Matrix Representations of the Thermo-dynamic Functions used for Studying the Burning of Gas Combustibles

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Abstract. The paper contains data regarding the processes that occur art normal pressure and the variations of enthalpy (ΔH), entropy (ΔS), molar isobar heat (ΔC_p), isobar potential (ΔG). The variations of enthalpy and molar isobar heat are useful in the calculation of the thermic balance-sheet, and those in connection with the isobar potential are useful for the calculation of the balances.
The enthalpy H(T) and entropy S(T) are linear combinations of the temperature functions $U_j(T)$ and $V_j(T)$, being taken as a basis for the calculation of isobar potential. The indicated proprieties for each component can be calculated, if we know the approximation function for the isobar molar heat and the known value of the propriety at a temperature T_0.

In order to find the $a_j,\ j = 1, 2, ..., 5$, coefficients we consider known the values of the molar isobar heat at five values of absolute temperature, after which we apply the linear algebra method.

1. Introduction

The efficient burning of the gas combustibles is a technical problem of major importance for industrial installations in order to make a bigger combustible economy. The way the burning process takes place leads to obtaining quality products in different technological processes.

The diffusive burning (diffusive flames) is used in the majority of the burning installations that use gas combustibles, which means that the mixing process between the gas combustibles and the air needed for burning takes place right in the burning space, with two jets (combustible gases and air), separately introduced in the burning chamber. In order to obtain diffusive flames with features that allow the unfolding of different technological processes in optimal conditions, it is necessary to know the physical, chemical and geometrical factors that influence the flame features. Knowing these factors and the influence they exert can lead to achieving some flames with well-established features according to different phases of the technological processes.

2. Processes that take place at constant pressure

The thermo-dynamic study of the processes that take place in a system needs the knowing of different system function modifications. So, for the processes that occur at constant pressure the enthalpy, (ΔH), entropy (ΔS), molar isobar heat (ΔC_p), isobar potential (ΔG), values and also the numeric value of the balance constant. (K_p) the data regarding the variations of enthalpy and molar isobar heat are useful for the calculation of thermo balance-sheet, and those regarding the variation of the isobar potential for the calculation of the balances.

The graphical analytical representation of the thermo dynamical functions as temperature allows the reduction of the data at a simple matrix of the thermodynamic properties. Values as the enthalpy, entropy and others can be obtain from the matrix of the thermodynamic properties through simple matrix operation. The matrix equations allow the calculation of some large systems through numerical methods wit specialized programs.

3. Fundamental equations for simple substances

For individual substances in a certain phase, the isobar molar heats are approximated according to the temperature by polynomial expression of the following form:

$$C_p(T) = a_1 + a_2 T + a_3 T^{-2}, \quad (1)$$

$$C_p(T) = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^{-2},$$

or through linear combinations of some functions $\varphi_j(T)$ cu $j = 1, 2 \ldots n$:

$$C_p(T) = \sum_{j=1}^{n} a_j \cdot \varphi_j(T), \quad (2)$$

where a_j are constants that depend of the product nature and $\varphi_j(T)$ are given functions.

Using the derivates of the enthalpy H and entropy S in rapport with the temperature at constant pressure:

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p(T); \quad \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p(T)}{T} \quad (3)$$

we have:

$$H(T_1) = H(T_0) + \int_{T_0}^{T_1} C_p(T) \cdot dT, \quad (4)$$

$$S(T_1) = S(T_0) + \int_{T_0}^{T_1} \frac{C_p(T)}{T} \cdot dT. \quad (5)$$

We replace (2) in (4) and (5) deduce:

$$H(T_1) = H(T_0) + \sum_{j=1}^{n} a_j \cdot \int_{T_0}^{T_1} \varphi_j(T) \cdot dT, \quad (6)$$

$$S(T_1) = S(T_0) + \sum_{j=1}^{n} a_j \cdot \int_{T_0}^{T_1} \frac{\varphi_j(T)}{T} \cdot dT. \quad (7)$$

The temperature is adopted $T_j < T_0$ and we transform the integrals form the relations (6), (7) in the following form:

$$\int_{T_0}^{T_1} \varphi_j(T) \cdot dT = \int_{T_j}^{T_1} \varphi_j(T) \cdot dT - \int_{T_j}^{T_0} \varphi_j(T) \cdot dT, \tag{8}$$

$$\int_{T_0}^{T_1} \frac{\varphi_j(T)}{T} \cdot dT = \int_{T_j}^{T_1} \frac{\varphi_j(T)}{T} \cdot dT - \int_{T_j}^{T_0} \frac{\varphi_j(T)}{T} \cdot dT. \tag{9}$$

This kind of integrals' representation in two components allows the introduction of the functions:

$$U_j(T) = \int_{T_j}^{T} \varphi_j(T) \cdot dT, \tag{10}$$

$$V_j(T) = \int_{T_j}^{T} \frac{\varphi_j(T)}{T} \cdot dT, \tag{11}$$

and the relations (8) and (9) take the form:

$$\int_{T_0}^{T_1} \varphi_j(T) \cdot dT = U_j(T_1) - U_j(T_0), \tag{12}$$

$$\int_{T_0}^{T_1} \frac{\varphi_j(T)}{T} \cdot dT = V_j(T_1) - V_j(T_0). \tag{13}$$

We mark the temperature T_1 with T and replacing the relations (12) and (13) in (6) and (7), we have:

$$H(T) = \left[H(T_0) - \sum_{j=1}^{n} a_j \cdot U_j(T_0) \right] + \sum_{j=1}^{n} a_j \cdot U_j(T), \tag{14}$$

$$S(T) = \left[S(T_0) - \sum_{j=1}^{n} a_j \cdot V_j(T_0) \right] + \sum_{j=1}^{n} a_j \cdot V_j(T). \tag{15}$$

Introducing the notations:

$$a_{n+1} = H(T_0) - \sum_{j=1}^{n} a_j \cdot U_j(T_0) \quad ; \quad U_{n+1} = 1 \quad ; \quad V_{n+1} = 0, \quad (16)$$

$$a_{n+2} = S(T_0) - \sum_{j=1}^{n} a_j \cdot V_j(T) \quad ; \quad U_{n+2} = 0 \quad ; \quad V_{n+2}(T) = 1, \quad (17)$$

the expressions (14) and (15) take the form:

$$H(T) = \sum_{j=1}^{n+2} a_j \cdot U_j(T), \quad (18)$$

$$S(T) = \sum_{j=1}^{n+2} a_j \cdot V_j(T). \quad (19)$$

In this form, the enthalpy H(T) and entropy S(T) are linear combinations of the temperature functions $U_j(T)$ and $V_j(T)$, being taken as basis in the calculation of the isobar potential:

$$G(T) = H(T) - T \cdot .S(T). \quad (20)$$

Getting to know the entropy allows the finding of temperature influences on isobar G potential, because:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S(T), \quad (21)$$

$$G(T) = G(T_0) - \int_{T_0}^{T} S(T) \cdot dT. \quad (22)$$

Replacing the expressions (18) and (19) in (20) we have:

$$G(T) = \sum_{j=1}^{n+2} a_j \cdot W_j(T), \quad (23)$$

where.

$$W_j(T) = U_j(T) - T \cdot V_j(T). \quad (24)$$

The enthalpy, entropy and the isobar potential of simple substances at a given pressure can be calculated as linear combinations of known temperature functions that do not depend of the concrete product nature for which the calculation is performed. The properties of each product can be calculated if we know the approximation function for the molar isobar heat and the corresponding value of the property at a certain temperature T_0.

4. Systems with more components

The relations (18), (19) and (23) were written for simple substances, in order to express the enthalpy, entropy and the isobar potential for the systems with more components through functions with identical form, I being the component index:

$$H_i(T) = \sum_{j=1}^{n+2} a_{i\,j} \cdot U_j , \tag{25}$$

$$S_i(T) = \sum_{j=1}^{n+2} a_{i\,j} \cdot V_j , \tag{26}$$

$$G_i(T) = \sum_{j=1}^{n+2} a_{i\,j} \cdot W_j . \tag{27}$$

If we neglect the mixture effect, the enthalpy H of the whole system is a sum of the partial enthalpies:

$$H(T) = \sum_{i=1}^{m} \nu_i \cdot H_i(T) , \tag{28}$$

where ν_i is the mol number of the I substance form the system. Analog expressions can be written for the entropy and the isobar potential:

$$S(T) = \sum_{i=1}^{m} \nu_i \cdot S_i(T) , \tag{29}$$

$$G(T) = \sum_{i=1}^{m} \nu_i \cdot G_i(T) . \tag{30}$$

For a system with more components the notion of isobar potential reaction (ΔG) and of standard isobar potential of the reaction ($\Delta G^{\ 0}$):

$$\Delta G = \Delta H - T \cdot .\Delta S , \tag{31}$$

$$\Delta G^0 = -R \cdot T \cdot \ln(K_p), \tag{32}$$

where K_p is the balance constant.

The modification of the enthalpy during the reaction determines the temperature influence on **ln(**K_p**) ,** because

$$\left(\frac{\partial \ln(K_p)}{\partial T}\right)_p = \frac{\Delta H(T)}{R \cdot T^2}, \tag{33}$$

where from

$$\ln(K_p(T)) = \ln(K_p(T_0)) + \int_{T_0}^{T} \frac{\Delta H(T)}{R \cdot T^2} \cdot dT. \tag{34}$$

Replacing in the (34) relation the expressions for ΔH (T) by the variation of the molar heat ΔC_p and using the relation (2) for the molar heat, it results for $\ln(K_p)$ a representation in a form of linear combinations of known temperature functions that do not depend on the nature of the products for which the calculation is made.

Introducing the expression (25), (26), (27) in (28), (29) and (30) we have:

$$H(T) = \sum_{i=1}^{m} \nu_i \cdot \left(\sum_{j=1}^{n+2} a_{i\,j} \cdot U_j \right) = \sum_{i=1}^{m} \sum_{j=1}^{n+2} \nu_i \cdot a_{i\,j} \cdot U_j, \tag{35}$$

$$S(T) = \sum_{i=1}^{m} \nu_i \cdot \left(\sum_{j=1}^{n+2} a_{i\,j} \cdot V_j \right) = \sum_{i=1}^{m} \sum_{j=1}^{n+2} \nu_i \cdot a_{i\,j} \cdot V_j, \tag{36}$$

$$G(T) = \sum_{i=1}^{m} \nu_i \left(\sum_{j=1}^{n+2} a_{i\,j} \cdot W_j \right) = \sum_{i=1}^{m} \sum_{j=1}^{n+2} \nu_i \cdot a_{i\,j} \cdot W_j. \tag{37}$$

5. Matrix notations

We introduce the column vectors: **X, U, V, W** and the matrix A according to the equalities:

$$\nu = \begin{bmatrix} \nu_1 \\ \nu_2 \\ \vdots \\ \nu_m \end{bmatrix}, \; U = \begin{bmatrix} U_1 \\ U_2 \\ \vdots \\ U_{n+2} \end{bmatrix}, \; V = \begin{bmatrix} V_1 \\ V_2 \\ \vdots \\ V_{n+2} \end{bmatrix}, \; W = \begin{bmatrix} W_1 \\ W_2 \\ \vdots \\ W_{n+2} \end{bmatrix}, \quad (38)$$

$$A = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1,n+2} \\ a_{21} & a_{22} & \cdots & a_{2,n+2} \\ \vdots & \vdots & \vdots & \vdots \\ a_{m,1} & a_{m,2} & \cdots & a_{m,n+2} \end{bmatrix}. \quad (39)$$

The expressions (35), (36), (37) can be written as a matrix in the following form:

$$H(T) = \nu^T \cdot A \cdot U = U^T \cdot A^T \cdot \nu, \quad (40)$$

$$S(T) = \nu^T \cdot A \cdot V = V^T \cdot A^T \cdot \nu, \quad (41)$$

$$G(T) = \nu^T \cdot A \cdot W = W^T \cdot A^T \cdot \nu. \quad (42)$$

Te values $a_{i\,j}$ can be interpreted as components of the A_i^T vectors that correspond to the thermodynamic properties. Each line of the matrix A corresponds to one of the analyzed system's substances. The A matrix is named thermodynamic matrix, a one line of it is a thermodynamic vector for the i substance. The elements $a_{i\,j}$ of the matrix A do not depend on the temperature T, but on the products' nature, unlike the components of the vectors **U, V, W** that depend only on the T and not on the product's nature. The expression for each property is generally the product of three matrix, each including important information for the system that do not depend on other parts. The vectors **U,** **V** and **W** are determined by the system's temperature, the matrix A is determined of the qualitative composition of the system, that means of the existing system products' composition, and ν is determined by the quantitative composition of the system.

This kind of equalities can be obtained also for the thermodynamic functions of the reactions: ΔH , ΔS , ΔG , that also depend on temperature. In this case, the stoichiometric coefficients of the chemical equation are considered as ν_i .

According to (32) we have the following expression for the balance constants:

$$\ln(K_p) = -\frac{1}{R \cdot T}\left(\nu^T \cdot A \cdot W\right). \tag{43}$$

The equation (40), (41) and (42) were obtained in the hypothesis of neglecting the mixing effects. If we give up this supposition, then the partial molar enthalpy and the mixture entropy of the substance i, ΔH_i and ΔS_i , are introduced and they are added at H_i and S_i in (25), (26) and (27). The thermodynamic functions of the system take the following form:

$$H(T) = \nu^T \cdot \left(A \cdot U + \Delta H\right) \tag{44}$$

$$S(T) = \nu^T \cdot \left(A \cdot V + \Delta S\right), \tag{45}$$

$$\Delta G = \Delta H - T\Delta S \tag{46}$$

where ΔH and ΔS are column vectors with the components ΔH_i and ΔS_i .

In ideal mixtures we have:

$$\Delta H_i = 0, \tag{47}$$

$$\Delta S_i = -R \cdot \ln(\nu_i). \tag{48}$$

If the condition (47) is not fulfilled, that means $\Delta H_i \neq 0$, bat the relation (48) is in vigor, the mixtures are named regular. In applications we presume known the followings: the mixture composition (ν), the temperature (T) and the pressure (p). if chemical reactions are taking place within the system for a given p, the thermodynamic functions H, S and G depend not only on the T, but also on time, and for a given initial composition the ulterior composition will be determined by the kinetics of the system processes. For the balance state we calculate at the beginning the balance composition and then we appeal to the relations (44), (45) and (46) or (40), (41) and (42).

6. Calculation of the thermodynamic properties

We adopt the molar isobar heat on the following form:

$$C_p(T) = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^{-2}, \qquad (49)$$

so that:

$$\varphi_1(T) = 1\,,\ \varphi_2(T) = T\,,\ \varphi_3(T) = T^2\,,\ \varphi_4(T) = T^3\,,\ \varphi_5(T) = T^{-2} \qquad (50)$$

At the calculation of the functions U_j şi V_j for the arbitrary temperature T_j the 0 K value is adopted.

6.1 Finding the $a_j,\ j = 1,2,\ldots 5$, coefficients for different substances.

We consider known the values of the isobar molar heats foe some substances at five values at the absolute temperature. In order to find the coefficients $a_j,\ j = \overline{1,5}$ from the relation (49) we apply the method of linear algebra. It results a linear algebraic system of five equations with five unknowns that can be solved by matrix method. The unknowns are given as elements of the matrix A, and its coefficients are the elements of the matrix Z:

$$Z = \begin{pmatrix} 1 & T1 & T1^2 & T1^3 & T1^{-2} \\ 1 & T2 & T2^2 & T2^3 & T2^{-2} \\ 1 & T3 & T3^2 & T3^3 & T3^{-2} \\ 1 & T4 & T4^2 & T4^3 & T4^{-2} \\ 1 & T5 & T5^2 & T5^3 & T5^{-2} \end{pmatrix} \qquad A = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ a_5 \end{pmatrix}$$

The coefficients $a_j,\ j = \overline{1,5}$ are determined multiplying the matrix:

$$A = Z^{-1} \cdot C_p$$

The numerical values of the coefficients $a_j,\ j=\overline{1,5}$ are given in the table 1.

Table 1

O_2	Temperature T $[K]$	Molar isobar heat$(1\ \text{bar})$ C_p $\left[\frac{kJ}{kmol \cdot K}\right]$	Coefficients of the molar isobar heat calculated by the method of the linear algebra a_j
1	300	31,963	32,099
2	800	35,212	$5{,}139 \cdot 10^{-3}$
3	1200	36,552	$-1{,}347 \cdot 10^{-6}$
4	1900	38,269	$1{,}912 \cdot 10^{-10}$
5	2500	39,489	$-1{,}485 \cdot 10^{5}$
Air			
1	300	30,313	27,269
2	800	33,454	0,011
3	1200	35,045	$-4{,}479 \cdot 10^{-6}$
4	1900	36,510	$7{,}034 \cdot 10^{-10}$
5	2500	37,348	$1{,}601 \cdot 10^{4}$
H_2			
1	300	29,350	26,292
2	800	30,481	$1{,}024 \cdot 10^{-3}$
3	1200	32,198	$8.1 \cdot 10^{-8}$
4	1900	34,835	$-1{,}944 \cdot 10^{-10}$
5	2500	36,343	$1{,}394 \cdot 10^{5}$
CO_2			
1	300	47,020	41.489
2	800	51,268	0.018
3	1200	58,073	$-7{,}638 \cdot 10^{-6}$

4	1900	60,209	$1,143\cdot10^{-9}$
5	2500	61,004	$-2,939\cdot10^{5}$
CO			
1	300	30,272	27,131
2	800	33,621	0,012
3	1200	35,212	$-4,967\cdot10^{-6}$
4	1900	36,510	$7,756\cdot10^{-10}$
5	2500	37,138	$8,539\cdot10^{3}$

Methane CH_4	Temperature T $[K]$	Molar isobar heat $(1\ \text{bar})\ C_p$ $\left[\frac{kJ}{kg\cdot K}\right]$	Coefficients of the molar isobar heat calculated by the method of the linear algebra a_j
1	100	2,254	2,35
2	300	2,663	$7,681\cdot10^{-4}$
3	500	2,972	$1,386\cdot10^{-6}$
4	800	3,433	$-8,13\cdot10^{-10}$
5	1000	3,690	$-1,863\cdot10^{3}$
Ethane C_2H_6			
1	100	1,825	3,389
2	200	2,033	-0,012
3	300	2,191	$3,995\cdot10^{-5}$
4	400	2,437	$-3,609\cdot10^{-8}$
5	500	2,598	$-6,788\cdot10^{3}$
Propane			
1	100	1,708	1,505
2	200	1,911	$2,03\cdot10^{-3}$
3	300	2,114	0

4	400	2,317	0
5	500	2,520	$-1,05 \cdot 10^{-10}$

6.2. Calculation of the enthalpy, entropy and isobar potential

With the aid of the molar isobar heats' coefficients, we calculate the enthalpy, entropy and isobar potential with the relations:

$$H(T) = H(T_0) + \int_{T_0}^{T} C_p(T)\, dT\,;\; S(T) = S(T_0) + \int_{T_0}^{T} \frac{C_p(T)}{T}\, dT\,;$$

$$G(T) = H(T) - TS(T)\,.$$

Conclusions

For the air, we consider T_0=200 (K) and the enthalpy, entropy and isobar potential have the following representations:

$$H(T_0) = 5764{,}8\ \text{kJ/kmol}\,,\quad S(T_0) = 172{,}392\ \text{kJ/kmol.K}$$

$$C_p(T) = 27{,}269 + 0{,}011 \cdot T - 4{,}479 \cdot 10^{-6} \cdot T^2 + 7{,}034 \cdot 10^{-10} \cdot T^3 + 1{,}601 \cdot 10^4 \cdot T^{-2}$$

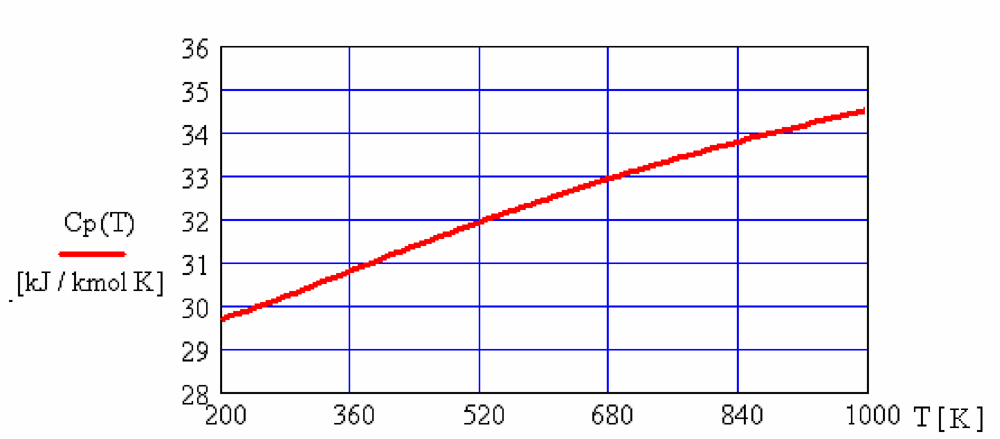

Fig. 1 Variation of the air molar isobar heat with the temperature

$$H(T) := H(T0) + \int_{T0}^{T} Cp(T)\,dT \qquad S(T) := S(T0) + \int_{T0}^{T} \frac{Cp(T)}{T}\,dT$$

$$G(T) := H(T) - T \cdot S(T)$$

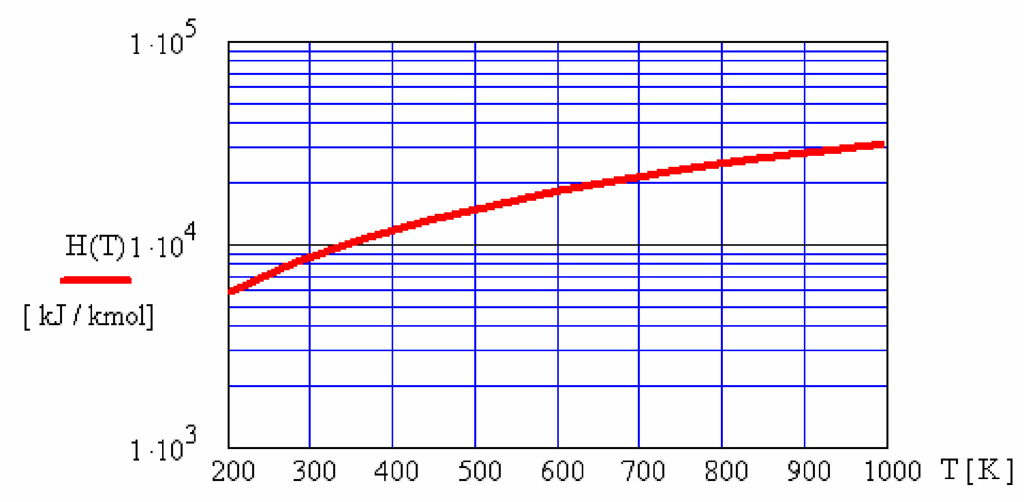

Fig.2. Dependency of the air specific enthalpy with the temperature

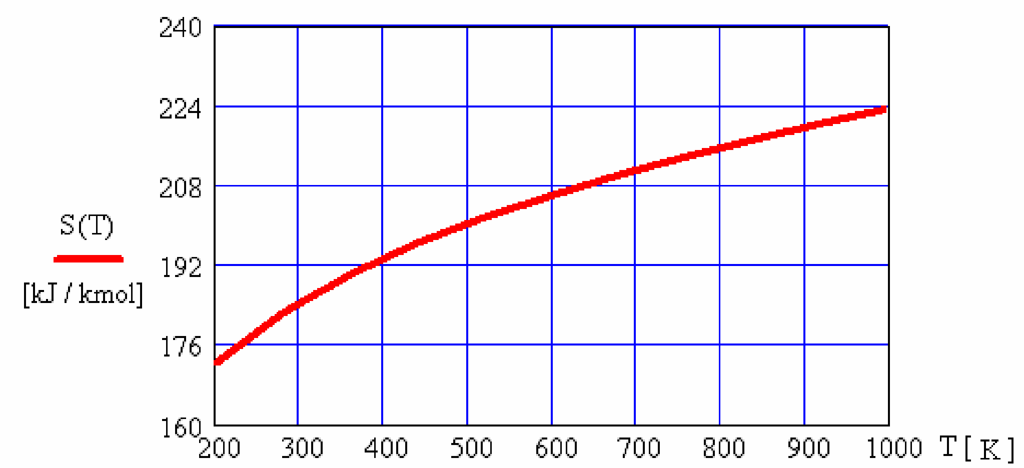

Fig. 3 Variation of air entropy with the temperature

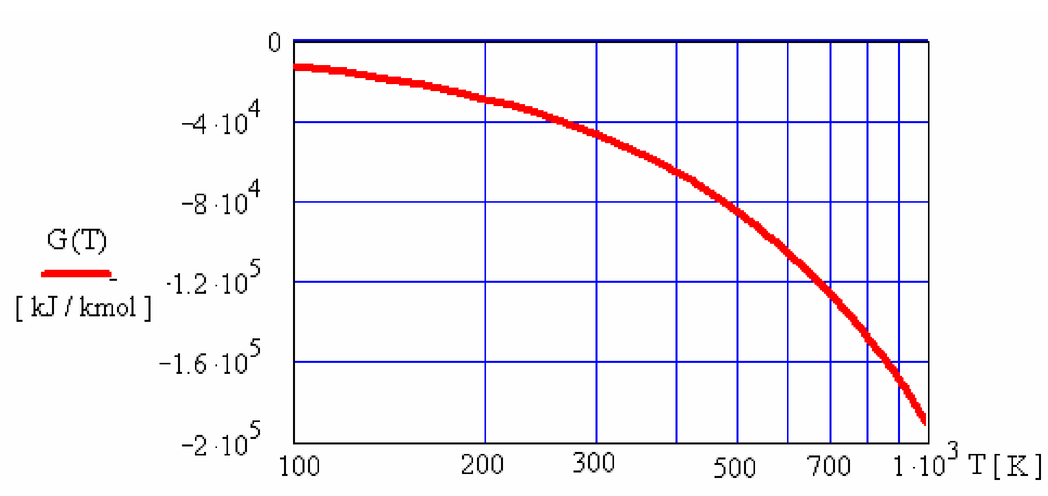

Fig. 4 Variation of the air isobar potential with the temperature

For the methane (CH_4) enthalpy, entropy and isobar potential have the following numeric values:

T [K]	H(T) [kJ / kmol]	S(T) [kJ / kmol]	G(T) [kJ / kmol]
200	289.68063	189.76912	-37664.14252
300	548.235	190.81533	-56696.36467
400	822.10313	191.60215	-75818.75686
500	1111.4182	192.24709	-95012.12702
600	1416.44663	192.80279	-114265.22534
700	1737.14443	193.29684	-133570.64163
800	2073.04638	193.74515	-152923.07478
900	2423.229	194.15745	-172318.4752
1000	2786.29583	194.53987	-191753.571

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