Int. J. Heat Mass Transfer. Vol. 10, pp. 1451–1457. Pergamon Press Ltd. 1967. Printed in Great Britain

SHORTER COMMUNICATIONS

HIGH TEMPERATURE ENTHALPY-COMPOSITION CHARTS FOR CARBON–NITROGEN MIXTURES

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(*Received* 22 *August* 1966 *and in revised form* 3 *April* 1967)

INTRODUCTION

TRANSPIRATION cooling of a plasma jet anode is one technique of coping with the high temperatures encountered in plasma technology. Porous carbon (graphite) is currently receiving consideration, a practical cooling gas being air. Because nitrogen is the dominant component of air, the carbon–nitrogen system was selected as having both scientific and engineering interest.

In previous work, with graphite cathodes, difficulties were encountered as a consequence of graphite evaporation from the hot cathode spot, these traces of carbon in the working gas being undesirable for many applications. The rate of ablation of a transpiration-cooled porous carbon anode was found to be quite small. Nevertheless it appears desirable to investigate this mass transfer in more detail. Enthalpy-composition diagrams are very useful for such calculations and methods of analysis have been worked out using such charts [1, 2]. The research described in this note was undertaken with the aim to provide the information necessary for analysis of this form. It should also be helpful in the diagnosis by spectroscopy, for instance, of nitrogen plasma jets with traces of carbon.

The present work deals with the calculation of the thermodynamic properties of carbon–nitrogen mixtures from 1000°K to 15000°K and at various pressures between 10^{-3} and 10^{2} atm. Thermal equilibrium, ideal solution behavior of the solid–gas mixture and ideal gas behavior of the gas phase were assumed. The non-ideal effects will be most pronounced at high pressures.

The equilibrium system studied was composed of the following reaction components. C_β (graphite), C_1, C_2, C_3, N, N_2, CN, C_2N_2, C^+, N^+, N_2^+, CN^+, e^-.

THERMODYNAMIC FUNCTIONS

The Gibbs' free energy function $(F^\circ - H_0^\circ)/RT$, enthalpy $(H^\circ - H_0^\circ)/RT$ and entropy S°/R for all reaction gas components were calculated by statistical mechanics methods through evaluation of the partition function. No intermolecular forces are considered in these calculations. For monatomic and polyatomic gases the rigid rotator–harmonic oscillator approximation is used and for diatomic gases we included vibrational anharmonicity and stretching effects. An effort was made to obtain the most recent spectroscopic and heat formation data. These are not included here because of limited space, but for those interested, they can be found in [3]. The thermodynamic functions of graphite are taken from Fickett and Cowan [4].

EQUILIBRIUM COMPOSITIONS

The free energy method of White, Johnson and Dantzig [5] was used to calculate the equilibrium compositions at given temperature T(°K) and pressure P (atm). The original method was generalized to include the condensed phase and electrically charge particles.

ENTHALPY COMPOSITION CHARTS

The enthalpy composition charts for six different total pressures (10^{-3}, 10^{-2}, 10^{-1}, 1, 10, 100 atm) were constructed by the following procedures:

The thermodynamic functions for each pure component were calculated by the methods of statistical mechanics using spectroscopic data as already described.

To represent the concentration of carbon and nitrogen atoms in the mixture, the quantity ψ is defined as follows

$$\psi = \frac{\text{number of moles of carbon atom}}{\text{total moles of atom}} = \frac{n_{C_\beta}}{n_N + n_{C_\beta}}.$$

At sufficiently low temperatures, where, for any pressure, chemical reaction is negligible, this would involve only graphite, C_β, and gaseous nitrogen, N_2. As the temperature

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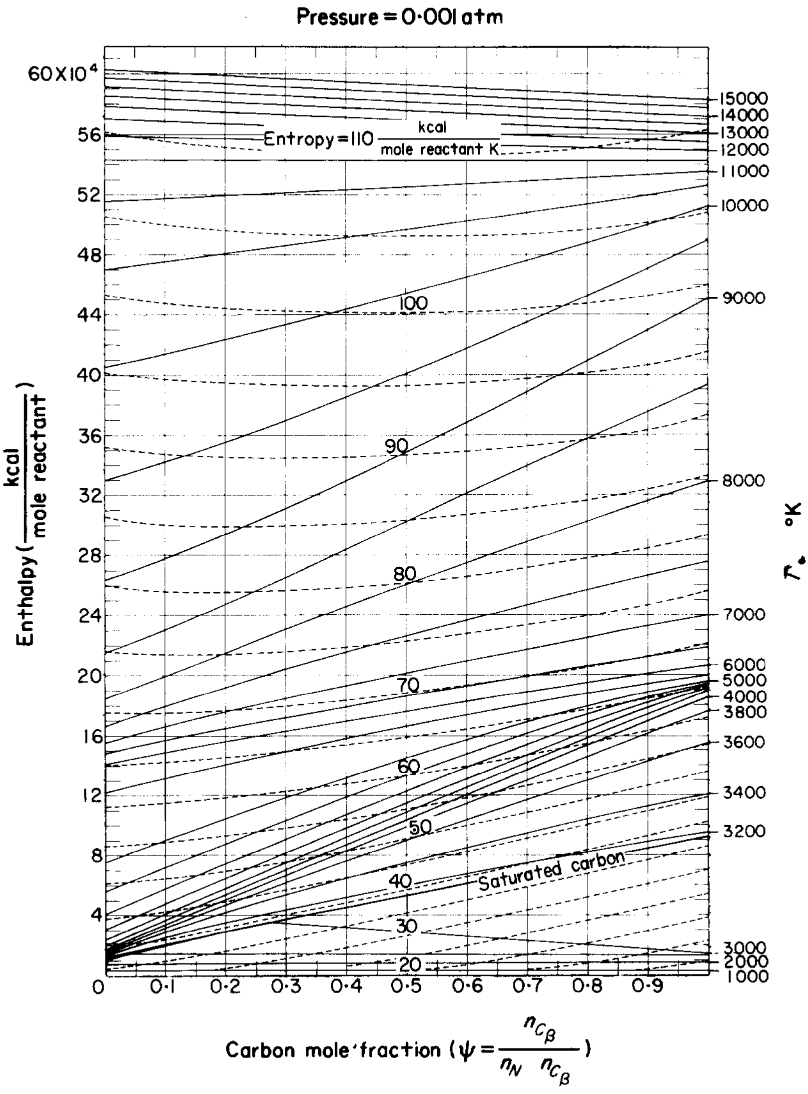

FIG. 1. Enthalpy-composition chart, 0·001 atm.

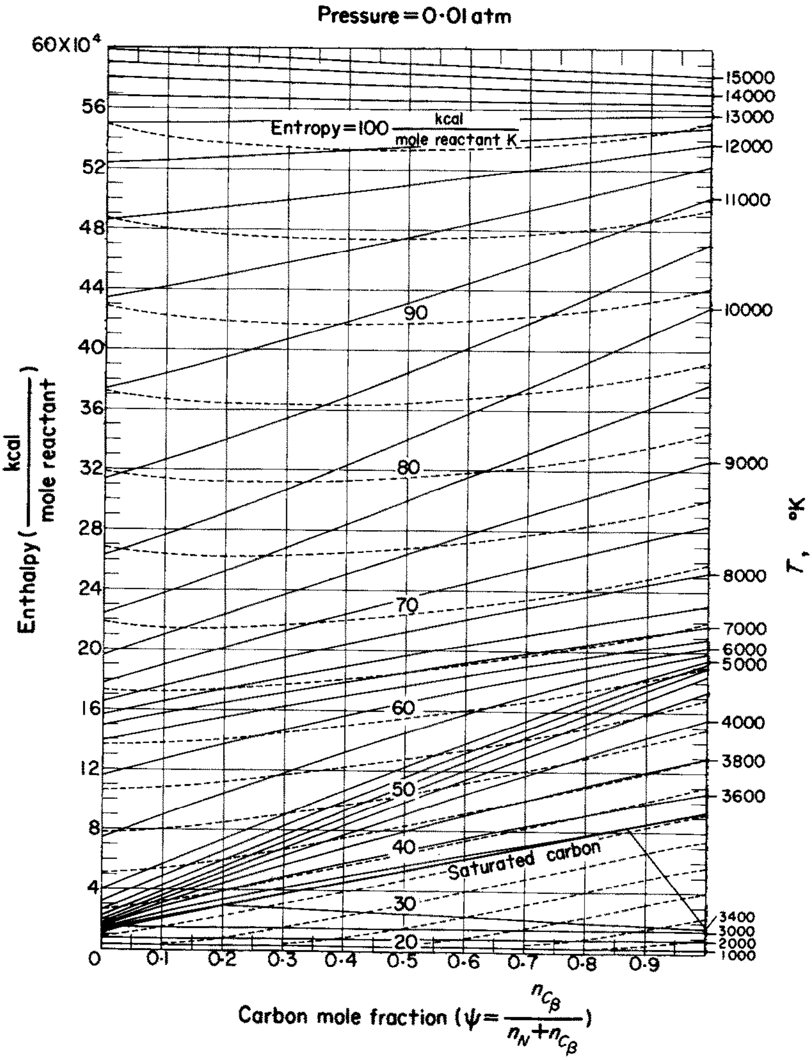

FIG. 2. Enthalpy-composition chart, 0·01 atm.

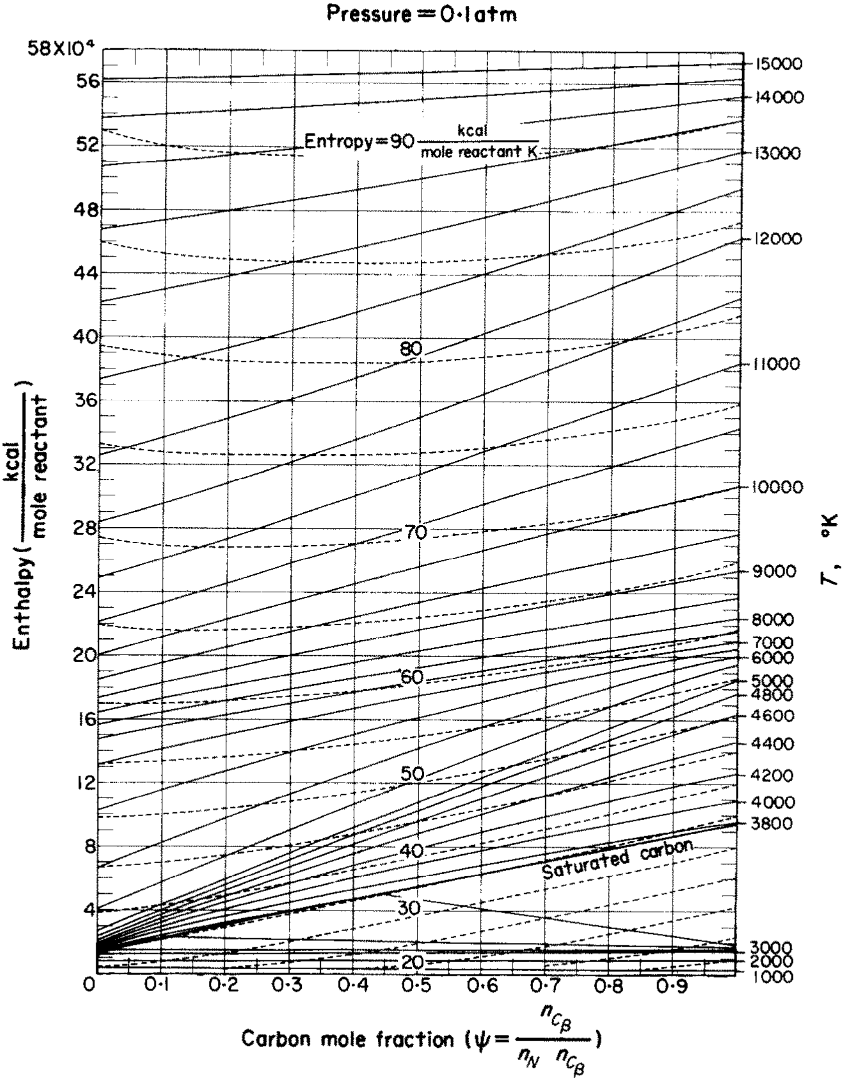

FIG. 3. Enthalpy-composition, 0·1 atm.

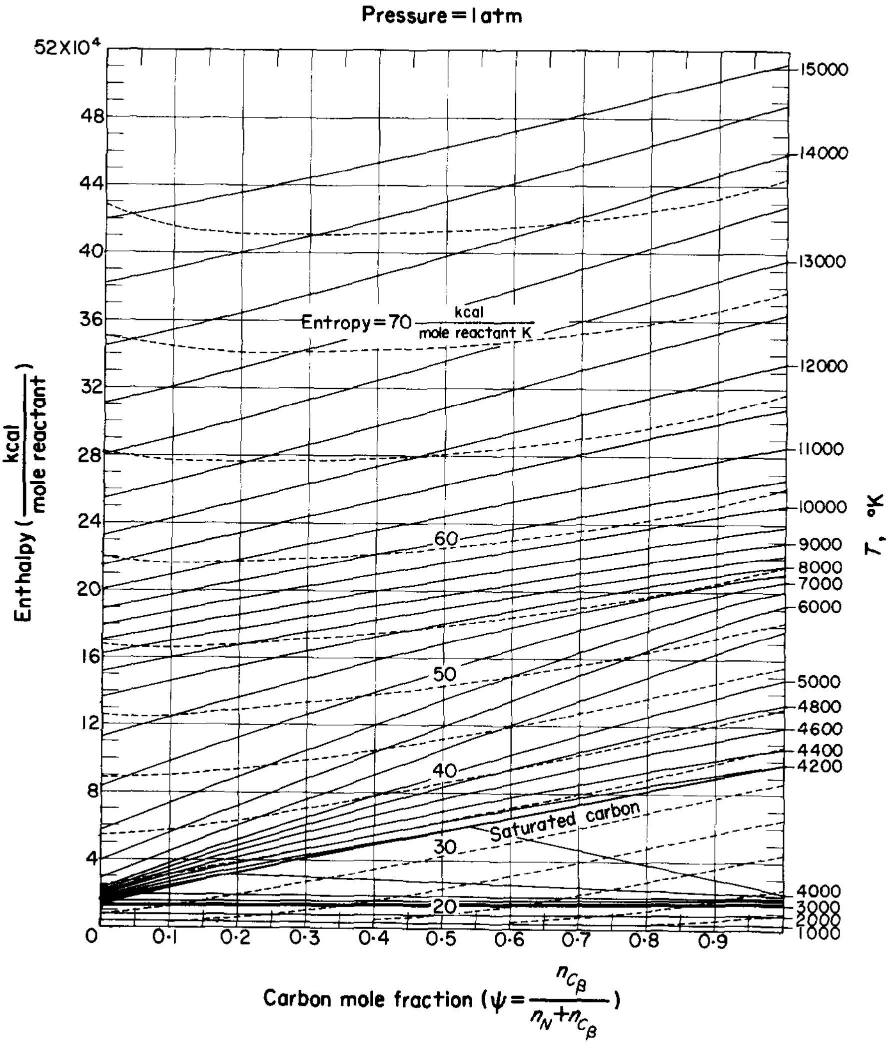

FIG. 4. Enthalpy-composition chart, 1 atm.

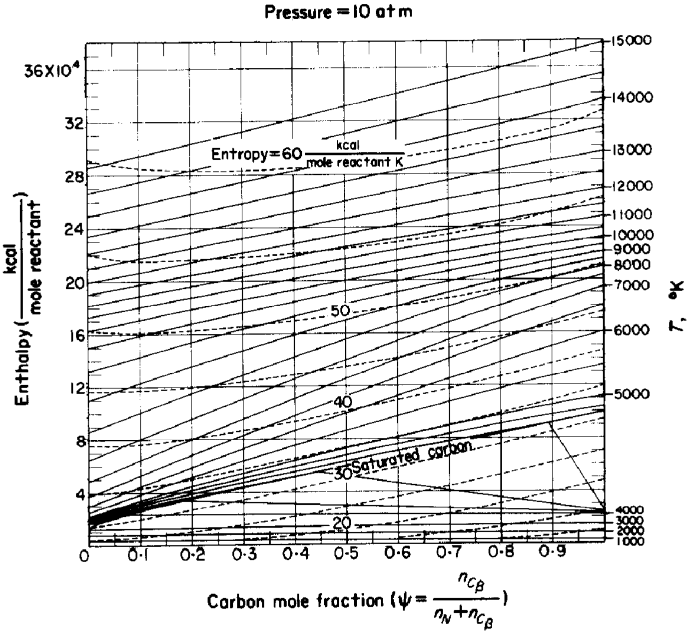

FIG. 5. Enthalpy-composition chart, 10 atm.

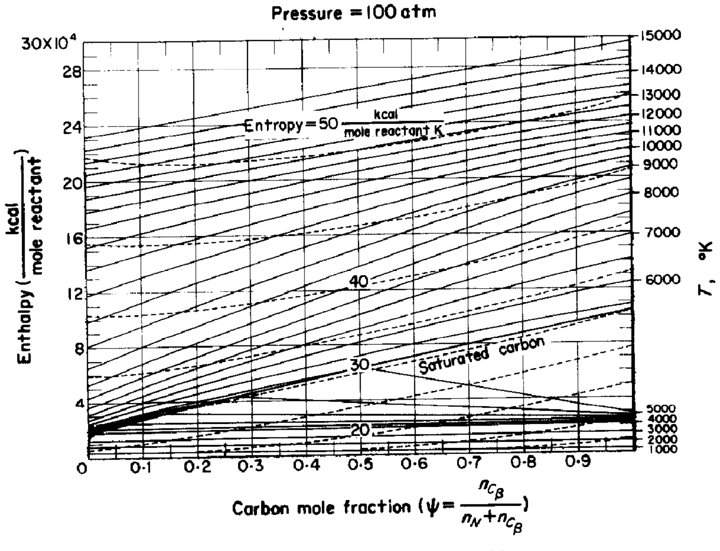

FIG. 6. Enthalpy-composition chart, 100 atm.

increases, sublimation, chemical reaction, dissociation, and ionization occur. In order to find the equilibrium composition, the method used is that of minimizing the free energy. The thermodynamic functions of the equilibrium mixture based on 1 mol of initial reactant are calculated by the equations for an ideal mixture.

The enthalpy composition charts are then constructed with the calculated values of $H^\circ(P, T, \psi)$. Taking H° as the ordinate and ψ as the abscissa, the constant temperature and entropy lines are shown in the charts. The carbon saturation line is also indicated, having been determined for given ψ by the temperature at which C_β disappears in the equilibrium composition. For the pressures 0·001, 0·01, 0·10, 1·0, 10, and 100 atmospheres, enthalpy-composition charts are given in Figs. 1 through 6, respectively.

ACKNOWLEDGEMENT

The authors wish to express their appreciation to the Aerospace Research Laboratories, Office of Aerospace Research, U.S. Air Force for support under Contract 33(657)-7380, Project 7063, Task 7063-03.

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Int. J. Heat Mass Transfer. Vol. 10, pp. 1457–1462. Pergamon Press Ltd. 1967. Printed in Great Britain.

THREE-FLUID HEAT EXCHANGER EFFECTIVENESS

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(*Received* 9 *September* 1966 *and in revised form* 19 *April* 1967)

NOMENCLATURE

A_1, A_2, A_3,	areas as illustrated in Fig. 1;
$A_{(1)}$,	variable area corresponding to surface 1;
A_k,	longitudinal heat conduction area;
$B_1, \ldots, B_6$,	functions defined by equations (11–14), (20) and (21);
c_p,	specific heat at constant pressure;
C,	$= \dot{m}c_p$, capacity rate;
e_c,	$= (T_{c_2} - T_{c_1})/(T_{h_1} - T_{c_1})$, cold fluid temperature ratio;
e_i,	$= (T_{i_2} - T_{i_1})/(T_{h_1} - T_{i_1})$, intermediate fluid temperature ratio;
ϵ,	heat exchanger effectiveness;
k,	thermal conductivity of the separating surface material;
L,	length of the separating surface in the longitudinal direction;
$\dot{m}$,	mass flow rate;
N_{tu},	$= U_1A_1/C_c$, dimensionless number of heat transfer units;
$\dot{Q}$,	heat-transfer rate;
r_2, r_3,	roots of the characteristic equation;
R_1, R_2, R_3,	$= 1/U_1A_1$, $1/U_2A_2$, $1/U_3A_3$, thermal resistances;
S_2, S_3,	functions defined by equations (15) and (16);
T_h, T_i, T_c,	fluid temperatures;
$T_{h_1}, T_{i_1}, T_{c_1}$,	inlet fluid temperatures;
$T_{h_2}, T_{i_2}, T_{c_2}$,	outlet fluid temperatures;
T_{ho},	hot fluid temperature defined by equation (4);
U_1, U_2, U_3,	over-all heat-transfer coefficients (see Fig. 1);
X,	$= (T_{h_1} - T_{i_1})/(T_{h_1} - T_{c_1})$, inlet temperature ratio.

Subscripts

c,	cold fluid (fluid with the lowest inlet temperature);

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