

# Sensitivity of the chemical exergy for atmospheric gases and gaseous fuels to variations in ambient conditions

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**Abstract** – Variation of the chemical exergy with ambient temperature from  $-30\text{ }^{\circ}\text{C}$  to  $45\text{ }^{\circ}\text{C}$ , pressure from 0.6 to 1.1 bar, and relative humidity (RH) from 10% to 100% was investigated for gaseous fuels and atmospheric gases on the basis of Szargut's model. It was found that the variation is significant. At ambient pressure at 1 atm and RH at 70%, the chemical exergy of hydrogen increased 0.7-0.8% per  $10\text{ }^{\circ}\text{C}$  of lower ambient temperature, while for methane the increase was 0.25-0.30%. For other gaseous hydrocarbons the increase was 0.08-0.20%. An error analysis verified that the uncertainties in the results were 2-3 orders of magnitudes less than the results. It was shown that assuming the atmospheric mole fraction of water vapor constant when varying the temperature, leads to unrealistic and even unphysical results, giving the opposite behavior of the model. Calculating the change of chemical exergy over certain processes showed that separation of air gases is potentially most efficient in cold climate, while water electrolysis to hydrogen is favorable in warmer climate. Combustion reactors and fuel cells are potentially most efficient in cold climate.

Key words: second law of thermodynamics, chemical exergy, ambient conditions, dead state, reference state, humidity.

## 1 Introduction

Depletion of cheap energy resources leads to greater interest both in energy conservation and search for new fields of oil and gas. The latter brings the exploration and extraction industry more and more into the Arctic. The cold climate presents severe challenges to the technology and to design and operation of the equipment. On the other hand, it is well known that a lower ambient temperature gives a greater potential for thermal energy conversion. This additional potential has been investigated in a number of studies. It is utilized when convenient, although sometimes counteracted by some equipment producers (e.g. by requiring preheating of low-temperature intake air to gas-turbine compressors).

The "reference state" usually found in collections of thermochemical data has a pressure of 1 atm (sometimes 1 bar) and a temperature of  $25\text{ }^{\circ}\text{C}$ . This state feels relevant in an indoor laboratory, and may even be representative for the outdoor conditions in some parts of the world. However, when seen from the shores of the Arctic Ocean, or even more from inland

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locations of the Arctic, a temperature of 25 °C does not feel very relevant for the locally experienced temperatures.

Large areas have winter month-average temperatures below 0 °C, while the extreme situation is found in North-East Siberia, with a January month-average temperature below –50 °C. The other extreme is found in Sahara and the Middle-East, with month averages above 40 °C. The moisture content will vary according to the temperature and the relative humidity. The average ambient pressure depends on the elevation, from 1.06 bar at 400 m below sea level to 0.60 bar at 4200 m above, and 0.32 bar at 8800 m [1], showing some variation with the local weather conditions.

Considerable work has been conducted over a long time to establish the basis for exergy analyses of industrial processes. In recent decades, many efforts have been made to figure out the determination of the chemical exergies of different substances [2,3,4,5,6] (cf. review in [6]). In this aspect, the chemical exergies of gaseous hydrocarbons may be regarded as a well established task. However, it is well known that thermal properties related to chemical reactions show some variation with temperature and pressure. Furthermore, the composition of the local atmosphere plays a role in determining the chemical exergy of a substance. Hence, some variation with ambient conditions should be expected. The purpose of this study is to investigate the variation of chemical exergy as a function of the state of the atmosphere. This variation of chemical exergy is hardly considered in previous studies concerning performance sensitivity to ambient conditions.

One issue debated in the literature is the basic assumptions for chemical exergy. Some proposed models are based on the condition that the reference environment should be a system in equilibrium. This can be said to be a consequence of the understanding that the environment should not be able to produce any work. Other models are based on the fact that the real environment is not in global equilibrium. Relevant examples in the present context are that the atmosphere rarely is saturated with water vapor, and that the air, ocean, and earth surface have different temperatures.

In the present study, the effects of varying local ambient conditions on the chemical exergy have been investigated. First the models for chemical exergy of atmospheric gases, liquid and solid water, and gaseous substances are reviewed. The effects of varying ambient temperature, moisture content, and pressure are assessed. Also the effect of increased CO<sub>2</sub> content in the atmosphere is tested. Subsequently, the effects on the change of chemical exergy through some technical processes are investigated: Air-gas separation, water electrolysis, combustion with all products mixed, and solid-oxide fuel-cell like reactors.

## **2 Background**

### **2.1 Fuels, heating values, and temperature**

Commercially, fuels are usually evaluated according to their lower heating value (LHV). This shows a small variation with temperature, which is incorporated in international and national technical standards. An ISO standard [7] specifies a “standard reference condition” for natural gas to 15 °C (288.15 K), 1 atm (101325 Pa). An informative annex of [7] lists reference temperatures from various national standards, ranging from 0 °C to 25 °C, which to some extent reflects the variation in local ambient conditions. The standard also specifies

conversion factors for recalculating LHV from one set of conditions to another. For instance, the LHV at 0 °C should be 0.03% higher than that of 25 °C. This difference is negligible to ordinary users of fuels. However, for large quantities, it might be of interest. For instance, 0.03% of the total Norwegian export of natural gas in 2005 was 1 PJ, which corresponded to 9% of the domestic end use.

## 2.2 Chemical exergy and thermomechanical flow exergy

The flow exergy of a substance is the theoretically obtainable work when the substance is brought into total equilibrium with the local environment. It can be split into chemical exergy and thermomechanical flow exergy,

$$\varepsilon = \varepsilon^{\text{ch}} + \varepsilon^{\text{tm}}. \quad (1)$$

The thermomechanical exergy (also known as physical exergy) represents the deviation in temperature and pressure between the flowing matter and the ambient. It also includes the potential and kinetic energy, although these contributions are not treated in the present study. The chemical exergy represents the deviation in chemical composition between the flowing matter and the local environment.

The molar thermomechanical flow exergy is expressed as

$$\varepsilon^{\text{tm}} = h - h_0 - T_0(s - s_0), \quad (2)$$

where  $h$  and  $s$  are the molar enthalpy and entropy, respectively, of the flowing matter, while  $h_0 = h(T_0, p_0)$  and  $s_0 = s(T_0, p_0)$ .

## 2.3 Thermomechanical exergy and temperature

The ratio of maximum obtainable work to obtainable (or supplied) heat increases with higher gas temperature and lower ambient temperature. In gas-turbine power plants, the turbine inlet temperature (TIT) is a crucial parameter for efficiency. A modern gas turbine may have a TIT of 1300 °C and a pressure ratio of 25. The overall thermal efficiency, the ratio of net power to rate of fuel LHV, of the best real installations (combined cycles) is close to 60%.

Considerable efforts are made to increase the TIT and, hence, the efficiency. With some idealizations for the flue gas flowing from combustor to turbine, the theoretically obtainable work-to-heat ratio can be expressed as

$$\frac{w_{\text{max}}}{q} = \frac{\varepsilon^{\text{tm}} - w_c}{h - h_0 - w_c} \approx 1 - \frac{T_0}{(T - T_0)(p/p_0)^{R/c_p}} \left( \ln \frac{T}{T_0} - \frac{R}{c_p} \ln \frac{p}{p_0} \right). \quad (3)$$

Here,  $w_c$  is the work required for isentropic compression of the gas from  $p_0$  to  $p$ ,  $c_p$  is the molar specific heating capacity averaged over the relevant temperature interval, and  $R$  is the universal gas constant. With a realistic temperature of  $T=1573.15$  K (1300 °C), an ambient temperature of  $T_0 = 298.15$  K (25 °C), and a pressure ratio of  $p/p_0 = 25$ , the ratio of Eq. (3) is 71%. A rise of the temperature from 1300 to 1400 °C increases the ratio by 1.0 %-point. Alternatively, the same increase is seen by reducing the ambient temperature from 25 to 8 °C, and also by increasing the pressure ratio from 25 to 36.

The efforts made to increase the TIT illustrates that differences in exergy of magnitude 1%, or even less, are of interest for technological development.

The amount of moisture in the air will affect the mass flow rate and heating capacity of the working fluid. Hence, the ISO standard for gas-turbine testing [8] specifies “standard conditions”, including relative humidity (RH), of the intake air. In this standard, temperature and pressure are equal to that of natural gas cited above, and the RH is 60%.

### 3 Determining the chemical exergy for off-reference ambient pressure, temperature and humidity.

#### 3.1 Local ambient conditions

The state of the local atmosphere is determined by the temperature,  $T_0$ , pressure,  $p_0$ , and the composition. The relative content of gases other than water vapor can be regarded constant. Therefore, the composition is given by the moisture content. The atmospheric mole fraction of water vapor can be expressed as

$$X_{\text{H}_2\text{O}}^e = \varphi p_{g0} / p_0, \quad (4)$$

where  $\varphi$  is the relative humidity (RH) and  $p_{g0}$  is the saturation pressure at temperature  $T_0$ . It is important to note that the saturation pressure of water, i.e. the partial pressure of water vapor at unity RH, has a strong variation with temperature.

When the mole fractions  $X_i^{\text{dry}}$  of dry air (i.e. without  $\text{H}_2\text{O}$ ) are assumed constant, the local atmospheric mole fractions of gases other than  $\text{H}_2\text{O}$  can be expressed as

$$X_i^e = (1 - X_{\text{H}_2\text{O}}^e) X_i^{\text{dry}}. \quad (5)$$

This mole fraction corresponds to the atmospheric partial pressure  $p_i^e = X_i^e \cdot p_0$  of the species.

These expressions imply the assumption of ideal gases for all atmospheric gases. For consistency, the temperature and pressure of the locally available liquid water or ice were assumed to be those of the atmosphere.

#### 3.2 Chemical exergy of atmospheric gases, liquid water, and ice

The molar chemical exergy of an atmospheric gas is expressed as

$$\varepsilon_i^{\text{ch}} = -RT_0 \ln X_i^e, \quad (6)$$

where  $R$  is the universal gas constant. This is equal to the work obtained from a reversible, isothermal ( $T_0$ ) expansion from atmospheric pressure ( $p_0$ ) to the atmospheric partial pressure ( $p_i^e$ ).

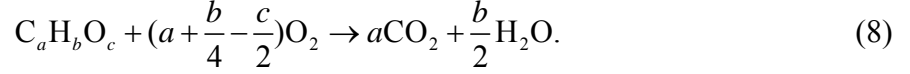
The molar chemical exergy of liquid water can be expressed as [9]

$$\varepsilon_w^{\text{ch}} = v(p_0 - p_{g0}) - RT_0 \ln \varphi, \quad (7)$$

where  $v$  is the molar volume of compressed water. Here, this expression was assumed valid for solid water (ice) as well.

### 3.3 Gaseous fuels

The stoichiometric reaction between a fuel and oxygen can be written as



For hydrocarbons  $c=0$ , for hydrogen  $a=c=0$  and  $b=2$ , while for carbon monoxide  $b=0$  and  $a=c=1$ . The chemical exergy is determined from

$$\varepsilon_i^{\text{ch}} = -\Delta G(T_0, p_0) + \sum_{j \neq i} \nu_j \varepsilon_j^{\text{ch}}, \quad (9)$$

where the chemical exergies of all products and co-reactants are evaluated at ambient temperature and pressure. Water ( $H_2O$ ) is evaluated in gaseous state. The change of Gibbs function for the reaction is

$$\Delta G(T, p) = \sum_j \nu_j g_j(T, p) \quad (10)$$

when reactants are supplied and products released separately each at the relevant state  $(T, p)$ .

Here,  $g_j(T, p)$  is the molar Gibbs function of each pure species and  $\nu_j$  is the stoichiometric coefficient of each species in the reaction, with negative values for the reactants and positive for products, thus  $\nu_{C_a H_b O_c} = -1$ ,  $\nu_{O_2} = -(a + b/4 - c/2)$ ,  $\nu_{CO_2} = a$ , and  $\nu_{H_2O} = b/2$ .

Correspondingly, the entropy and enthalpy changes are,

$$\Delta S(T, p) = \sum_j \nu_j s_j(T, p) \quad (11)$$

and

$$\Delta H(T, p) = \sum_j \nu_j h_j(T, p), \quad (12)$$

where, respectively,  $s_j(T, p)$  and  $h_j(T, p)$  are the molar entropy and enthalpy of each pure species. For fuels, the quantity of Eq. (12) equals the negative of the lower heating value (LHV),  $h_{\text{LHV}}$ , at the specified state. The relation between the three quantities is

$$\Delta G(T, p) = \Delta H(T, p) - T \Delta S(T, p). \quad (13)$$

Data for the molar Gibbs functions, molar entropy, and molar enthalpies are available for a certain reference state  $(T_{\text{ref}}, p_{\text{ref}})$ , usually 25 °C (298.15 K) and 1 atm (101235 Pa). Similarly, the molar enthalpies and entropies are available at this reference state. For deviating conditions, the expressions of Eqs. (10) and (12), assuming ideal gases, are elaborated as

$$-\Delta G(T_0, p_0) = -\Delta G^{\text{ref}} + (T_{\text{ref}} - T_0)(-\Delta S^{\text{ref}}) + W_1 + W_2. \quad (14)$$

$$-\Delta H(T_0) = h_{\text{LHV}}(T_0) = -\Delta H^{\text{ref}} + \sum_j \nu_j \int_{T_{\text{ref}}}^{T_0} c_{p,j}(T) dT \quad (15)$$

Here, the notation  $\Delta G^{\text{ref}} = \Delta G(T_{\text{ref}}, p_{\text{ref}})$ ,  $\Delta S^{\text{ref}} = \Delta S(T_{\text{ref}}, p_{\text{ref}})$ , and  $\Delta H^{\text{ref}} = \Delta H(T_{\text{ref}})$ , is used and for shortness

$$W_1 = \sum_j \nu_j \int_{T_{\text{ref}}}^{T_0} c_{p,j}(T) \left(1 - \frac{T_0}{T}\right) dT \quad (16)$$

and

$$W_2 = T_0 R \sum_j \nu_j \ln \frac{p_0}{p_{\text{ref}}}. \quad (17)$$

Thus, the chemical exergy at a certain state can be expressed [2,9] as

$$\varepsilon_i^{\text{ch}} = -\Delta G^{\text{ref}} + (T_{\text{ref}} - T_0)(-\Delta S^{\text{ref}}) + W_1 + W_2 + \sum_{j \neq i} \nu_j \varepsilon_j^{\text{ch}}, \quad (18)$$

where the summation in the last term is made over products and co-reactants (here: CO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>) but not the substance itself. According to Szargut [2], the terms here denoted  $W_1$  and  $W_2$  can be neglected.

Using Eq.(13), alternative expressions of the two first right-hand-side terms of Eq.(14) are obtained:

$$-\Delta G^{\text{ref}} + (T_{\text{ref}} - T_0)(-\Delta S^{\text{ref}}) = -\Delta G^{\text{ref}} \frac{T_0}{T_{\text{ref}}} + \frac{T_{\text{ref}} - T_0}{T_{\text{ref}}} (-\Delta H^{\text{ref}}), \quad (19)$$

or

$$-\Delta G^{\text{ref}} + (T_{\text{ref}} - T_0)(-\Delta S^{\text{ref}}) = -\Delta H^{\text{ref}} - T_0(-\Delta S^{\text{ref}}). \quad (20)$$

By using Eqs. (19) and (6), the chemical exergy from Eq.(18) can be re-expressed in terms of the chemical exergy at the reference condition:

$$\varepsilon_i^{\text{ch}} = \varepsilon_i^{\text{ch,ref}} \frac{T_0}{T_{\text{ref}}} + \frac{T_{\text{ref}} - T_0}{T_{\text{ref}}} (-\Delta H^{\text{ref}}) + W_1 + W_2 + T_0 R \sum_{j \neq i} \nu_j \ln \frac{X_j^{\text{ref}}}{X_j^e}. \quad (21)$$

Here,  $\varepsilon_i^{\text{ch,ref}}$  and  $X_j^{\text{ref}}$  are values at the reference state  $(T_{\text{ref}}, p_{\text{ref}}, \varphi_{\text{ref}})$ . For a substance with  $c < b/2$  in Eq. (8), the last term will be positive when  $X_j^e$  is less than  $X_j^{\text{ref}}$ . This is the case when  $T_0 < T_{\text{ref}}$  with unchanged  $\varphi$  and  $p_0$ , and when  $p_0 > p_{\text{ref}}$  with unchanged  $\varphi$  and  $T_0$ . Hence, for hydrocarbons, this term will contribute to a larger chemical exergy for a lower ambient temperature. The expression in Eq. (21) is similar to the model presented by Kotas [5,10], except that he omitted the last three terms. Neglect of the last term implies that the absolute moisture content is unchanged with temperature (see below).

### 3.4 Gas mixtures

For a mixture of gases, the molar chemical exergy can be expressed as

$$\varepsilon_{\text{mix}}^{\text{ch}} = \sum_i X_i \varepsilon_i^{\text{ch}} + RT_0 \sum_i X_i \ln X_i. \quad (22)$$

Here, the molar chemical exergies of the individual gases are expressed either from Eq.(18) or Eq. (6), and  $X_i$  is its mole fraction in the mixture.

### 3.5 Previous investigations

The model above, Eq.(18), was outlined by Morris and Szargut [2,11]. They chose 25 °C (298.15 K), 1 atm (101325 Pa), and 70% RH, as the reference state and discussed briefly the consequences of the choice of RH. One important effect (cf. [12]) of choosing an RH somewhat less than 100% is that liquid water is attributed a thermodynamic value according to Eq. (7). However, the consequences of ambient conditions different from the reference were not investigated.

With the basic assumption of an environment in equilibrium, Ahrendts [3] suggested to use 25 °C, 1.019 atm (103250 Pa), and 100% RH as the standard or reference state for chemical exergy. One effect of this choice is a lower chemical exergy for gaseous and liquid water, the latter being very small.

Based on Szargut's model, Kotas [5,10] gave a more elaborate presentation for use in thermal engineering. He also chose 25 °C, 1 atm as the reference state. For the humidity, he specified an H<sub>2</sub>O partial pressure of 0.0088 bar (following [2]). This partial pressure corresponds to an RH of 27.8% at 25 °C, and is equal to the saturation pressure at 5.1 °C. When presenting the model for variation with ambient state, he neglected the three last terms of Eqs. (18) and (21). Neglect of the last term of the two equations implies that the atmospheric mole fraction of H<sub>2</sub>O is held constant at all temperatures. With a pressure of 1 atm, this means e.g. an RH of 9% at 45 °C or 100% at 5.1 °C. Below 5.1 °C, this partial pressure implies supersaturation (subcooling), which is an unstable situation.

These and some other suggestions were reviewed by Gallo and Milanez [13] and some more by Muñoz and Michaelides [14]. They compared the outcome of the different models in terms of chemical exergy for various substances at one single ambient state. A similar comparison was included by Rosen and Dincer [15].

The only investigations specifically on the variation of chemical exergy with ambient conditions seemed to be conducted by Garfias and Rivero [16,17]. In the latter paper, they showed the behavior of chemical exergy of atmospheric gases with varying RH, temperature, pressure, and CO<sub>2</sub> content. The study presented in [16] includes variation of chemical exergy of hydrocarbons with ambient temperature. The models were based on the models of Szargut and Kotas described above. The ambient pressure and H<sub>2</sub>O mole fraction were kept constant, similar to Kotas' assumption. Hence, the comparison was essentially a comparison between two different constant H<sub>2</sub>O mole fractions (0.0087 and 0.0219) at different temperatures.

In a study on aerospace engines, Etele and Rosen [18] investigated the variation of fuel exergy with altitude. The combination of lower pressure and lower temperature when rising from sea level (288 K, 1.013 bar) to 11000 m altitude (217 K, 0.227 bar), assuming constant atmospheric mole fraction of H<sub>2</sub>O, caused a reduction in chemical exergy of approximately 0.7%. A further rise in elevation to 15000 m (217 K, 0.120 bar; i.e. constant temperature) increased the chemical exergy by 0.1%. These figures corresponded to a 1.5%-point reduction in the overall engine exergy efficiency. In the study, the atmospheric water vapor mole fraction was held constant and equal to that of saturation at 13.5 °C.

A number of studies are published that shows the effects on certain devices at varying ambient conditions. The majority of these focuses on the effect on thermomechanical exergy, and the chemical exergy is most often not adjusted with the ambient conditions.

## 4 Calculations

### 4.1 Atmospheric conditions and thermochemical data

The atmospheric state at a location shows daily and seasonal variations. Different locations have different local climates depending of latitude, elevation, relation to open ocean, etc. In this study, the ambient temperature was varied from  $-30$  to  $45$  °C. Although actual temperatures may occur outside this range (in particular, below), it includes the design temperature of most installations of interest. The ambient pressure was varied from 0.6 to 1.2 bar, which includes most relevant design values, except for very high mountains, aviation, deep mines, and sub-sea operations. The relative humidity was varied from 0.1 to unity.

The investigated substances are in gaseous form over these ranges of properties, except water ( $\text{H}_2\text{O}$ ), butane, pentane, and hexane, which have fictitious gaseous states for temperatures below the saturation temperature. However, when the substances occur at sufficiently low partial pressures in mixtures, these fictitious states can be used.

Data for Gibbs functions, enthalpies, and entropies at the reference state,  $T_{\text{ref}}=298.15$  K and  $p_{\text{ref}}=101325$  Pa, were obtained from [19]. Data for saturation pressure of water at the various temperatures were also found in this source. The saturation pressure has a strong variation, from 38.1 Pa at  $-30$  °C and 618 Pa at  $0$  °C, to 9593 Pa at  $45$  °C. Temperature-dependent functions for ideal-gas specific heats were [19,20] were integrated analytically for use in Eqs. (15) and (16). The composition of dry air [1] (referring to the US Standard Atmosphere 1976), was updated with more recent data for  $\text{CO}_2$ , 375 ppm for 2004 [21], and the  $\text{O}_2$  content was reduced with the same amount. The dry-air mole fractions were then 0.78084 for  $\text{N}_2$ , 0.209415 for  $\text{O}_2$ , 0.000375 for  $\text{CO}_2$ , and 0.00934 for Ar. Following Szargut's proposal [9], the reference relative humidity,  $\varphi_{\text{ref}}$ , was set to 0.70. At  $25$  °C, 1 atm, this means a mole fraction of 0.02189 for  $\text{H}_2\text{O}$ .

All calculations were made in a spreadsheet.

Table 1 shows the calculated chemical exergies at the reference conditions  $25$  °C, 1 atm, 70% RH. In the following, deviations from these values will be presented as relative deviations, that is,

$$\text{Relative deviation} = \frac{\varepsilon_i^{\text{ch}}}{\varepsilon_i^{\text{ch,ref}}} - 1. \quad (23)$$

The nominator of the first term is the chemical exergy determined at the actual ambient temperature, pressure, and humidity. The denominator is the chemical exergy determined at the reference conditions.

### 4.2 Variation with temperature and moisture content

The variation of chemical exergy with ambient temperature is shown in Figure 1 for the atmospheric gases nitrogen ( $\text{N}_2$ ), oxygen ( $\text{O}_2$ ), carbon dioxide, argon, and water vapor at ambient pressure 1 atm and RH of 70%. Hydrogen ( $\text{H}_2$ ) is included in the graph as well. It



was observed that, due to the variation of saturation pressure, water vapor has a very large relative variation in chemical exergy over the range of ambient temperature. The other atmospheric gases showed the opposite tendency compared with H<sub>2</sub>O. This was mainly due to the proportionality with ambient temperature, cf. Eq.(6). The effect of varying mole fraction of the specific gas according to the dilution by H<sub>2</sub>O, Eq.(5), played a modest role, except for nitrogen. Figure 2 shows the variation of chemical exergy for nitrogen for varying ambient temperature and RH. As the maximum dilution with water vapor rises with temperature, also the variation with RH is seen to increase. For oxygen, the corresponding variation at 45 °C ranged from 5 to 11% of relative deviation, and for CO<sub>2</sub> from 6.1 to 7.2%.

Also shown in Figure 2 for N<sub>2</sub> is a series where the atmospheric partial pressure of H<sub>2</sub>O was kept constant at 880 Pa. This is the reference value chosen by Kotas [5,10]. It is seen that this model gave a somewhat different variation of chemical exergy with ambient temperature. If extrapolated below the saturation temperature for this pressure, 5.1 °C, it gave a value for the chemical exergy higher than that of 100% RH. Although subcooled vapor can exist in some cases, the situation is unstable. As a general model, it must be regarded unphysical below the saturation temperature. For high temperatures, on the other side, this value of H<sub>2</sub>O partial pressure corresponds to unrealistically low RH.

The variation of chemical exergy with ambient temperature for hydrogen, gaseous hydrocarbons, and carbon monoxide is shown in Figure 3 for ambient pressure 1 atm and 70% RH. This relative variation was much less than for the atmospheric gases, however, appreciable. The variation depended, not unexpectedly, on the hydrogen content and, hence, on the amount of H<sub>2</sub>O in the stoichiometric product. The variation was the least for CO, which was reduced by 0.07 %-points for each 10 °C of higher temperature. The chemical exergy for butane was reduced by 0.09 %-points per 10 °C of higher temperature above 0 °C, and by 0.13 %-points below 0 °C. For methane the figures were 0.24 and 0.30 %-points above and below 0 °C, respectively. The hydrogen chemical exergy was reduced by 0.72 %-points per 10 °C of increased temperature above 0 °C, and by 0.81 %-points below 0 °C.

The effect of RH is shown in Figure 4 for methane. It is seen that within these ranges of ambient RH and temperature, the chemical exergy of methane varied with 3 %-points. Within the RH range at a given ambient temperature, the variation in chemical exergy was more than 1 %-point. Also shown in the figures is the variation of chemical exergy with temperature when the atmospheric partial pressure of H<sub>2</sub>O is kept constant at 880 Pa (see above). It is seen that this model gives the opposite variation of chemical exergy with ambient temperature. Furthermore, as this is the saturation pressure at 5.1 °C, it will be unphysical below that temperature.

The corresponding variations for the other hydrocarbons were similar to that of methane, but somewhat smaller, mainly due to the smaller variation with ambient temperature (cf. Figure 3). For butane, Figure 5, the variation with RH over the range 0.1 to 1.0 at 15 °C was approximately 1 %-point.

The chemical exergy of CO was negligibly affected by the ambient RH. The biggest variation was seen for hydrogen, ranging from a relative deviation of -1.8% at 100% RH, 45 °C to 5.8% at 10% RH, -30 °C. At 15 °C and a variation over the RH range from 0.1 to 1.0, the chemical exergy varied with 2.4 %-points.

Variation in chemical exergy with RH at 1 atm, 25 °C is shown for atmospheric gases and hydrogen in Figure 6 and for some fuels in Figure 7. The magnitude of the deviation from the reference value appeared to depend on the ratio of hydrogen to carbon in the fuel. The H-to-C ratio was more important than the size of the molecule.

### 4.3 Variation with atmospheric pressure and temperature

Figure 8 shows the effect of ambient pressure on the chemical exergy for methane. As seen, the range of pressures investigated gave a variation of less than 0.5 %-point for a given temperature. This graph was made for 70% ambient RH, and the same relative variation was seen at e.g. 30% RH. For the heavier hydrocarbons, the variation was even narrower, e.g. for butane, Figure 9, approximately 0.20–0.25 %-points for the range of pressures. Also for CO, the variation was modest, from 0.22 %-points at –30 °C to 0.33 %-points at 45 °C. For hydrogen, the variation was larger; from 0.77 to 1.05 %-points.

Lowering the ambient pressure at constant temperature and RH leads to a higher mole fraction of water vapor, Eq. (4), and thus to a reduced chemical exergy, Eq. (6). This reduces the mole fractions of the other atmospheric gases and, hence, increases their chemical exergies. The effect is strongly reduced at lower temperatures due to the lower saturation pressure of water. At 70% RH, the reduction of ambient pressure from 1 atm to 0.6 bar increased the chemical exergy of nitrogen by 2.7%-points at 45 °C, by 1% at 25 °C, and less than 0.2%-points below 0 °C. For oxygen, the increase was 0.6%-points at 45 °C. For CO<sub>2</sub> and argon, the increase was negligible.

### 4.4 Increase of CO<sub>2</sub> content in atmosphere

The CO<sub>2</sub> content of the atmosphere has increased during the past two or three centuries. The effect of this on chemical exergy was investigated by increasing the dry-air mole fraction of CO<sub>2</sub> from 280 ppm to 377 ppm and reducing the O<sub>2</sub> content correspondingly (see above).

The main effect was seen on the chemical exergy of CO<sub>2</sub>, which decreased by 4.4 %-points at –30 °C and by 3.3 %-points at 45 °C. Due to the adjustment in O<sub>2</sub> content, its chemical exergy increased by approximately 0.03%-points. The chemical exergy of CO increased with 0.21 %-points (at –30 °C) to 0.28 %-points (at 45 °C). The investigated hydrocarbons showed increased values at 0.08–0.09 %-points for methane (lowest carbon-to-hydrogen ratio) to 0.10–0.12 %-points for acetylene (highest C-to-H ratio). For hydrogen the change in chemical exergy was very small, due only to the adjustment in O<sub>2</sub> content and can be neglected.

### 4.5 Relative contributions to the chemical exergy and uncertainties in the results

When investigating the relative magnitudes of the terms in Eq. (18), it appeared that the main contribution came from the first right-hand-side (RHS) term ( $-\Delta G^{\text{ref}}$ ), while the variation was mainly due to the last term. The ratio of the third term,  $W_1$  (the  $c_p$ -term), to the first on the RHS was within  $\pm 2 \cdot 10^{-4}$  for all the investigated fuels and temperatures. Hence, for practical purposes this term can be neglected. The ratio of the pressure term  $W_2$  to the first term was

within  $\pm 3 \cdot 10^{-3}$  at the lowest investigated ambient pressure (0.6 bar). At pressures closer to the reference (1 atm), the impact of the term was even smaller, and zero at 1 atm. Thus, it may be argued that this term can be neglected. On the other hand, the term is rather easy to calculate. For the fuels with no net molar change ( $\sum_j \nu_j = 0$ ), i.e. methane and ethylene, the pressure term is zero in any case. The second RHS term had a magnitude relative to the first term in the range 0.1 to 0.4% for hydrocarbons at the lowest temperature ( $-30$  °C), and 1.1% and 1.8%, respectively, for  $H_2$  and CO. Table 2 shows the relative magnitudes of the terms in Eq. (18) for hydrogen and butane.

The data sources used in this study do not specify the accuracy of the data. Uncertainties in enthalpies of formation and entropy at the reference state are available from [22] for hydrogen, CO, methane, pentane, and hexane, and for  $CO_2$ ,  $H_2O$ , and  $O_2$ . These uncertainties have an impact on the quantities  $\Delta H^{ref}$  and  $\Delta S^{ref}$  at the reference state, and thus on  $\Delta G^{ref}$ . Based on these uncertainty data, the absolute error in LHV, chemical exergy (Eq.(18) with Eq.(20) introduced), and the Relative Deviation (RD) (Eq.(23)) were estimated. This gave uncertainties in the LHV of 0.05–0.06% for the hydrocarbons, 0.11% for CO, and less than 0.02% for hydrogen. For the chemical exergy, the uncertainty estimates were 0.05% for pentane and hexane, 0.08% for methane, 0.11% for CO, and less than 0.02% for hydrogen. In these estimates, the entropy-data uncertainties had an impact that was from one-fourth to one-seventh of that of the enthalpy data for the hydrocarbons, and less for CO and hydrogen.

The main results of this study, the relative variations of the chemical exergies, were to a lesser degree affected by these uncertainties. The uncertainty of the RD was estimated to  $4 \cdot 10^{-5}$  for methane,  $2 \cdot 10^{-5}$  for pentane, hexane, and CO, and  $1 \cdot 10^{-5}$  or less for hydrogen. Here, the enthalpy and entropy uncertainties had about the same impact for hydrogen, while the entropy uncertainties were the more important for the other five fuels. The error estimates showed only a weak variation with ambient conditions.

Provided that the uncertainty of the water saturation pressure at a given temperature was 1% or less, the error analysis showed that it had no significance on the errors for fuels. The uncertainty of the dry-air oxygen mole fraction was also found to have no effect on the error estimates for the fuels.

In summary, the uncertainties in the chemical-exergy results were found to be less than the sensitivity to ambient conditions. They were mainly due to uncertainties in enthalpy and entropy at the reference condition. The uncertainty of the relative deviation was two to three orders of magnitude less than the result itself.

## 5 Chemical-exergy change in some industrial processes

In exergy analyses, the objective is often not to determine the absolute values of exergy but to evaluate exergy changes. As some terms of the exergy model will appear on both the inflow and the outflow sides of a device balance, the dependency on ambient conditions of a change may differ from that of the absolute value. This will be investigated for four different devices in this section.

### 5.1 Separation of air gases

The chemical exergy of an atmospheric gas is interpreted as the minimum work required to separate it from atmospheric air. However, this is when the atmosphere is regarded as a reservoir, i.e. the composition is unaffected by the separation. A real device will drain a certain flow of air and separate the desired gas (or gases) from this. The separation process can be illustrated as shown Figure 10. The drained air is split into two or more flows: The separated gas(es) and the remaining gas mixture (depleted air). The minimum work, i.e. the exergy change, for separation of a single species  $i$  can be expressed as

$$\frac{\Delta E^{ch}}{(n_i \mathcal{E}_i^{ch})_{sep}} - 1 = \frac{(1 - \beta X_i^e) \ln(1 - \beta X_i^e) - X_i^e (1 - \beta) \ln(1 - \beta)}{\beta X_i^e \ln X_i^e}. \quad (24)$$

Here, the denominator is the chemical exergy of the separated gas. The nominator of the first LHS term,  $\Delta E^{ch}$ , is the change of chemical exergy over the device. The degree of separation,  $\beta$ , is the ratio of moles of species  $i$  separated to the total amount of this species in the inflow air. Equation (24) expresses the additional minimum work required for a separation device relative to the chemical exergy of the separated substance. This fraction depends on the ambient condition through the atmospheric mole fraction of the species. The additional required minimum work is seen to be reduced when the value of  $X_i^e$  is lowered, i.e. higher RH, lower ambient pressure, or higher ambient temperature (opposite for H<sub>2</sub>O). Also a lower degree of separation gives a lower value of Eq. (24). The required minimum work approaches the chemical exergy of the separated species as the degree of separation goes to zero. This corresponds to a device that is extracting the gas from the atmosphere directly, without affecting its composition (i.e. the atmosphere is a reservoir).

It should be noted that Eq.(24) has to be modified if any water condenses in the remaining gas. That is, if the quantity  $(\beta X_i^e)$  exceeds the value of  $(1 - \varphi)$ . The effluent chemical exergy is then reduced, and also the change of chemical exergy and the quantity of (the LHS of) Eq.(24). This is increasingly relevant for higher moisture content (higher ambient temperature and higher RH), for extraction of gases with a large mole fraction in air, and a large degree of separation. The question of regarding the condensed (i.e. distilled) water as a valuable output (cf. Szargut's argument [12] for a reference RH lower than 1) is not further treated in this study.

Figure 11 shows the variation of the quantity of the RHS of Eq.(24) with the degree of separation for each of the gases N<sub>2</sub>, O<sub>2</sub>, and Ar. In Series I-III, only one gas was separated, and the shown cases are for ambient conditions at 1 atm, 0 °C, and 90% RH. These results were not significantly different from the corresponding cases with 30% RH (not shown). They followed Eq.(24) closely, even though some water was condensed for high degrees of separation for N<sub>2</sub>, and O<sub>2</sub>. Also shown is the simultaneous separation of N<sub>2</sub> and O<sub>2</sub> ( $\beta_{N_2} = \beta_{O_2}$ ), and of all three gases ( $\beta_{N_2} = \beta_{O_2} = \beta_{Ar}$ ) for ambient conditions 0 °C, 30% RH and 90% RH, and all three gases at 25 °C, 90% RH. Here, the effect of varying atmospheric moisture content is seen. All these cases were calculated at 1 atm ambient pressure.

In summary, it was observed that both the chemical exergy of atmospheric gases (other than H<sub>2</sub>O) and the additional required minimum work for a separation device increased with higher absolute moisture content and with higher ambient temperature. Hence, a certain air-gas separation plant should potentially be more efficient in a cold climate than in a warm (and moist) climate.

## 5.2 Water electrolysis

In a water electrolyzer two electrodes are submerged in liquid water. At one, gaseous hydrogen is formed and at the other, gaseous oxygen is formed. The gases are collected separately, and can be assumed saturated with water vapor. The exergy change over the device depends on the ambient temperature both directly and through the ratio of vapor pressure to ambient pressure. In the calculations, it appeared that this change deviated very little from the chemical exergy of hydrogen. At 70 RH it was from 0.3% to 0.4% larger in the range of ambient temperature from 55 to 0°C, and this deviation was slightly reduced with a lower ambient pressure. The chemical exergy change (while not the chemical exergy of hydrogen) is independent of the RH. Hence, the variation of chemical exergy of hydrogen is representative for the required minimum exergy supply to the electrolytic cell. Thus, water electrolysis in a warmer climate should be potentially more efficient than in a cold climate.

## 5.3 Reactor with all products mixed with excess air (combustor).

The chemical exergy for a substance is defined with separate effluents at atmospheric partial pressures. Real devices have one or more outflows of mixtures. A conventional combustor has a fuel inflow, an air inflow, and an exhaust comprising combustion products and excess air. Except at very large excess air, some of the product water in the exhaust will be condensed at ambient temperature and pressure. This water (or ice) can be regarded as a separate effluent stream. The amount of condensed water will depend both on the relative humidity of the air, and on the amount of excess air. The amount of excess air can be expressed by the air excess number,  $\lambda$ , which is the ratio of the actual and theoretical amounts of air (and the reciprocal of the equivalence ratio). The change in chemical exergy over the device can then be expressed as the chemical exergy of the fuel minus that of the gaseous exhaust mixture and of the condensed exhaust H<sub>2</sub>O:

$$\Delta E_{\text{burner}}^{\text{ch}} = n_{\text{fu}} \varepsilon_{\text{fu}}^{\text{ch}} - E_{\text{exhaust(g)}}^{\text{ch}} - n_{\text{cond}} \varepsilon_{\text{H}_2\text{O(liquid)}}^{\text{ch}} \quad (25)$$

This change (per amount of fuel) appeared to be only slightly lower than the chemical exergy of the fuel, and showed the same variation with ambient temperature. For hydrogen in complete reaction with the theoretical amount of air ( $\lambda=1$ ), the calculated values of  $\Delta E_{\text{burner}}^{\text{ch}}/n_{\text{fu}}$  were from 0.6% (at -30 °C) to 1.0% (at 45 °C) lower than the fuel chemical exergy at 1 atm, 70% RH. For the investigated hydrocarbons, the chemical-exergy change  $\Delta E_{\text{burner}}^{\text{ch}}/n_{\text{fu}}$  was approximately 98% of the fuel chemical exergy, and was reduced by 0.6% from -30 °C to 45 °C of ambient temperature. For CO the difference was more notable, as the change varied from 95.3% to 93.8% over the range of ambient temperatures. When excess air was increased, the change of Eq. (25) was slightly increased towards the fuel chemical exergy.

When the ambient pressure was varied, the change of Eq. (25) followed the variation seen in fuel chemical exergy. The variation with RH, however, was small since the H<sub>2</sub>O chemical exergy cancels on the RHS of the equation. An exception was seen at high values of ambient temperature and low RH. Then less or no product water condenses, and the last terms of Eq. (25) were reduced.

In summary, the change of chemical exergy per amount of fuel over a burner with varying ambient condition was nearly proportional to the chemical exergy of the fuel determined at the actual ambient temperature and at chosen values of RH and pressure. Hence, the exergy obtainable from a burner can be approximated to the chemical exergy of the fuel at the actual ambient temperature but at chosen (and constant) reference values for RH and pressure (e.g. 70% and 1 atm). It should be noticed, however, that this implies that the H<sub>2</sub>O mole fraction varies with the temperature. When a certain degree of accuracy is required, CO should be regarded as an exception from this approximation. If full accuracy is required, the chemical exergies of influents and effluents can be calculated according to the model in Sec.3.

#### 5.4 Reactor with products separated from excess air (SOFC, oxygen transfer membrane combustor)

Another type of device is the solid-oxide fuel cell (SOFC). Also, if an oxygen-permeable membrane could be devised in a combustor, this would give the same overall effect. Here, fuel is supplied on the anode side and air at the cathode side. Oxygen is transported through the electrolyte and reacts with the fuel on the anode side, giving an effluent of CO<sub>2</sub> and H<sub>2</sub>O. At ambient temperature and pressure, the major part of the H<sub>2</sub>O will be condensed, 95% at 45 °C and 99% at 15 °C when methane is the fuel. The cathode effluent is the remaining oxygen-depleted air. At high RH (above 80%) and low excess air, some water will condense since the fraction of non-H<sub>2</sub>O gases is reduced. The change in chemical exergy over the device can then be expressed as

$$\Delta E_{\text{SOFC}}^{\text{ch}} = n_{\text{fu}} \epsilon_{\text{fu}}^{\text{ch}} - E_{\text{anode-prod.}}^{\text{ch}} - E_{\text{depleted-air(g)}}^{\text{ch}} - n_{\text{cond}} \epsilon_{\text{H}_2\text{O(liq)}}^{\text{ch}} \quad (26)$$

Fuel cells are relevant mainly for hydrogen and methane. However, also butane was investigated here. For H<sub>2</sub> the change according to Eq. (26) was very close to that of the burner above. The change with RH and excess air was very small. For methane and butane, the change was another one percent lower compared to the fuel chemical exergy at 1 atm pressure, 70% RH, and the relevant ambient temperature. The variation with RH was very small, while the chemical-exergy change was a little increased with higher excess air. The variation with ambient pressure was similar to that of the fuel chemical exergy.

Thus, the conclusion for the burner above also holds for an SOFC. The exergy obtainable from an SOFC can as an approximation be assumed proportional to the chemical exergy of the fuel at the actual ambient temperature and chosen (and constant) reference values for RH and pressure (e.g. 70% and 1 atm).

## 6 Discussion

From the analysis above it is apparent that the variation in ambient humidity plays a significant role. The saturation pressure of water has a strong dependency of temperature; showing two orders of magnitude change over the investigated range of temperatures. The relative humidity (RH), however, has a modest variation, usually observed within a range from 30 to 90%. Hence, when the value of the chemical exergy is to be adjusted for the ambient conditions, the strongly varying mole fraction of water vapor has to be considered. Taking, for simplicity or other reasons, this mole fraction constant, leads to either unrealistically low RH for higher temperatures or to unphysically high RH for low

temperatures. Moreover, as shown above, a constant H<sub>2</sub>O mole fraction gives the opposite gradient of chemical exergy with ambient temperature in comparison with a constant and realistic RH.

The analysis showed that the effect of ambient conditions on the chemical exergy is within 1% for the investigated fuels, except for methane and hydrogen. An obvious question that rises is whether this matters. Isn't this a too small deviation to bother about? And, furthermore, we do not have any equipment that can utilize this potential anyhow.

Two comments to this are: First, theoretically, this deviation has to be accounted for in order to provide consistent calculations. Second, with the knowledge of this added potential, the technological community is challenged to invent remedies to utilize it. A couple of examples, exhaust-condensing thermal plants and the “ice-bar” heat pump, can be used to illustrate this. Both are examples of non-conventional solutions for improved resource utilization: Low-temperature heat from exhaust, including latent heat of product water vapor, is often not utilized in thermal plants. Corrosion due to acidic condensed water and large heat-exchanger areas are two of the reasons for this. However, in recent years the low-temperature heat has gained a large interest both for power plants and heating plants. For domestic heating appliances, condensing heaters have come into widespread use [23] during the last two decades. Air-based heat pumps for room heating in cold climate are customarily designed to avoid icing in the outdoor heat exchanger. This requires a de-icing function, which costs some exergy and loss of efficiency. An alternative approach is seen in the ice-bar heat pump [24]. This device utilizes the latent heat of atmospheric vapor and builds up a bar of ice during operation, which eventually evaporates in the warmer season.

The question “does this small amount matter?” can also be answered by pointing towards the ISO-standard for natural gas [7]. The industry has found it convenient to include the deviation in heating value into a standard. The deviation from the value at the reference conditions is much larger for chemical exergy than it is for heating value, both in absolute terms and relative to the thermomechanical component.

Another question is whether the varying chemical exergy should be used. Or should a reference value be used, regardless of the ambient conditions? The answer depends to a large extent on the purpose of the analysis. When the method is used to optimize a specific plant, the relevant knowledge is how the input (fuel, electricity, etc.) best can be utilized. It is important then to know the input exergy relative to the output exergy of the plant, and to see what is utilized and what is lost. In this case, the chemical exergy should be accurately calculated with respect to the ambient conditions. If, on the other hand, the purpose is to compare installations at different locations, it may be interesting to evaluate the plants on a generic basis, e.g. output per unit of input mass. In that case, the chemical exergy of the substance at reference conditions may be the useful measure. However, as discussed in Sec.5.1 on atmospheric air separation and Sec. 5.2 on water electrolysis, the locally determined chemical exergy will make clear which location is the most beneficial for a certain device.

## 7 Conclusions

The effects of ambient temperature, atmospheric moisture content and pressure on the chemical exergy have been investigated for atmospheric gases and gaseous fuels. It appears that the ambient conditions have significant influence on the values of chemical exergy.

All the investigated fuels showed larger chemical exergy at lower temperature at constant pressure and relative humidity. Also lower RH gave a higher chemical exergy, except for CO. Over ranges from  $-30\text{ }^{\circ}\text{C}$  to  $45\text{ }^{\circ}\text{C}$  of temperature and 30 to 90% of relative humidity, the chemical exergy of methane varied by 3% and hydrogen by 7%.

A notable result was that if keeping the absolute humidity (i.e. constant atmospheric mole fraction of  $\text{H}_2\text{O}$ ) constant – as is done in the literature, the opposite variation of chemical exergy with temperature is observed. This condition, however, readily leads to unrealistic, or even unphysical, situations when the temperature has more than a small variation.

A lower ambient pressure also gave significant reduction in chemical exergy, although more modest compared to variation of temperature and RH.

An increase in atmospheric content of  $\text{CO}_2$ , as observed during the past three centuries, causes small increases in hydrocarbon chemical exergy, although significant only for CO and  $\text{CO}_2$ .

Evaluating the change of chemical exergy over a air-gas separation unit showed that such units are potentially more efficient in a cold climate than in a warm (and moist) one, as the required minimum work increases with higher absolute moisture content and with higher ambient temperature. The opposite result was found for a water-to-hydrogen electrolysis cell, which showed a lower minimum electric input per mole of hydrogen at higher temperatures.

The chemical exergy change over reactors like combustors (all reaction products and excess air mixed) and solid-oxide fuel cells (reaction products separated from depleted and excess air) was seen to follow the temperature variation observed for the fuel chemical exergy. The dependency on relative humidity was, however less.

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Tables

**Table 1** Chemical exergies determined at the chosen reference conditions, 25 °C, 1 atm, 70% relative humidity.

Species	Chemical exergy (kJ/mol)	Species	Chemical exergy (kJ/mol)
nitrogen, N <sub>2</sub>	0.6681	methane, CH <sub>4</sub>	831.47
oxygen, O <sub>2</sub>	3.9305	ethane, C <sub>2</sub> H <sub>6</sub>	1495.5
carbon dioxide, CO <sub>2</sub>	19.610	ethylene, C <sub>2</sub> H <sub>4</sub>	1360.4
argon, Ar	11.640	acetylene, C <sub>2</sub> H <sub>2</sub>	1265.4
water, H <sub>2</sub> O (g)	9.474	propane, C <sub>3</sub> H <sub>8</sub>	2151.1
water, H <sub>2</sub> O (liq)	0.8842	n-butane, C <sub>4</sub> H <sub>10</sub>	2805.0
hydrogen, H <sub>2</sub>	236.098	n-pentane, C <sub>5</sub> H <sub>12</sub>	3458.7
carbon monoxide, CO	274.87	n-hexane, C <sub>6</sub> H <sub>14</sub>	4113.3

**Table 2** Relative contribution from the terms in Eq. (18)

$T_0$ (°C)	$\frac{(T_{\text{ref}} - T_0)\Delta S^{\text{ref}}}{-\Delta G^{\text{ref}}}$	$\frac{W_1}{-\Delta G^{\text{ref}}}$	$\frac{W_2}{-\Delta G^{\text{ref}}}$	$\frac{\sum_{j \neq i} \nu_j \epsilon_j^{\text{ch}}}{-\Delta G^{\text{ref}}}$	
			$p_0 = 0.6 \text{ bar}$	$p_0 = 0.6 \text{ bar}$	$p_0 = 1 \text{ atm}$
Hydrogen, H <sub>2</sub>					
45	$-0.39 \cdot 10^{-2}$	$-0.28 \cdot 10^{-4}$	$-3.03 \cdot 10^{-3}$	$0.97 \cdot 10^{-2}$	$2.20 \cdot 10^{-2}$
35	$-0.19 \cdot 10^{-2}$	$-0.07 \cdot 10^{-4}$	$-2.94 \cdot 10^{-3}$	$1.56 \cdot 10^{-2}$	$2.74 \cdot 10^{-2}$
25	0	0	$-2.84 \cdot 10^{-3}$	$2.14 \cdot 10^{-2}$	$3.28 \cdot 10^{-2}$
15	$0.19 \cdot 10^{-2}$	$-0.07 \cdot 10^{-4}$	$-2.75 \cdot 10^{-3}$	$2.71 \cdot 10^{-2}$	$3.83 \cdot 10^{-2}$
0	$0.49 \cdot 10^{-2}$	$-0.47 \cdot 10^{-4}$	$-2.60 \cdot 10^{-3}$	$3.28 \cdot 10^{-2}$	$4.64 \cdot 10^{-2}$
-10	$0.68 \cdot 10^{-2}$	$-0.93 \cdot 10^{-4}$	$-2.51 \cdot 10^{-3}$	$4.12 \cdot 10^{-2}$	$5.30 \cdot 10^{-2}$
-20	$0.87 \cdot 10^{-2}$	$-1.56 \cdot 10^{-4}$	$-2.41 \cdot 10^{-3}$	$4.80 \cdot 10^{-2}$	$5.95 \cdot 10^{-2}$
-30	$1.07 \cdot 10^{-2}$	$-2.35 \cdot 10^{-4}$	$-2.32 \cdot 10^{-3}$	$5.47 \cdot 10^{-2}$	$6.60 \cdot 10^{-2}$
Butane, C <sub>4</sub> H <sub>10</sub>					
45	$0.12 \cdot 10^{-2}$	$1.54 \cdot 10^{-4}$	$0.77 \cdot 10^{-3}$	$3.13 \cdot 10^{-2}$	$3.40 \cdot 10^{-2}$
35	$0.06 \cdot 10^{-2}$	$0.72 \cdot 10^{-4}$	$0.75 \cdot 10^{-3}$	$3.30 \cdot 10^{-2}$	$3.55 \cdot 10^{-2}$
25	0	0	$0.72 \cdot 10^{-3}$	$3.46 \cdot 10^{-2}$	$3.71 \cdot 10^{-2}$
15	$-0.06 \cdot 10^{-2}$	$-0.64 \cdot 10^{-4}$	$0.70 \cdot 10^{-3}$	$3.63 \cdot 10^{-2}$	$3.86 \cdot 10^{-2}$
0	$-0.14 \cdot 10^{-2}$	$-1.42 \cdot 10^{-4}$	$0.66 \cdot 10^{-3}$	$3.87 \cdot 10^{-2}$	$4.09 \cdot 10^{-2}$
-10	$-0.20 \cdot 10^{-2}$	$-1.83 \cdot 10^{-4}$	$0.64 \cdot 10^{-3}$	$4.07 \cdot 10^{-2}$	$4.29 \cdot 10^{-2}$
-20	$-0.26 \cdot 10^{-2}$	$-2.14 \cdot 10^{-4}$	$0.61 \cdot 10^{-3}$	$4.28 \cdot 10^{-2}$	$4.48 \cdot 10^{-2}$
-30	$-0.32 \cdot 10^{-2}$	$-2.35 \cdot 10^{-4}$	$0.59 \cdot 10^{-3}$	$4.48 \cdot 10^{-2}$	$4.68 \cdot 10^{-2}$

## Figures

**Figure 1** Variation of chemical exergy with ambient temperature for some atmospheric gases and hydrogen at ambient pressure 1 atm and 70% ambient relative humidity. Relative deviation in % from value at reference condition 25 °C, 1 atm, 70% RH, cf. Eq.(23).

**Figure 2** Variation of chemical exergy (cf. Eq.(23)) for nitrogen at ambient pressure 1 atm and varying ambient temperature and relative humidity (RH); the last series is for partial pressure of H<sub>2</sub>O held constant at 880 kPa.

**Figure 3** Variation of chemical exergy (cf. Eq.(23)) with ambient temperature for hydrogen, CO, and some gaseous hydrocarbons at ambient pressure 1 atm and 70% ambient relative humidity.

**Figure 4** Variation of chemical exergy (cf. Eq.(23)) for methane at ambient pressure 1 atm and varying ambient temperature and relative humidity (RH); the last series is for partial pressure of H<sub>2</sub>O held constant at 880 kPa.

**Figure 5** Variation of chemical exergy (cf. Eq.(23)) for butane at ambient pressure 1 atm and varying ambient temperature and relative humidity; the last series is for partial pressure of H<sub>2</sub>O held constant at 880 kPa.

**Figure 6** Variation of chemical exergy (cf. Eq.(23)) with ambient relative humidity for some atmospheric gases and hydrogen at ambient pressure 1 atm and temperature 25 °C.

**Figure 7** Variation of chemical exergy (cf. Eq.(23)) with ambient relative humidity for some fuels at ambient pressure 1 atm and temperature 25 °C.

**Figure 8** Variation of chemical exergy (cf. Eq.(23)) for methane at 70% ambient relative humidity and varying ambient temperature and pressure.

**Figure 9** Variation of chemical exergy (cf. Eq.(23)) for butane at 70% ambient relative humidity and varying ambient temperature and pressure.

**Figure 10** Schematic view of air-gas separation process.

**Figure 11** Additional minimum required exergy for separation of gas(es) from atmospheric air (cf. Eq. (24)) as a function of degree of separation. (I): separation of N<sub>2</sub> at 90%RH; (II): O<sub>2</sub> at 90% RH; (III): Ar at 90% RH; (IV): N<sub>2</sub> and O<sub>2</sub> at 30% RH; (V): N<sub>2</sub> and O<sub>2</sub> at 90% RH; (VI): N<sub>2</sub>, O<sub>2</sub> and Ar at 30% RH; (VII): N<sub>2</sub>, O<sub>2</sub> and Ar at 90% RH; all series at 0 °C, 1 atm. (VIII): N<sub>2</sub>, O<sub>2</sub> and Ar at 90% RH, 1atm, 25 °C.

Figures

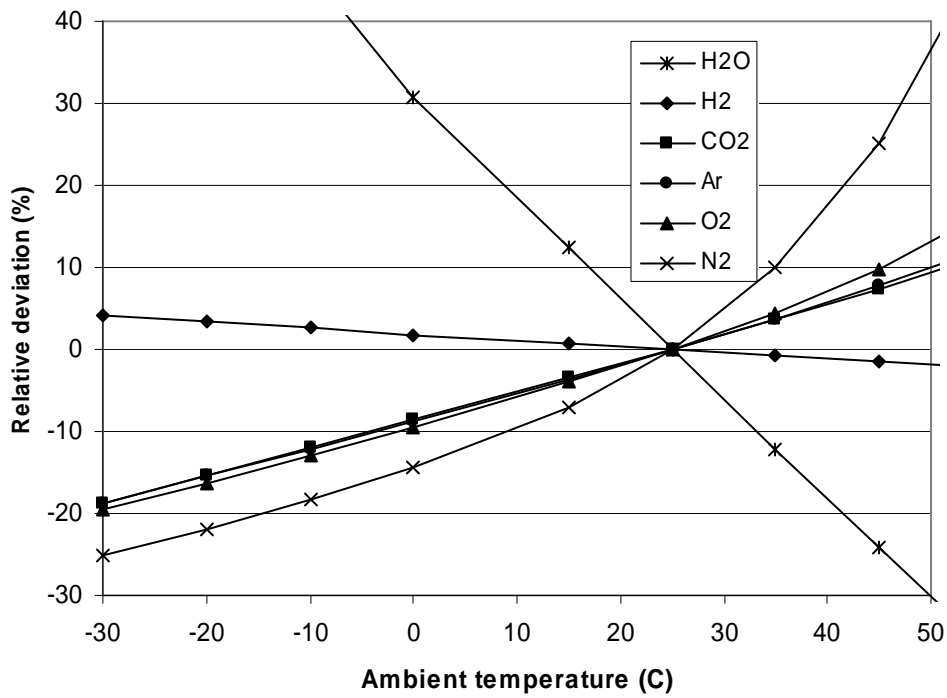


Fig.1

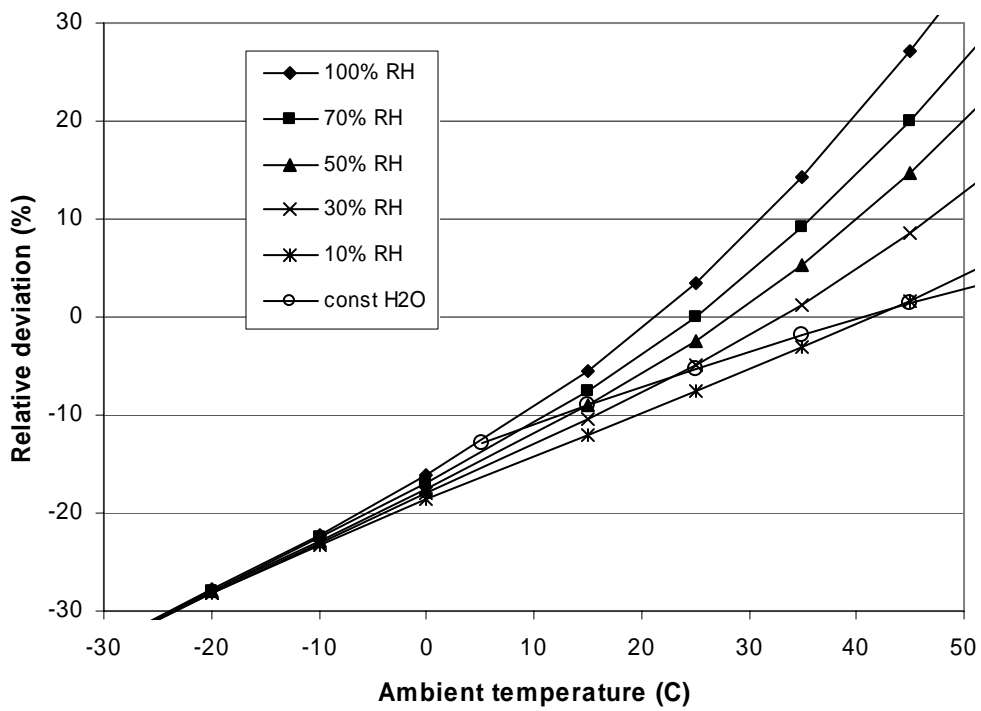


Fig 2

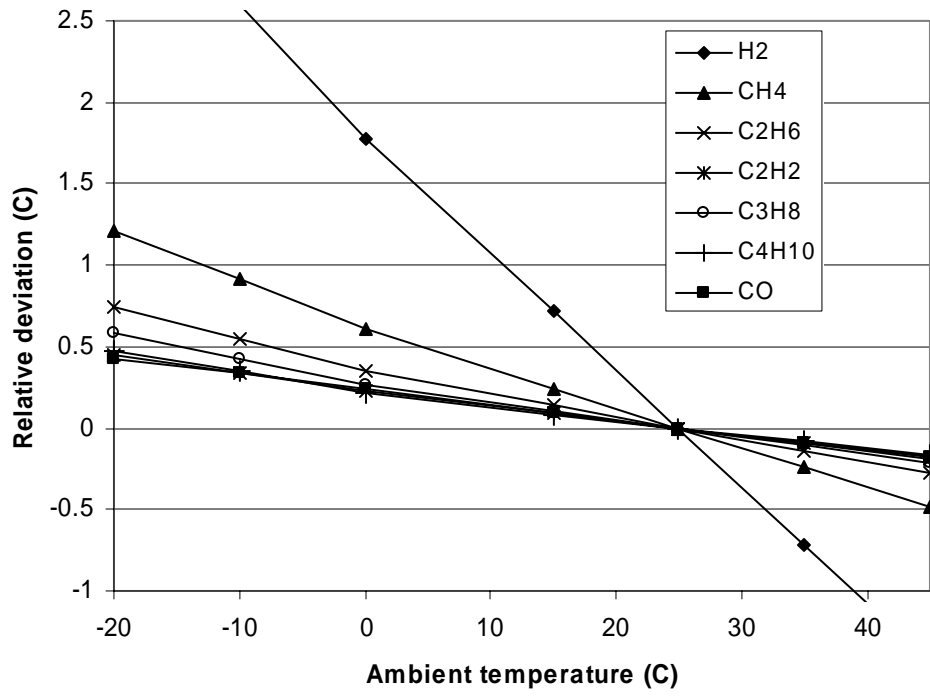


Fig.3

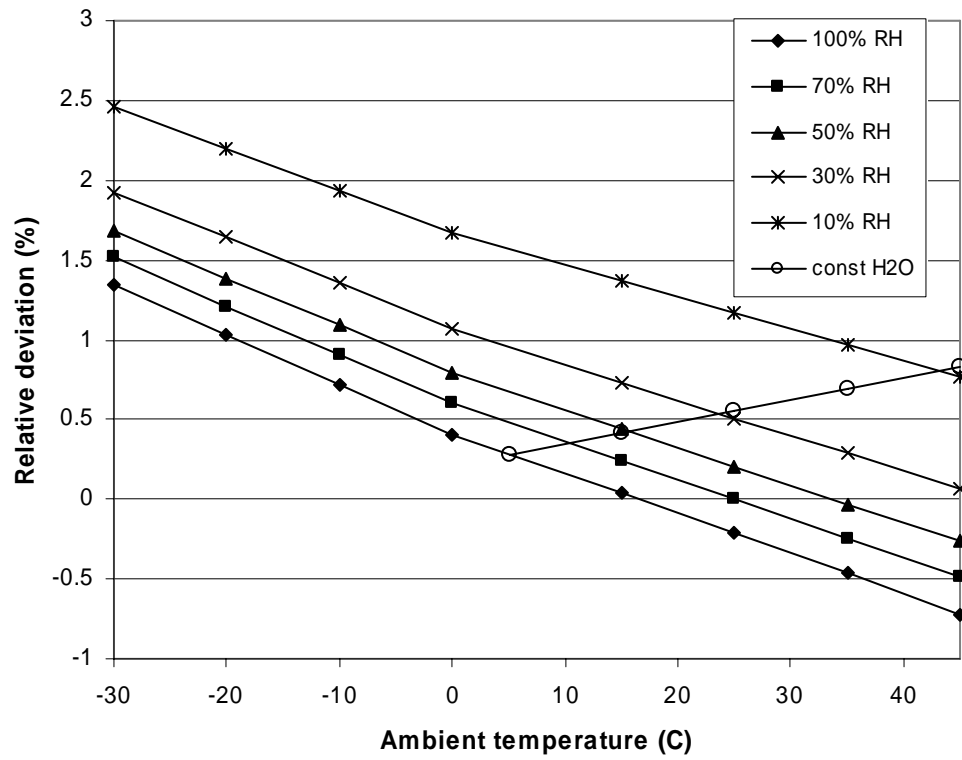


Fig.4

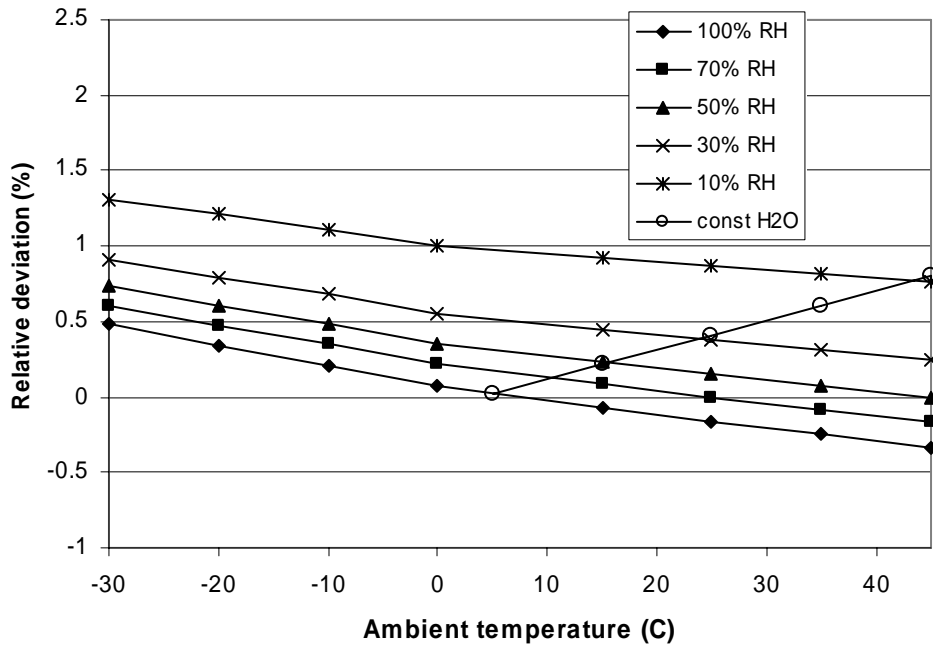


Fig.5

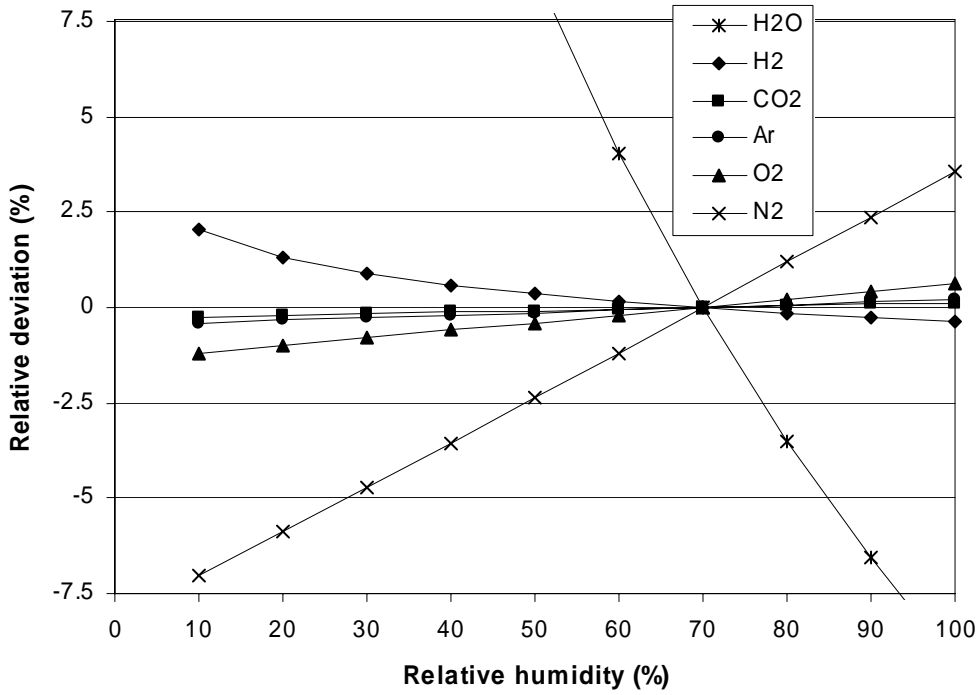


Fig.6

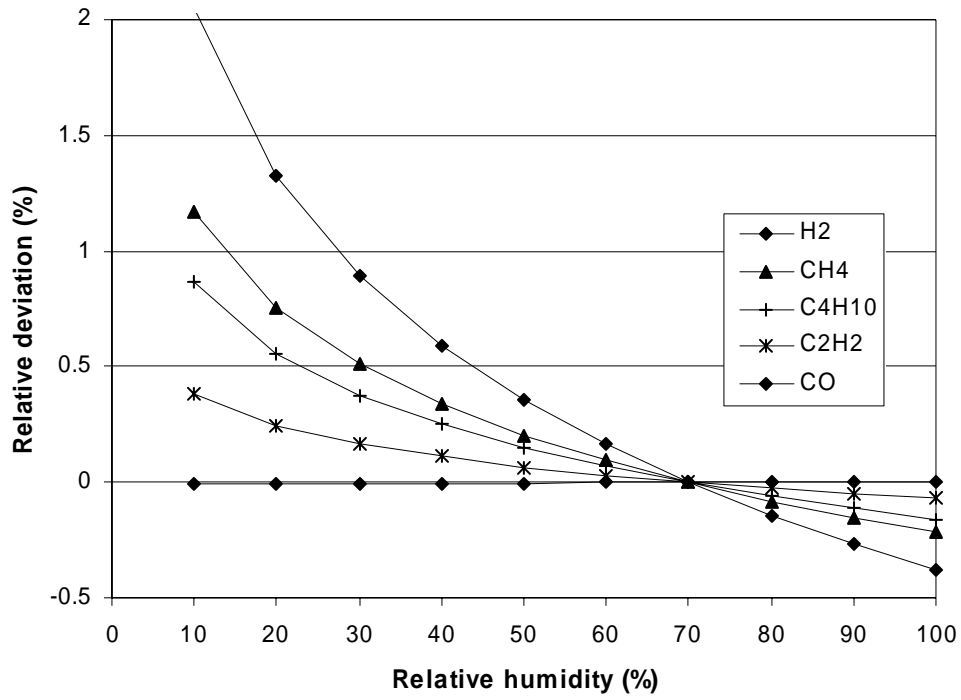


Fig.7

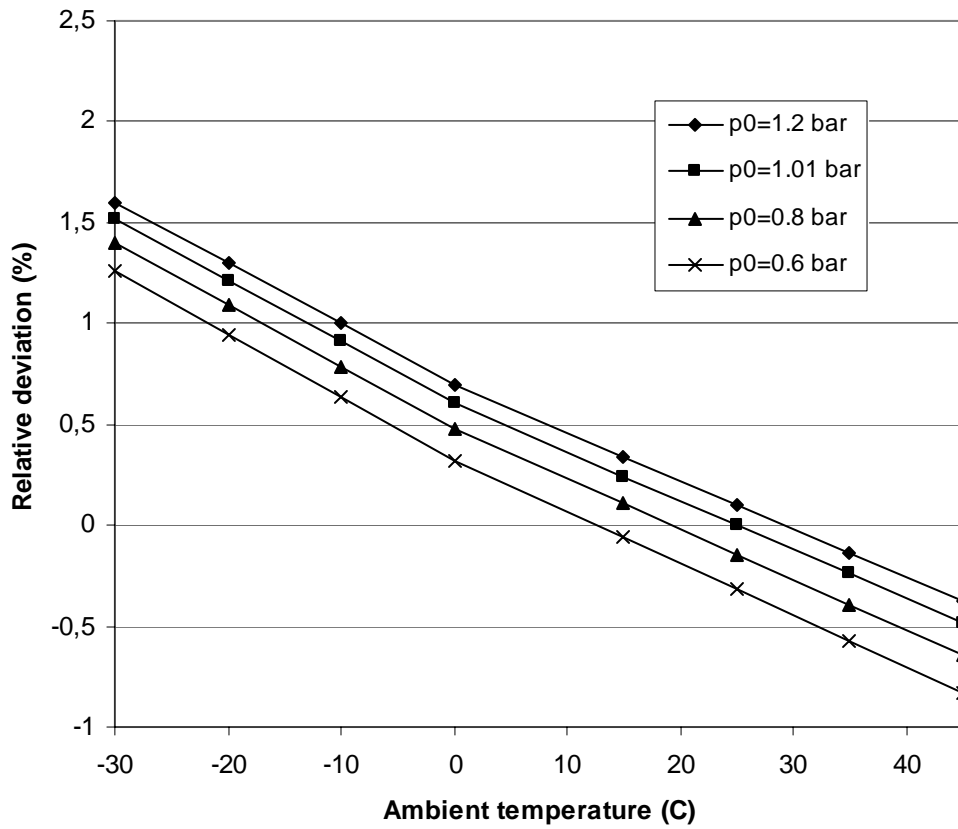


Fig.8

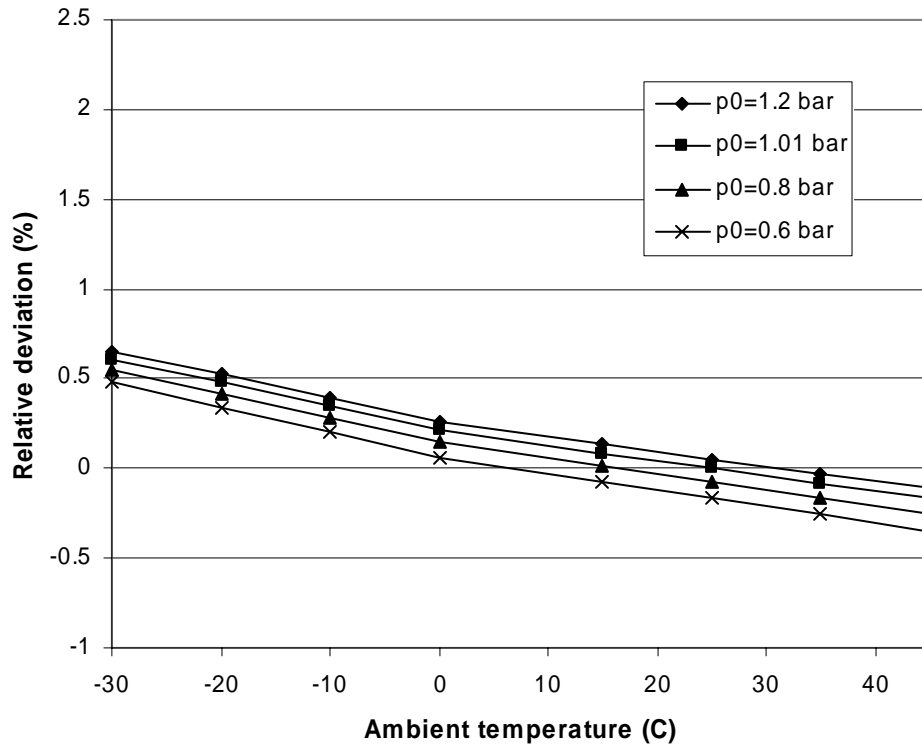


Fig.9

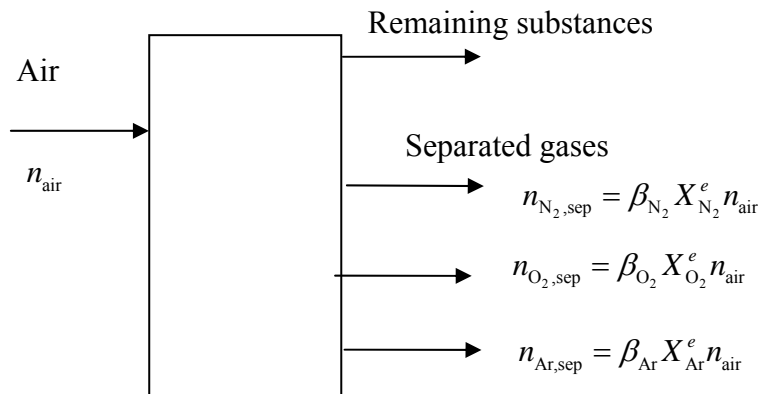


Fig.10



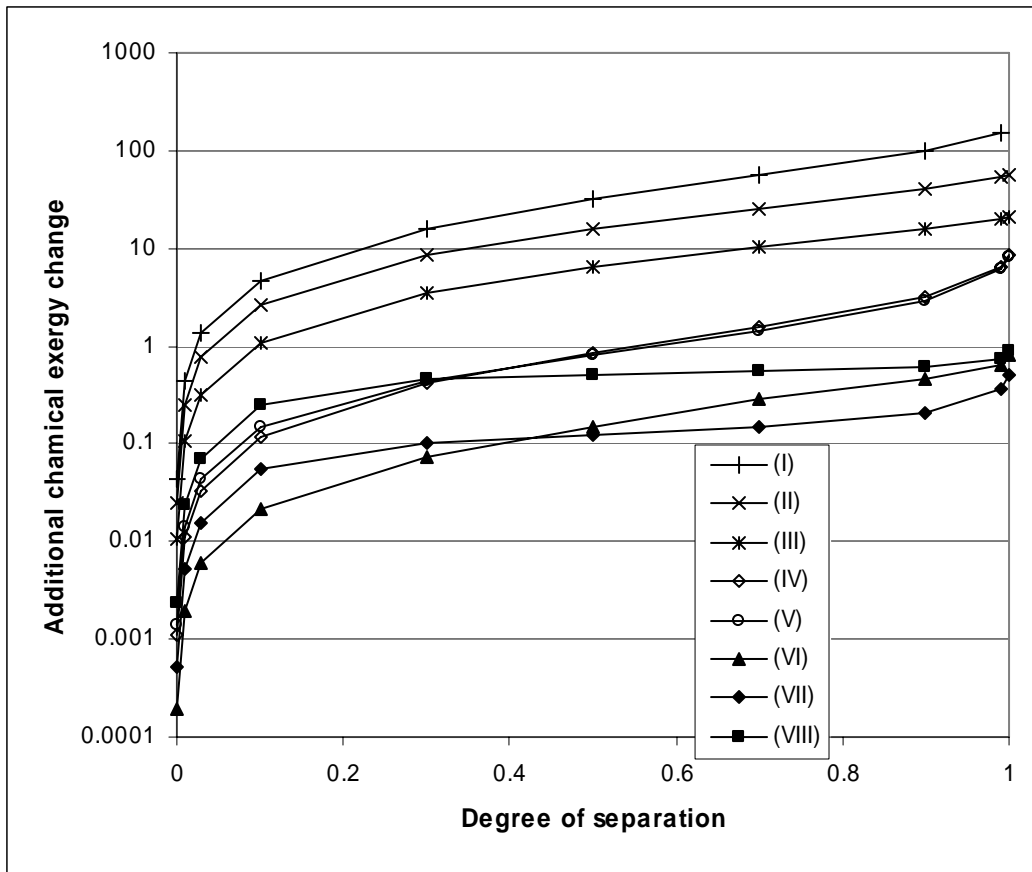


Fig.11