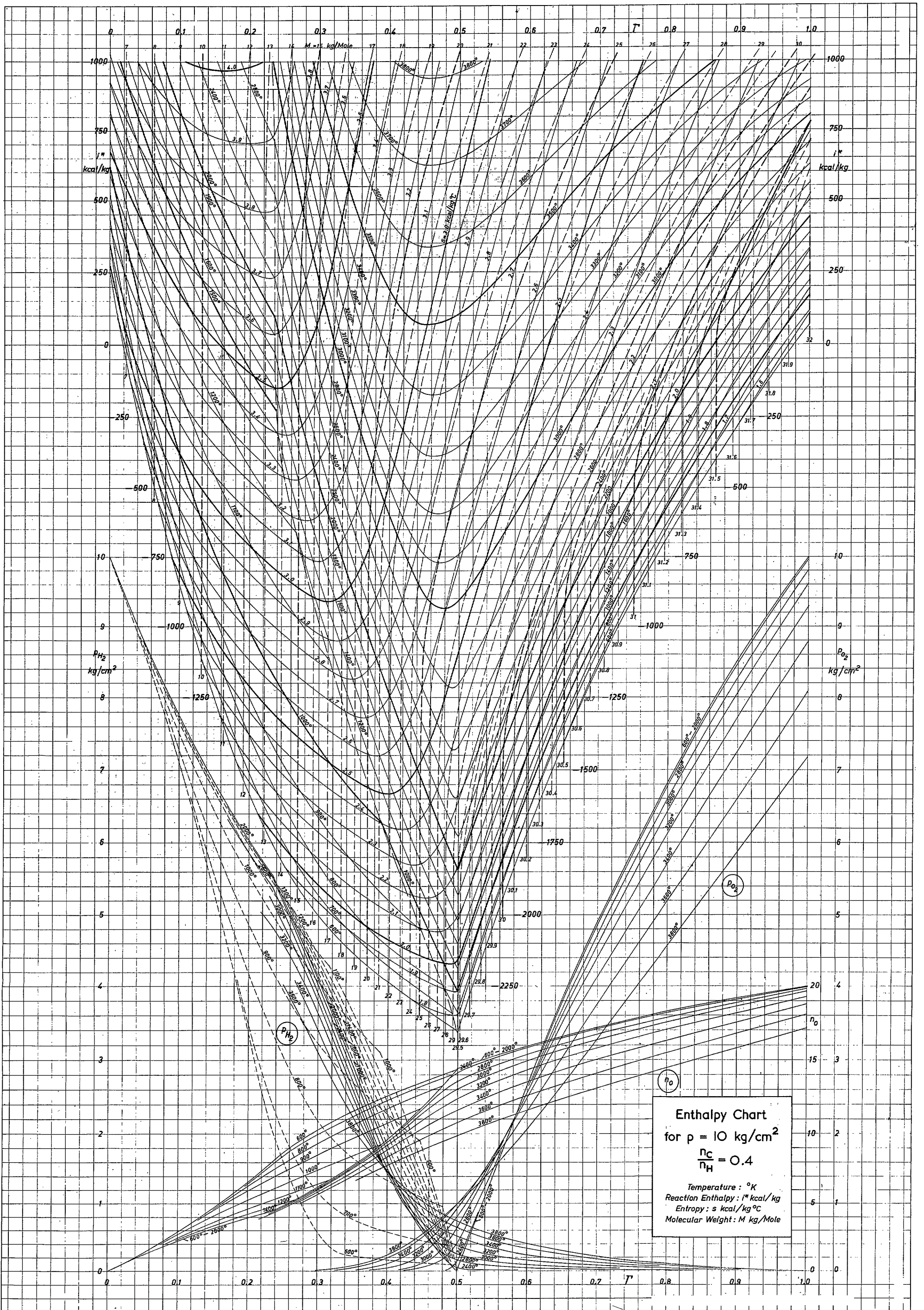
TABLE 4

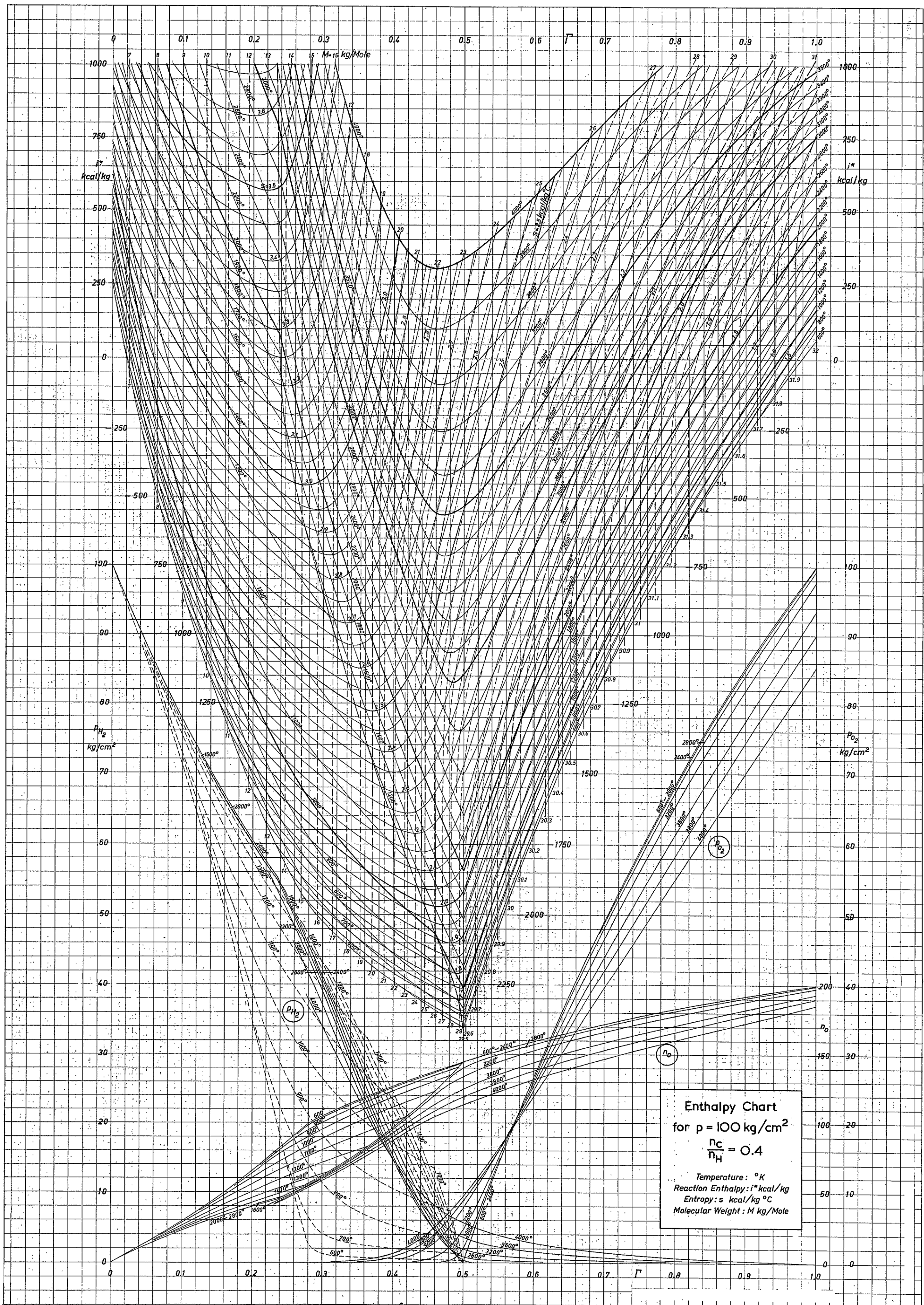
Equilibrium constants K

T (deg) K	H ₂ O	OH	O	H	NO	CO ₂	CO	CO ₂ CO	C ₂ C	CO*	p_c	p_{c_2}
298.16	1.097×10^{40}	4.002×10^{-7}	5.452×10^{-41}	4.867×10^{-36}	6.253×10^{-16}	1.234×10^{69}	1.135×10^{24}	1.087×10^{45}				
300	6.024×10^{39}	4.430×10^{-7}	5.543×10^{-41}	8.190×10^{-36}	8.203×10^{-16}	4.648×10^{68}	8.625×10^{23}	5.389×10^{44}				
400	1.707×10^{29}	2.769×10^{-5}	6.027×10^{-30}	2.204×10^{-26}	6.771×10^{-12}	3.436×10^{51}	1.361×10^{19}	2.526×10^{32}				
500	7.556×10^{22}	3.308×10^{-4}	1.838×10^{-23}	1.042×10^{-20}	1.568×10^{-9}	1.811×10^{41}	1.820×10^{16}	9.953×10^{24}				
600	4.223×10^{18}	1.765×10^{-3}	3.951×10^{-19}	6.473×10^{-17}	5.912×10^{-8}	2.517×10^{34}	2.203×10^{14}	1.144×10^{20}				
700	3.768×10^{15}	5.589×10^{-3}	4.993×10^{-16}	3.377×10^{-14}	7.917×10^{-7}	3.183×10^{29}	9.370×10^{12}	3.394×10^{16}				
800	1.910×10^{13}	1.345×10^{-2}	1.068×10^{-13}	3.740×10^{-12}	5.541×10^{-6}	6.709×10^{25}	8.692×10^{11}	7.718×10^{13}				
900	3.095×10^{11}	2.656×10^{-2}	6.983×10^{-12}	1.469×10^{-10}	2.516×10^{-5}	9.250×10^{22}	1.357×10^{11}	6.819×10^{11}				
1000	1.132×10^{10}	4.566×10^{-2}	1.986×10^{-10}	2.788×10^{-9}	8.432×10^{-5}	4.749×10^{20}	3.052×10^{10}	1.556×10^{10}			2.1547×10^{-20}	1.9470×10^{-27}
1100	7.514×10^8	7.099×10^{-2}	3.087×10^{-9}	3.125×10^{-8}	2.272×10^{-4}	6.345×10^{18}	8.948×10^9	7.092×10^8				
1200	7.792×10^7	1.025×10^{-1}	3.048×10^{-8}	2.346×10^{-7}	5.188×10^{-4}	1.738×10^{17}	3.200×10^9	5.427×10^7			7.9630×10^{-18}	4.6214×10^{-24}
1300	1.139×10^7	1.393×10^{-1}	2.120×10^{-7}	1.299×10^{-6}	1.043×10^{-3}	8.248×10^{15}	1.333×10^9	6.181×10^6			1.0903×10^{-15}	2.9581×10^{-21}
1400	2.190×10^6	1.812×10^{-1}	1.118×10^{-6}	5.391×10^{-6}	1.897×10^{-3}	6.040×10^{14}	6.269×10^8	9.652×10^5			6.9586×10^{-14}	6.9177×10^{-19}
1500	5.226×10^5	2.279×10^{-1}	4.755×10^{-6}	2.029×10^{-5}	3.195×10^{-3}	6.287×10^{13}	3.247×10^8	1.933×10^5	2.1849×10^6	4.8390×10^{18}	2.4398×10^{-12}	7.3398×10^{-17}
1600	1.491×10^5	2.777×10^{-1}	1.681×10^{-5}	6.203×10^{-5}	5.028×10^{-3}	8.649×10^{12}	1.820×10^8	4.751×10^4			5.2961×10^{-11}	4.1419×10^{-15}
1700	4.928×10^4	3.309×10^{-1}	5.143×10^{-5}	1.670×10^{-4}	7.511×10^{-3}	1.502×10^{12}	1.088×10^8	1.378×10^4	1.8280×10^5	1.9071×10^{17}	7.7940×10^{-10}	1.4000×10^{-13}
1800	1.838×10^4	3.856×10^{-1}	1.386×10^{-4}	4.027×10^{-4}	1.072×10^{-2}	3.215×10^{11}	6.870×10^7	4.612×10^3	3.6934×10^4	1.0979×10^{16}	8.3288×10^{-9}	3.1046×10^{-12}
1900	7.603×10^3	4.425×10^{-1}	3.383×10^{-4}	8.889×10^{-4}	1.476×10^{-2}	7.306×10^{10}	4.541×10^7	2.4827×10^3	8.8952×10^3	8.6690×10^{14}	6.8182×10^{-8}	4.8474×10^{-11}
2000	3.436×10^3	5.002×10^{-1}	7.535×10^{-4}	1.812×10^{-3}	1.971×10^{-2}	2.239×10^{10}	3.118×10^7	7.180×10^2	2.4827×10^3	8.9288×10^{13}	4.4604×10^{-7}	5.6341×10^{-10}
2100	1.672×10^3	5.595×10^{-1}	1.557×10^{-3}	3.454×10^{-3}	2.548×10^{-2}	7.183×10^9	2.213×10^7	3.248×10^2	7.8622×10^2	1.8055×10^{12}	2.4118×10^{-6}	5.0971×10^{-9}
2200	8.682×10^2	6.192×10^{-1}	3.024×10^{-3}	6.227×10^{-3}	3.230×10^{-2}	2.553×10^9	1.617×10^7	1.577×10^2	2.7757×10^2	3.3455×10^{11}	1.1079×10^{-5}	3.7209×10^{-8}
2300	4.777×10^2	6.786×10^{-1}	5.506×10^{-3}	1.064×10^{-2}	4.004×10^{-2}	9.932×10^8	1.213×10^7	8.196×10^1	1.0750×10^2	7.1805×10^{10}	4.4209×10^{-5}	2.2575×10^{-7}
2400	2.760×10^2	7.369×10^{-1}	9.575×10^{-3}	1.742×10^{-2}	4.878×10^{-2}	4.175×10^8	9.292×10^6	4.498×10^1	4.5170×10^1	4.9527×10^9	1.5609×10^{-4}	1.1662×10^{-6}
2500	1.666×10^2	7.976×10^{-1}	1.597×10^{-2}	2.747×10^{-2}	5.856×10^{-2}	1.880×10^8	7.265×10^6	2.588×10^1	2.0396×10^1	1.7504×10^{10}	4.9527×10^{-4}	5.2355×10^{-6}
2600	1.044×10^2	8.569×10^{-1}	2.559×10^{-2}	4.182×10^{-2}	6.924×10^{-2}	8.998×10^7	5.832×10^6	1.557×10^1	9.7976	4.7736×10^9	1.4303×10^{-3}	2.0773×10^{-5}
2700	6.770×10^1	9.141×10^{-1}	3.949×10^{-2}	6.166×10^{-2}	8.077×10^{-2}	4.542×10^7	4.663×10^6	9.748	4.9742	1.4375×10^9	3.8015×10^{-3}	7.3905×10^{-5}
2800	4.485×10^1	9.712×10^{-1}	5.948×10^{-2}	8.879×10^{-2}	9.337×10^{-2}	2.405×10^7	3.814×10^6	6.299	2.6519	4.7249×10^8	9.3840×10^{-3}	2.3866×10^{-4}
2900	3.109×10^1	1.028	8.649×10^{-2}	1.244×10^{-1}	1.067×10^{-1}	1.330×10^7	3.159×10^6	4.207	1.4785	1.6807×10^8	2.1688×10^{-2}	7.0688×10^{-4}
3000	2.192×10^1	1.078	1.228×10^{-1}	1.703×10^{-1}	1.208×10^{-1}	7.639×10^6	2.644×10^6	2.888	8.5814×10^{-1}	6.4181×10^7	4.7253×10^{-2}	1.9380×10^{-3}
3100	1.583×10^1	1.137	1.707×10^{-1}	2.288×10^{-1}	1.357×10^{-1}	4.549×10^6	2.237×10^6	2.035	5.1621×10^{-1}	2.6113×10^7	9.7632×10^{-2}	4.9561×10^{-3}
3200	1.165×10^1	1.191	2.327×10^{-1}	3.022×10^{-1}	1.514×10^{-1}	2.798×10^6	1.911×10^6	1.464	3.2052×10^{-1}	1.1263×10^7	1.9229×10^{-1}	1.1904×10^{-2}
3300	8.724	1.242	3.112×10^{-1}	3.935×10^{-1}	1.678×10^{-1}	1.772×10^6	1.645×10^6	1.077	2.0482×10^{-1}	5.1192×10^6	3.6264×10^{-1}	2.7014×10^{-2}
3400	6.654	1.294	4.091×10^{-1}	5.014×10^{-1}	1.846×10^{-1}	1.151×10^6	1.427×10^6	0.8066	1.3441×10^{-1}	2.4369×10^6	6.5750×10^{-1}	5.8223×10^{-2}
3500	5.138	1.339	5.279×10^{-1}	6.321×10^{-1}	2.017×10^{-1}	7.629×10^5	1.244×10^6	0.6130	9.0454×10^{-2}	1.2120×10^6	1.1500	1.1972×10^{-1}
3600	4.033	1.386	6.730×10^{-1}	7.856×10^{-1}	2.195×10^{-1}	5.195×10^5	1.094×10^6	0.4753	6.2206×10^{-2}	6.2564×10^5	1.9467	2.3587×10^{-1}
3700	3.211	1.433	8.479×10^{-1}	9.664×10^{-1}	2.382×10^{-1}	3.608×10^5	9.673×10^5	0.3733	4.3671×10^{-2}	3.3589×10^5	3.1979	4.4680×10^{-1}
3800	2.586	1.480	1.055	1.175	2.572×10^{-1}	2.554×10^5	8.603×10^5	0.2972	3.1235×10^{-2}	1.8624×10^5	5.1100	8.1640×10^{-1}
3900	2.105	1.527	1.301	1.420	2.771×10^{-1}	1.838×10^5	7.691×10^5	0.2390	2.2737×10^{-2}	1.0664×10^5	7.9610	1.4431
4000	1.732	1.571	1.584	1.694	2.968×10^{-1}	1.345×10^5	6.911×10^5	0.1947	1.6812×10^{-2}	6.2806×10^4	12.1159	2.4741
									1.2613×10^{-2}	3.7971×10^4	18.0433	4.1235









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