Environment. Technology. Resources. Rezekne, Latvia
Proceedings of the 15th International Scientific and Practical Conference. Volume I, 300-305

Thermodynamic Empirism for Describing Atmospheric Pollutants

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Abstract. **Humanity is currently subject to excessive pollution of the Biosphere and the atmosphere that comes from anthropogenic activity. The global warming is the most acute problem that has a negative impact on the state of the biosphere as a whole. The long empirical analysis on the state of the atmosphere makes it possible to develop quantitative expressions that give a dependence of the atmospheric temperature variation depending on the accumulation of anthropogenic polluting gases with greenhouse effect. One of the gases with a greenhouse effect is carbon dioxide, which has a major contribution to global warming. The method suggested in the paper focuses on the empirical analysis with the application of the thermodynamic laws describing the state of the atmosphere and gives the results of the validation within certain limits of the variation of the atmospheric temperature as the dependence of the accumulated concentration of the polluting gases with greenhouse effect. The relational connection between variations of concentrations and of the temperature is found by the equation of state of the ideal gas, assuming that the atmosphere can be described by this equation and the combination with the adiabatic thermodynamical equation leads to the expression which contains those variations. Annually, the monitoring stations record variations of concentrations and temperatures. The last 40 years the average temperature of the atmosphere is elevated up to 1^0C. The respective calculations by the application of thermodynamic expressions lead to the same order of 1 ^{0}C. It is explained by the application of thermodynamic physico-chemical laws that the rate of photosynthesis is comparatively low compared to the rate of additional excessive accumulation of carbon dioxide that comes from anthropogenic activity. The importance of the suggested method allows us to conclude about the validation of the method with the direct application of analytical expressions of the state of the atmosphere. Statistical analysis is very widely applied in general for data analysis, but it would be recommendable physico-chemical laws to be applied directly with a wider retrospective and the most important thing is that it allows the control of both the real recorded values and to be compared with those calculated by the thermodynamic method. The practical importance of this expression is based on the fact that the anthropogenic accumulation of carbon dioxide is followed by the accumulation of heat excess in the atmosphere, and in its turn to the increasing of the average global temperature of the atmosphere. One thing it is important to mention that the effect which takes place must be explained and this explanation is given by physical-chemical methods based on thermodynamic phenomena for the atmosphere.**

Keywords: adiabatical constant, biosphere, greenhouse gases, pollutants.

I. INTRODUCTION

The acute problem of contemporary humanity is the solving of the acute state of the atmospheric pollution. High levels of anthropogenic pollutant gases lead to high values of atmospheric temperatures. Global warming and all effects in the atmosphere could be described by classical physical laws. The presence of the pollutants in both gas and aerosols has a negative effect on the evolution of the biosphere and further on the state of the atmosphere. Modern anthropogenic activity is characterized by the increasing of the concentrations of green house pollutant gases. One of the major green house components is carbon dioxide which has a ratio of

Print ISSN 1691-5402
Online ISSN 2256-070X
https://doi.org/10.17770/etr2024vol1.7980

75% in comparison to other pollutants and therefore the effect could be considered only on the base of carbon dioxide and the other components are of minor importance and almost have no influence. The empirical suggested method in this study is based on deeply analysis that applies in general the model of ideal gas. One of the empirical analyzes based on prolonged observations is the application of the laws of thermodynamics that describes the state of physical models of gases with the application of macroscopic parameters of the state of gases. The application of this suggested model of ideal gas for atmospheric air allows checking the calculated values with the real ones such as the effective molar mass of the air and the adiabatic constant. The validity of the suggested method is confirmed by re-calculation of the important parameters such as the molar mass and the adiabatic constant and which are coincident with the real ones.

The priority of the direct application of the known physical models to the atmospheric phenomena consists in the checking of the respective values which allow us to validate the suggested method for the direct application of the description of the state of the atmosphere.

II. Material and Methods

The composition of the dry air is complex and it contains 78,08 % nitrogen, 20,95% oxygen, 0,93% argon, 0,04% carbon dioxide and small amounts of other gases. [1] The state of the atmosphere can be described by macroscopic thermodynamic parameters such as temperature, pressure, volume. To some extent it can be considered that the state of the atmosphere can be described by the equation of ideal gas. [2], [3] For dry air is valid the adiabatic equation of the ideal gas [3]:

$$P(h)\cdot[T(h)]^{-\frac{\gamma}{\gamma-1}} = const \qquad (1)$$

where γ is the adiabatic constant of the air (γ ≈ 7/5).

The pressure of the atmosphere is maximal at sea level and decreases with altitude [4]. This is because the atmosphere is very nearly in hydrostatic equilibrium so that the pressure is equal to the weight of air above a given point. The change in pressure with altitude can be expressed by the density as [5]:

$$\frac{dP}{dh} = -\rho\cdot g = -\frac{M\cdot P\cdot g}{R\cdot T} \qquad (2)$$

where g is the gravitational acceleration; ρ is the density of air; h is the altitude; P is the pressure; R is the gas constant; T is the thermodynamic temperature; M is the molar mass. This change in pressure "2" originates from the barometric formula of troposphere [6]:

$$P(h) = P_o\cdot e^{-\frac{M\cdot g\cdot h}{R.T(h)}} \qquad (3)$$

The substitution of "3" into "1" gives the following result:

$$P_o\cdot e^{-\frac{M\cdot g\cdot h}{R.T}}\cdot[T(h)]^{-\frac{\gamma}{\gamma-1}} = const \qquad (4)$$

If the temperature depends on height, it would be better to obtain such expression of the value of temperature that depends on height by the application of "4":

$$[T(h)]^{-\frac{\gamma}{\gamma-1}} = \frac{const}{P_o}\cdot e^{\frac{Mgh}{RT(h)}} \qquad (5)$$

$$[T(h)]^{\frac{\gamma}{\gamma-1}} = \frac{P_o}{const\cdot e^{\frac{Mgh}{RT(h)}}} \qquad (6)$$

The process of logarithmization of "6" by natural logarithm gives the following result:

$$\frac{\gamma}{\gamma-1}\cdot\ln[T(h)] = \ln P_o - \ln(const) - \frac{Mgh}{RT(h)} \qquad (7)$$

$$T(h)\cdot\ln[T(h)] = \frac{T(h)\cdot(\gamma-1)}{\gamma}\cdot(\ln P_o - \ln(const)) - \frac{Mg\cdot(\gamma-1)h}{R\cdot\gamma} \qquad (8)$$

$$\ln[T(h)] = \frac{(\gamma-1)}{\gamma}\cdot(\ln P_o - \ln(const)) - \frac{Mg\cdot(\gamma-1)\cdot h}{R\cdot\gamma\cdot T(h)} \qquad (9)$$

The graphic of the dependence $\ln[T(h)] = f\left(\frac{h}{T}\right)$ is represented on the "Fig.1". For the case when *h=0*, then *h/T=0* and "9" is written as:

$$\ln[T(0)] = \frac{(\gamma-1)}{\gamma}\cdot(\ln P_o - \ln(const)) \qquad (10)$$

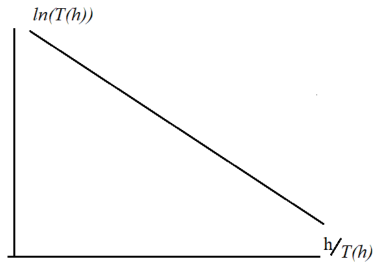

Fig.1 The dependence of $\ln[T(h)] = f\left(\frac{h}{T}\right)$

Such a way, it would be possible to recalculate the temperature at the null level *T(0)* and also the molar mass *M* by the slope of this graphic. The "10" could be applied for the small altitudes. Then:

$$\ln T = \frac{(\gamma-1)}{\gamma}\cdot(\ln P - \ln(const)) \qquad (11)$$

In order to describe the increasing of the temperature due to of the greenhouse effect, it would be better to differentiate "11":

$$\frac{\Delta T}{T} = \left(\frac{\gamma-1}{\gamma}\right)\cdot\frac{\Delta P}{P} \qquad (12)$$

The respective expression of the equation of the state of ideal gas: $P.V = \nu.R.T$; $P = C.R.T$; C is the molar concentration of the mixture of gas of the atmospheric air. The respective variation of pressure is:

$$\Delta P = R\cdot(\Delta T.C + \Delta C.T) \qquad (13)$$

The substitution of "13" into "12" gives:

$$\frac{\Delta T}{T} = \left(\frac{\gamma - 1}{\gamma}\right) \cdot \frac{R(\Delta T \cdot C + \Delta C \cdot T)}{P} = \left(\frac{\gamma - 1}{\gamma}\right) \cdot \frac{\Delta T.C + \Delta C.T}{C.T}$$

$$\Delta T = (\gamma - 1) \cdot \frac{\Delta C \cdot T}{C} \qquad (14)$$

The “14” shows quantitatively the increasing of the temperature of the atmosphere with the increasing of the molar concentration of greenhouse gases by the value ΔC.
The density of air at sea level is about 1,2 kg/m³. The molar concentration of the atmospheric air is calculated as:

$$C = \frac{\rho}{M} = \frac{1{,}2(kg/m^3)}{0{,}029(kg/mol)} = 41{,}37(mol/m^3) = 0{,}04137(mol/l)$$

The average mass of the atmosphere is about 5 quadrillion ($5{,}13\times10^{15}$) tones or 1/1,200,000 the mass of Earth [6]. The mass of the atmosphere that is $5{,}13.10^{18}$ kg allows to calculate the full volume of the atmosphere - $V_{atm.}$:

$$V_{atm} = \frac{m_{atm}}{M \cdot C} = \frac{5{,}13.10^{18}(kg)}{0{,}029(kg/mol) \cdot 0{,}04137(mol/l)} =$$
$$= 4275{,}96.10^{18}(l) = 4275{,}96.10^{15}(m^3) = 4{,}28.10^{18}(m^3)$$

Then, easily we can calculate the height of troposphere - *h*:

$$h = \frac{V_{atm}}{S_{Earth}} = \frac{4{,}28.10^{18}}{4.3{,}14.(6371.10^3)^2} =$$
$$8{,}39.10^{-9}.10^{18}.10^{-6} = 8{,}39.10^3(m) \cong 8{,}5(km)$$

The calculated value of molar concentration of air will be used to appreciate the change of the temperature as the result of increasing of greenhouse gases by the value ΔC. In general the average temperature of the atmospheric air is increasing almost linearly the last 50 years. [8] The graph is represented on the “Fig. 2”.

The opinions about the reason of the increasing of the temperatures are various, but the most observation is on the focusing of the increasing of the concentration of carbon dioxide that is one major greenhouse gas and the carbon dioxide has 75% effect from all others green house gases [9]. The registration of the concentrations of carbon dioxide [9] is represented by the diagram on the “Fig. 3”.

The changes of the values of temperatures and concentrations which are described by the “Fig. 2” and “Fig. 3” could be included into the “15” and the final result is the representation of the graphic $\Delta T = f(\Delta C)$ that in general is a linear dependence on the “Fig. 4”.

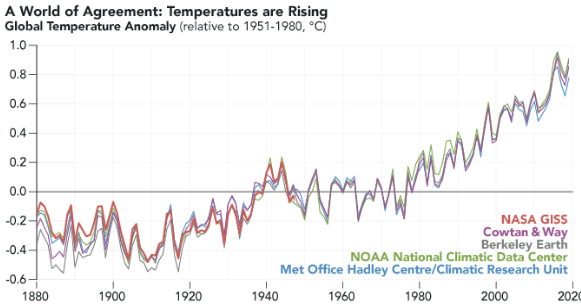

Fig. 2. The history of global change of the temperature [13]

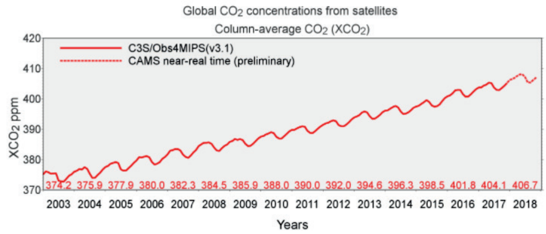

Fig. 3 The dynamics of the change of the concentration of CO_2 [14]

Such a way, the slope of the dependence of $\Delta T = f(\Delta C)$ allows to re-calculate the value of adiabatic constant γ. The numerical value of γ confirms the validity of the suggested quantitative expression of the temperature variation.

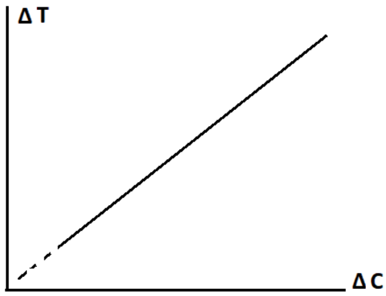

Fig. 4 The form of the dependence of $\Delta T = f(\Delta C)$

III. Results and Discussion

The values of temperatures and of the pressure are changeable with the altitude. The following Table 1 shows the results [7] of the measurements of these values.

Table 1 The important parameters of the atmosphere as the function of altitude [7]

Height h; m	Temperature t; (^{0}C)	Pressure; P; (10^4 ; Pa)	Density; ρ; kg/m3
0	15	10.13	1.225
1000	8.5	8.988	1.112
2000	2	7.95	1.007
3000	-4.49	7.012	0.9093
4000	-10.98	6.166	0.8194
5000	-17.47	5.405	0.7364
6000	-23.96	4.722	0.6601
7000	-30.45	4.111	0.59
8000	-36.94	3.565	0.5258

9000	-43.42	3.08	0.4671
10000	-49.9	2.65	0.4235

In order to validate "1" by the application of real values of the source [11], the following graphic $\ln[P(h)] = f(\ln[T(h)]$ is represented on the "Fig. 5". The procedure of natural logarithm of "1" is:

$$\ln\left[P(h)\cdot[T(h)]^{\frac{\gamma}{\gamma-1}}\right] = \ln[const] \quad ;$$

$$\ln[P(h)] = \frac{\gamma}{\gamma-1}\cdot\ln[T(h)] + \ln[const]$$

The slope of this linear dependence allows finding the adiabatic constant γ of air.

The correlation calculation of the linear dependence shows that $\frac{\gamma}{\gamma-1} = 5{,}2521 \Rightarrow \gamma = \frac{5{,}2521}{4{,}2521} \approx 1{,}23$

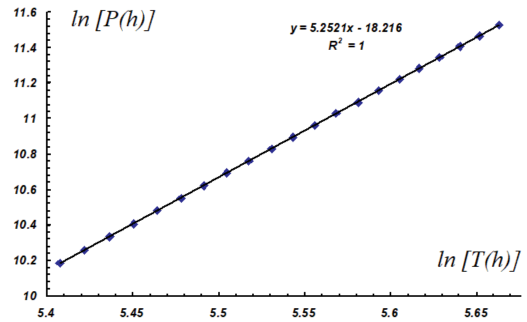

Fig.5 The functional dependence $\ln[P(h)] = f(\ln[T(h)]$

The obtained result of the adiabatic constant of the atmospheric air is of the same order of the results of the papers [10], [11]. In order to check the barometric formula written by "3" for the troposphere air it would be better to represent this expression by the logarithm of this expression. The linear dependence will validate the expression of the barometric formula: $\ln[P(h)] = \ln[P_o] - \frac{M.g}{R.T}.h\cdot$

The graphic of $\ln[P(h)] = f(h)$ is represented on the "Fig. 6".

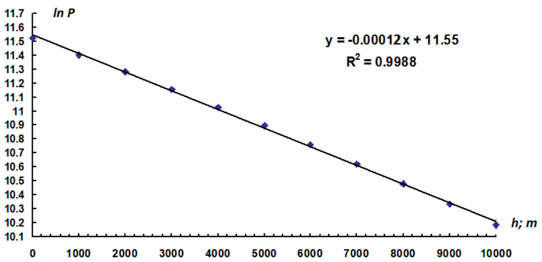

Fig. 6 The graphic of the dependence $\ln[P(h)] = f(h)$

The respective slope is: $\frac{M.g}{R.T} = 0{,}00012$

Then, the calculation of the molar mass of troposphere air is:

$$M = \frac{0{,}00012\cdot 8{,}31\cdot 288}{9{,}83} = 0{,}02921(kg/mol)$$

The calculated value of the molar mass of the troposphere air is of the same order like in [7].

$$\ln P_0 = 11{,}55 \;\Rightarrow\; P_0 = 103777(Pa) \approx 1{,}04\cdot 10^5(Pa)$$

The obtained value of the pressure of the troposphere air at the null level is of the same order of the value from the Table 1 [7]. The graphic of $\ln[T(h)] = f(h/T)$ is represented on the "Fig.7".

The correlational calculations show that:

$$\ln[T(0)] = \frac{(\gamma-1)}{\gamma}\cdot\left(\ln P_o - \ln(const)\right) = 5{,}6581$$

$$\ln[T(0)] = 5{,}6581; \quad T(0) = e^{5{,}6581} = 286{,}6(K);$$

The respective slope of the graphic is:

$$-\frac{Mg\cdot(\gamma-1)}{R\cdot\gamma} = -0{,}0057$$

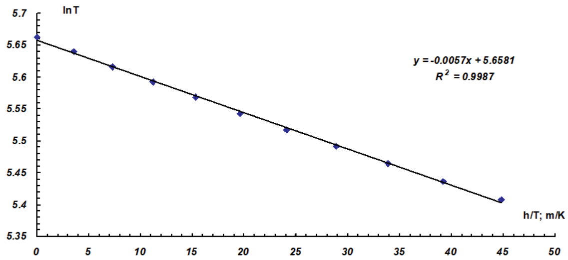

Fig. 7 The graphic of the dependence $\ln[T(h)] = f(h/T)$

Then, easily we can recalculate the molar mass of the troposphere air:

$$M = \frac{0{,}0057.R.\gamma}{g.(\gamma-1)} = \frac{0{,}0057\cdot 8{,}31\cdot 1{,}2}{9{,}83\cdot 0{,}2} = 0{,}0289(kg/mol)$$

The suggested method of the quantitative description of the variation of the atmospheric temperature ΔT with the increasing of the concentration of greenhouse gas CO_2 can be checked by the following Table 2 that is based on the results of the sources [9]. [12],

Table 2. The variation of temperature as the function of the increasing of the concentration of CO_2

Nº	Year	ΔT; ºC	C (CO_2); ppm	ΔC (CO_2); ppm	ΔC (CO_2); mg/m³
0	1980	0	338	0	0
1	1981	0,03	340	2	3,61
2	1982	0,05	341	3	5,41
3	1983	0,07	343	5	9,01
4	1984	0,09	345	7	12,63
5	1985	0,11	347	9	16,23
6	1986	0,13	348	10	18,03
7	1987	0,15	349	11	19,84
8	1988	0,18	350	12	21,64
9	1989	0,19	350.5	12,5	22,54
10	1990	0,22	351	13	23,44

11	1991	0,26	352	14	25,25
12	1992	0,32	353	15	27,05
13	1993	0,34	355	17	30,66
14	1994	0,36	357	19	34,26
15	1995	0,37	359	21	37,87
16	1996	0,39	360	22	39,67
17	1997	0,41	361	23	41,48
18	1998	0,42	362	24	43,28
19	1999	0,43	363	25	45,08
20	2000	0,45	365	27	48,69
21	2001	0,46	369	31	55,90
22	2002	0,47	373	35	63,12
23	2003	0,5	375	37	66,72
24	2004	0,54	376	38	68,52
25	2005	0,58	378	40	72,13
26	2006	0,59	379	41	73,93
27	2007	0,6	380	42	75,74
28	2008	0,61	381	43	77,54
29	2009	0,62	382	44	79,34
30	2010	0,63	383	45	81,15
31	2011	0,65	385	47	84,75
32	2012	0,68	393	55	99,18
33	2013	0,7	398	60	108,20
34	2014	0,74	401	63	113,61
35	2015	0,78	402	64	115,41
36	2016	0,8	406	68	122,63
37	2017	0,81	410	72	129,84
38	2018	0,82	412	74	133,44
39	2019	0,83	413	75	135,25
40	2020	0,85	415	77	138,85

The usually concentrations that are represented on the Table 2 as *ppm* values can be transformed into *mg/m³* by the application of the method given in [11]. So, the respective variation of *ppm* is:

$$\Delta C_{ppm} = \frac{24{,}4(l/mole)\cdot \Delta C[mg/m^3]}{M[g/mole]}$$

The variation of the concentrations of carbon dioxide $\Delta C[mg/m^3]$ in the atmosphere:

$$\Delta C[mg/m^3] = \frac{M[g/mole]\cdot \Delta C_{ppm}}{24{,}4}$$

The respective dependence of the variation of the temperature *ΔT* as the function of *ΔC* is represented on the "Fig. 8". The respective slope of the graphic ΔT=f(ΔC) is:

$$(\gamma-1)\cdot\frac{T}{C} = 0{,}006\left(\frac{{}^0C}{\frac{mg}{m^3}}\right) \equiv \frac{6\left(\frac{{}^0C}{g/m^3}\right)}{44(g/mol)} = 0{,}136\left(\frac{{}^0C}{\frac{mol}{m^3}}\right) = 136\left(\frac{{}^0C}{mol/l}\right)$$

The atmospheric air has the concentration:

$$C = 0{,}04137(mol/l) = 41{,}37(mol/m^3) \equiv 29(g/mol).41{,}37(mol/m^3) =$$
$$= 1199{,}73(g/m^3) = 1{,}199(kg/m^3) = 1{,}199(g/l)$$

The value of adiabatic constant γ is calculated from the expression below:

$$(\gamma-1) = \frac{0.136.C}{T} = \frac{0{,}136.41{,}37}{288} \approx 0{,}02\,;$$
$$\gamma = 1{,}02$$

Such a way, the "16" could be written simply by proportional linear coefficient *a* as:

$\Delta T_e = a.\Delta C$; (e)-empirical

$$a = (\gamma-1)\cdot\frac{T}{C} = 0{,}02\cdot\frac{288(K)}{0{,}04137(mol/m^3)} = 139\left(\frac{{}^0C}{mol/l}\right)$$

$$\Delta T_e = 0{,}006\cdot\Delta C\,;\quad [\Delta C]=mg/m^3;$$

or: $\Delta T_e = 136\cdot\Delta C$; [ΔC]=*mol/l*;

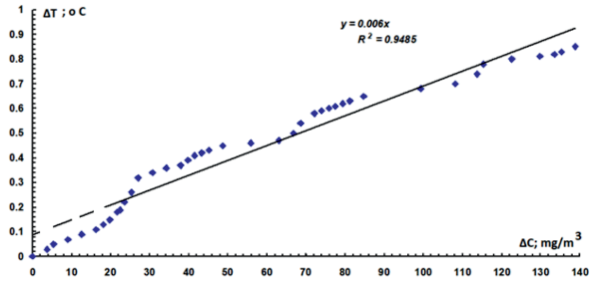

Fig. 8 The graphic of the dependence ΔT=f(ΔC)

The calculated values of ΔT_e by the empirical expression can be checked with the real variations of ΔT by the representation of the following graphic. On the "Fig. 9".

In order to have the important parameter like interval of time that can be included into the empirical expression, is necessary to represent the following dependence of the variation of concentration of carbon dioxide as the function of time and is represented on the "Fig. 10". The rate of increasing of CO_2 (speed of increasing of the concentration each year) is about *3,383((mg/m³)/year)*

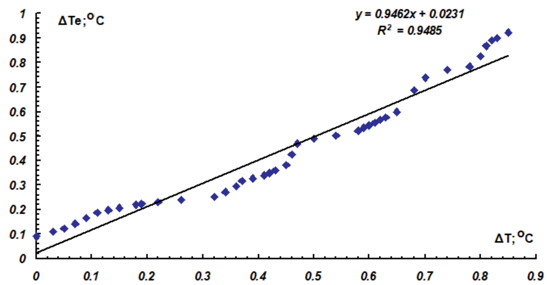

Fig. 9 The validity of empirical calculations of temperature variations

Such a way the empirical formula of the temperature variation can be written as:

$$\begin{cases} \Delta T_e(t) = 0{,}006 \cdot \Delta C(t) \\ \Delta C(t) = 3{,}3833 \cdot t; \\ [t] = years; \quad [\Delta C] = mg/m^3 \end{cases};$$

If each last years the concentration of carbon dioxide is increasing with the value of 3,383 *mg/m³,* then it would give the possibility to calculate the excess mass Δm_{CO2} during one year.

$$\Delta m_{CO_2} = \Delta C.V_{atm} = 3{,}383((mg/m^3)/year).4{,}27596.10^{18}(m^3) =$$
$$= 14{,}47.10^{18}(mg/year) = 14{,}47.10^{12}(kg/year) =$$
$$14{,}47.10^9(tons/year) = 14{,}47(Gtons/year)$$

The study [10] has such result about carbon dioxide: "Between 2009-18, however, the growth rate has been 2.3 *ppm per year*". Transposing *ppm* into mg/m³, then:

$$\Delta C[mg/m^3] = \frac{M[g/mole] \cdot \Delta C_{ppm}}{24{,}4} = \frac{44.2{,}3}{24{,}4} = 4{,}14((mg/m^3)/year)$$

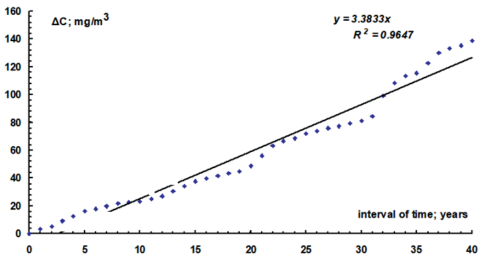

Fig. 10 The variation of the concentration of carbon dioxide as the function of time (starting reference year is 1980)

The result in this recent paper is 3,383 *(mg/m³)/year*. Then, the average value is 3,76 *(mg/m³)/year*. The respective admissible error of exactity is:

$$\varepsilon = \frac{|4{,}14 - 3{,}76|}{3{,}76} \cdot 100\% = \frac{38}{3{,}76} \approx 10\%$$

The comparison of the calculated value of the mass of carbon dioxide is of the same order within the limits of errors with the real one.

CONCLUSIONS

The suggested method of the recent study which is based on thermodynamic empirism gives us the possibility to obtain values that are calculated and that are of the same order with the real ones. The empirical expression allows us to predict the trend of the values of the future states of the atmosphere that are described by the variations of the pollutant concentrations. The validation of the suggested method is performed on the basis of known values such as the adiabatic constant of the atmospheric air. The importance of this empirical expression is based on the fact that if ΔC<0, i.e. the concentration of polluting gases decreases over time, then we could obtain a situation of the decreasing of the atmospheric temperature. Empirical intuition could give this result with the reality. The important problem of the World recently is to look for ways to solve the reduction of the emission of pollutants with such result that we could expect of the reduction of the atmospheric temperature and the attenuation of the global warming. This moment could be reached by the increasing of the forest areas with the aim of the acceleration of global photosynthesis.

ACKNOWLEDGMENTS

The work is supported by a project of the university Prof. Dr. Asen Zlatarov Burgas NIX-482/2023 "Application of Intuitionistic Fuzzy Logic in the Decision Making Process".

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