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# APPARENT LINEAR RELATIONSHIP, COMPENSATION LAW AND OTHERS. PART II

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## ABSTRACT

In estimating the Arrhenius equation coefficients from kinetic data, a linear relationship between the logarithm of the pre-exponential factor and the activation energy is assumed; this is called the "compensation law". From analysis of the estimation procedure, it was found that the coefficient of this last equation will be close to the geometrical average temperature in the experiments multiplied by the gas constant.

A similar effect was observed for the thermodynamic experiments. An apparent linear relationship exists between the enthalpy and entropy determined from the experimental free enthalpy results.

These presumptions were checked for 72 sets of experimental data recently presented in the literature and, in general, overestimations of the quality of the experiments were detected.

## INTRODUCTION

The theory presented in Part I of this study has been the basis for a re-analysis of many sets of experimental results available in the literature with respect to the possible occurrence of the expected relationship between the linear equation coefficients. The subjects of the analysis are data collected in articles published during the last two years by both Thermochimica Acta and the Journal of Thermal Analysis. Another set was found at random in High Temperature Science.

In this work, all data sets found during a review of the journals mentioned have been utilized. All of them represented a simultaneous change of two values determined as a result of elaborating the experimental results by means of the linear equation coefficients estimation. In most cases, the authors of the articles did not suggest the existence of any relationship between the value cited. It should be stressed that the only aim of our article was to draw attention to the possibility of making an error from an incorrect interpretation of the experimental results by means of the apparently safe method of least-squares. A re-estimation of the results presented has been left to the individual authors.

## ANALYSIS OF THE RELATIONSHIP BETWEEN THE LINEAR EQUATION COEFFICIENTS

The form of eqn. (25) * depends on the model equation used for a description of the relationship between the experimental results, as well as on the way the non-linear model equation describing the relationships of the measured values is transformed to a linear form [1]. They may be varied: by the logarithm, developing a series, utilizing the approximation equations, etc.

These variables $y$ and $x$ are not usually measured directly, but they are known functions of experimental values. In the case of the Arrhenius equation, the linearization leads to

$$\log_{10}(k) = \log_{10}(k_0) - E/[\log_e(10) RT] \tag{26}$$

which is the form most frequently used. $k$ is the reaction rate constant at temperature $T$, $E$ is the activation energy, $R$ the gas constant, $k_0$ the pre-exponential constant and $T$ the absolute temperature.

In comparison with eqn. (1)

$$y = \log_{10}(k) \tag{27a}$$

$$x = -1/[\log_e(10) RT] \tag{27b}$$

$$a = E \tag{27c}$$

$$b = \log_{10}(k_0) \tag{27d}$$

are obtained.

Thus the direction coefficient value $\alpha$ of eqn. (25) is approximately equal to

$$\alpha = \Sigma(1/T)/[\log_e(10) Rn] \tag{28}$$

where $n$ is the number of measurements.

In a case where the free enthalpy value (Gibbs function) is measured

$$G = H - TS \tag{29}$$

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* The numbering of equations remains the same for both parts of the article.

where $H$ is the enthalpy and $S$ the entropy, usually the substitutions

$$y = G/T \text{ or } y = -\log_e(K_i) \tag{30a}$$

$$x_i = 1/T \tag{30b}$$

$$a = H \quad \text{or } a = H/R \tag{30c}$$

$$b = -S \quad \text{or } b = -S/R \tag{30d}$$

are used, where $G$ is the free enthalpy value determined for temperature $T$, while $K$ is the equilibrium constant.

Thus the direction coefficient value for eqn. (25) is close to

$$\alpha = -\Sigma(1/T)/n \tag{31}$$

Analogous to the free enthalpy equation is the simple equation of vapour pressure change $p$ with temperature

$$\log_{10}(p) = A + B/T \tag{32a}$$

which leads to the substitution

$$y = \log_{10}(p) \tag{32b}$$

$$x = 1/T \tag{32c}$$

$$a = A \tag{32d}$$

$$b = B \tag{32e}$$

where $A$ and $B$ are the empirical equation coefficients. In this case the direction coefficient value of the "compensation" equation is also determined by eqn. (31).

The equation connecting the excess solubility enthalpy $H_e$ with a mean solution concentration $f_a$ is of a strictly empirical nature

$$H_e/(RTf_1f_2) = A + Bf_a \tag{33}$$

where $f_1$ and $f_2$ are the initial and final solution concentrations. In this case, the direction coefficient $\alpha$ of the "compensation" equation is directly equal to the negative mean value of the mean solution concentration.

$$\alpha = -\Sigma(f_a)/n \tag{34}$$

### *Method for the estimation of the "compensation" equation coefficients*

Unlike the classical least-squares method used to determine the coefficients of eqn. (1) and based on the minimization of the sum of the points square deviations from a straight line to the direction of the dependent variable axis, the coefficients of eqn. (25) have been determined by means of the equation based on the minimization of the distance of the points from the straight line, i.e. on the orthogonal regression.

In practice, the difference in values determined by these two methods is not too large. It is, however, of some significance due to the nature of the *a* and *b* values. It is not clear which of the coefficients of eqn. (1) should be recognized as an independent variable and which as a dependent one. There is no choice in this selection of method as only one of these values is prone to error. Both result from the same calculation procedure using the same set of measured results. In this case, it is natural that the orthogonal regression is applied.

## EXPERIMENTAL RESULTS

Table 1 gives the characteristics of the individual sets of experimental results. Each paper is identified by a letter and the sets of experimental results within each paper are labelled in numerical order.

Seventy-two sets of results have been collected from 22 papers: the first 56 sets are concerned with the determination of the Arrhenius equation coefficients; the next 12 sets involve the determination of the enthalpy and entropy from the free enthalpy equation; the subsequent two sets of results refer to the determination of the vapour pressure versus temperature equation coefficients; and the last two sets describe the change of the excess solubility enthalpy with the solution concentration.

The following information is given: the aim of the measurements; the method of measurement; and the factor differentiating the individual pairs of values in a given set of estimation results.

No bias was assumed towards the method of interpreting the individual experiments: the grouping of the sets of values by the authors of each work was a sufficient criterion for assuming a given set to be homogeneous.

The subjects of the papers analysed were as follows:

— the kinetics of dehydration and thermal decomposition, hydrolysis in acid, the martensitic transformation and the decomposition of explosives;

— the thermodynamics of: $GdF_3$ evaporation, fluoride synthesis, DNA and RNA transformation, and dissociation of barbituric acid derivatives;

— the change in pressure of organic substances; and

— the thermodynamics of polymer solubility in water solutions.

Various measurement techniques were used:

— measurement of the mass change during heating under isothermal conditions and with linear temperature increase (TG);

— differential thermal analysis (DTA);

— dynamic scanning calorimetry (DSC);

— dilatometry;

— potentiostatic titration;

— torsion–effusion method; and

— microcalorimetry.

TABLE 1

Experimental data

| No. | Data set code | Task of work | Measurement method | Variable factor |
|---|---|---|---|---|
| 1 | A01 | Thermal decomposition of $PbCO_3$ | Thermogravimetry at constant temperature | Pressure of $CO_2$ |
| 2 | A02 | Thermal decomposition of $PbCO_3 \cdot PbO$ | Thermogravimetry at constant temperature | Pressure of $CO_2$ |
| 3 | A03 | Thermal decomposition of $PbCO_3 \cdot 2PbO$ | Thermogravimetry at constant temperature | Pressure of $CO_2$ |
| 4 | A04 | Thermal decomposition of $2PbCO_3 \cdot Pb(OH)_2$ | Thermogravimetry at constant temperature | Pressure of $CO_2$ |
| 5 | A05 | Thermal decomposition of $2PbCO_3 \cdot PbO$ | Thermogravimetry at constant temperature | Pressure of $CO_2$ |
| 6 | A06 | Thermal decomposition of $PbCO_3 \cdot PbO$ | Thermogravimetry at constant temperature | Pressure of $CO_2$ |
| 7 | A07 | Thermal decomposition of $PbCO_3 \cdot 2PbO$ | Thermogravimetry at constant temperature | Pressure of $CO_2$ |
| 8 | A08 | Thermal decomposition of $PbCO_3$ | Thermogravimetry with linearly increasing temperature | Pressure of $CO_2$ |
| 9 | A09 | Thermal decomposition of $PbCO_3 \cdot PbO$ | Thermogravimetry with linearly increasing temperature | Pressure of $CO_2$ |
| 10 | A10 | Thermal decomposition of $PbCO_3 \cdot 2PbO$ | Thermogravimetry with linearly increasing temperature | Pressure of $CO_2$ |
| 11 | A11 | Thermal decomposition of $2PbCO_3 \cdot Pb(OH)_2$ | Thermogravimetry with linearly increasing temperature | Pressure of $CO_2$ |
| 12 | A12 | Thermal decomposition of $2PbCO_3 \cdot PbO$ | Thermogravimetry with linearly increasing temperature | Pressure of $CO_2$ |
| 13 | A13 | Thermal decomposition of $PbCO_3 \cdot PbO$ | Thermogravimetry with linearly increasing temperature | Pressure of $CO_2$ |
| 14 | A14 | Thermal decomposition of $PbCO_3 \cdot 2PbO$ | Thermogravimetry with linearly increasing temperature | Pressure of $CO_2$ |
| 15 | B01 | Oxidation kinetics of "$NbS_2$" | Thermogravimetry at constant temperature | Pressure of $O_2$ |
| 16 | C01 | Thermal decomposition of zinc acrylate | Thermogravimetry with linearly increasing temperature | Metal content in copolymer |
| 17 | C02 | Thermal decomposition of cobalt acrylate | Thermogravimetry with linearly increasing temperature | Metal content in copolymer |

TABLE 1 (continued)

| No. | Data set code | Task of work | Measurement method | Variable factor |
|---|---|---|---|---|
| 18 | C03 | Thermal decomposition of nickel acrylate | Thermogravimetry with linearly increasing temperature | Metal content in copolymer |
| 19 | C04 | Thermal decomposition of copper acrylate | Thermogravimetry with linearly increasing temperature | Metal content in copolymer |
| 20 | D01 | Thermal decomposition of $Cu(SAF)_2$ | Thermogravimetry with linearly increasing temperature | Different methods of the kinetic constants calculation |
| 21 | D02 | Thermal decomposition of $Cu(HNAF)_2$ | Thermogravimetry with linearly increasing temperature | Different methods of the kinetic constants calculation |
| 22 | D03 | Thermal decomposition of $Pd(SAF)_2Cl_2$ | Thermogravimetry with linearly increasing temperature | Different methods of the kinetic constants calculation |
| 23 | D04 | Thermal decomposition of $Pd(HNAF)_2Cl_2$ | Thermogravimetry with linearly increasing temperature | Different methods of the kinetic constants calculation |
| 24 | E01 | Thermal dehydration of $Ce_2(SO_4)\cdot nH_2O$ and $Ce_2(SO_4)\cdot nD_2O$ (Jander eqn.) | Thermogravimetry with linearly increasing temperature | Number of $H_2O$ or $D_2O$ molecules |
| 25 | E02 | Thermal dehydration of $Ce_2(SO_4)\cdot nH_2O$ and $Ce_2(SO_4)\cdot nD_2O$ (Ginstling eqn.) | Thermogravimetry with linearly increasing temperature | Number of $H_2O$ or $D_2O$ molecules |
| 26 | F01 | Thermal dehydration of Mg, Ca, Al, Cr, Fe Co, Ni, Zn, Mn and Cd complex salts with citric acid | Thermogravimetry with linearly increasing temperature | Kind of cation |
| 27 | G01 | Thermal dehydration of Cu and Zn salts of carboxylic acids | Thermogravimetry with linearly increasing temperature | Kind of salts |
| 28 | G02 | Thermal decomposition of Cu and Zn salts of carboxylic acids | Thermogravimetry with linearly increasing temperature | Kind of salts |
| 29 | H01 | Thermal decomposition of $(NH_4)_3M(SO_4)_3$ | Thermogravimetry at constant temperature | M = Al, Cr or Fe |
| 30 | H02 | Thermal decomposition of $NH_4M(SO_4)_2$ | Thermogravimetry at constant temperature | M = Al, Cr or Fe |
| 31 | H03 | Thermal decomposition of $M_2(SO_4)_3$ | Thermogravimetry at constant temperature | M = Al, Cr or Fe |
| 32 | I01 | Thermal decomposition of a series of polythiocarbonates | Thermogravimetry with linearly increasing temperature | Kind of polythiocarbonates |

TABLE 1 (continued)

| No. | Data set code | Task of work | Measurement method | Variable factor |
|---|---|---|---|---|
| 33 | I01 | Thermal dehydration of $(COOH)_2 \cdot 2H_2O$ | Thermogravimetry at constant temperature | Particle size in samples |
| 34 | I02 | Thermal dehydration of $(COOH)_2 \cdot 2H_2O$ | Termogravimetry with linearly increasing temperature | Different kinetic model equations |
| 35 | I03 | Thermal dehydration of $(COOH)_2 \cdot 2H_2O$ | Thermogravimetry with linearly increasing temperature | Particle size in samples |
| 36 | K01 | Exothermic decomposition of energetic materials: cast singgle base propellent | Differential scanning calorimetry | Different kinetic model equations (integral method) |
| 37 | K02 | Exothermic decomposition of energetic materials: cast single base propellent | Differential scanning calorimetry | Different kinetic model equations (differential method) |
| 38 | K03 | Exothermic decomposition of energetic materials: double base propellent | Differential scanning calorimetry | Different kinetic model equations (integral method) |
| 39 | K04 | Exothermic decomposition of energetic materials: double base propellent | Differential scanning calorimetry | Different kinetic model equations (differential method) |
| 40 | K05 | Exothermic decomposition of energetic materials: 1,4,5,8-tetranitro-1,4,5,8-zadecalin | Differential scanning calorimetry | Different kinetic model equations (integral method) |
| 41 | K06 | Exothermic decomposition of energetic materials: 1,4,5,8-tetranitro-1,4,5,8-zadecalin | Differential scanning calorimetry | Different kinetic model equations (differential method) |
| 42 | K07 | Exothermic decomposition of energetic materials: 2,6-dinitrophenol (trace 1) | Differential scanning calorimetry | Different kinetic model equations (integral method) |
| 43 | K08 | Exothermic decomposition of energetic materials: 2,6-dinitrophenol (trace 1) | Differential scanning calorimetry | Different kinetic model equations (differential method) |
| 44 | K09 | Exothermic decomposition of energetic materials: 2,6-dinitrophenol (trace 2) | Differential scanning calorimetry | Different kinetic model equations (integral method) |

TABLE 1 (continued)

| No. | Data set code | Task of work | Measurement method | Variable factor |
|---|---|---|---|---|
| 45 | K10 | Exothermic decomposition of energetic materials: 2,6-dinitrophenol (trace 2) | Differential scanning calorimetry | Different kinetic model equations (differential method) |
| 46 | K11 | Exothermic decomposition of energetic materials: 2,6-dinitrophenol (trace 3) | Differential scanning calorimetry | Different kinetic model equations (integral method) |
| 47 | K12 | Exothermic decomposition of energetic materials: 2,6-dini trophenol (trace 3) | Differential scanning calorimetry | Different kinetic model equations (differential method) |
| 48 | K13 | Exothermic decomposition of energetic materials: 2,6-dinitrophenol (trace 4) | Differential scanning calorimetry | Different kinetic model equations (integral method) |
| 49 | K14 | Exothermic decomposition of energetic materials: 2,6-dinitrophenol (trace 4) | Differential scanning calorimetry | Different kinetic model equations (differential method) |
| 50 | L01 | Decomposition of cellulose | Differential scanning calorimetry | Acid concentration, sample quantity, acid quantity |
| 51 | L02 | Decomposition of D-glucose | Differential scanning calorimetry | Acid concentration, sample quantity, acid quantity |
| 52 | M01 | Kinetics of the acid hydrolysis of cellulosic materials | Differential scanning calorimetry | Different kinds of cellulosic materials |
| 53 | N01 | Kinetics of the martensitic transformation in CuAlNi-43 alloy | Differential scanning calorimetry | Different kinetic model equations, scanning rate |
| 54 | P01 | First stage of thermal explosion tertiary butyl peroxybenzoate | Differential thermal analysis | Different kinetic model equations, mass of sample, atmosphere |
| 55 | P02 | First stage of thermal explosion of tertiary butyl peroxybenzoate | Low pressure autoclave | Pressure of $O_2$ |
| 56 | Q01 | Burning velocity of gas-less pyrotechnic mixtures | Thermodilatometry | Kind of pyrotechnic mixture |
| 57 | R01 | Thermodynamics of $GdF_3$ evaporation | Thermogravimetry at constant temperature with evolved gas detection | Sample preparation: Ta or Mo cell, cast or powder |

TABLE 1 (continued)

| No. | Data set code | Task of work | Measurement method | Variable factor |
|---|---|---|---|---|
| 58 | S01 | Thermodynamics of $MTeF_3$ synthesis | Literature data evaluation | M = Li, Na, K, Rb and Cs |
| 59 | S02 | Thermodynamics of MF synthesis | Literature data evaluation | M = Li, Na, K, Rb and Cs |
| 60 | T01 | Thermodynamics of inversion of B-DNA to Z-DNA | UV spectroscopy | Kind of polynucleotides |
| 61 | T02 | Thermodynamics of inversion of A-RNA to Z-RNA | UV spectroscopy | Kind of polynucleotides |
| 62 | U01 | Thermodynamics of dissociation of barbituric acid | Potentiometry | Relationship of dioxane to water |
| 63 | U02 | Thermodynamics of dissociation of barbituric acid compound, x = H | Potentiometry | Relationship of dioxane to water |
| 64 | U03 | Thermodynamics of dissociation of barbituric acid compound, x = OH | Potentiometry | Relationship of dioxane to water |
| 65 | U04 | Thermodynamics of dissociation of barbituric acid compound, $x = NO_2$ | Potentiometry | Relationship of dioxane to water |
| 66 | U05 | Thermodynamics of dissociation of barbituric acid compound, $x = CH_3$ | Potentiometry | Relationship of dioxane to water |
| 67 | U06 | Thermodynamics of dissociation of barbituric acid compound, x = COOH | Potentiometry | Relationship of dioxane to water |
| 68 | U07 | Thermodynamics of dissociation of barbituric acid compound, $x = OCH_3$ | Potentiometry | Relationship of dioxane to water |
| 69 | V01 | Vapour pressure of monophenylurea | Torsion–effusion method | Different experiments |
| 70 | V02 | Vapour pressure of diphenyl-1,3-urea | Torsion–effusion method | Different experiments |
| 71 | W01 | Heat of dilution of poly(acrylic acid)–water system | Flow microcalorimetry | Molecular weight of polymers |
| 72 | W02 | Heat of dilution of poly(acrylic acid)–(water–ethyl alcohol) mixture | Flow microcalorimetry | Volume fraction of ethyl alcohol |

Table 1 (footnotes)

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V D. Ferro and G. Della Gatta, Thermochim. Acta, 122 (1987) 189.
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The factors differentiating the values collected in a single set were:

— the kind of the material tested;

— the experimental parameters: $CO_2$ or $O_2$ partial pressure, weight of the sample and concentration of the solvent, form of the sample (solid or powdered, with or without particle size ranges), concentration of solution; and

— the elements of the calculation procedure: various model equations used in the calculations, utilization of only a part of the whole set of experimental results, various methods for linearization of the model equation.

Table 2 lists the results of the calculations of the "compensation" equation coefficients for the individual sets of experimental results. The code of the set, the number of value pairs used in the calculations of coefficients $a$ and $b$, the values of the "compensation" eqn. (25) coefficients and the correlation coefficients $r_e(a, b)$ calculated from the experimental data describing the correlation of the given "compensation" equation have been given.

Table 3 presents the statistical values with reference to the quality of the estimation process or the "compensation" equation coefficients, i.e. the

TABLE 2

Results of calculations

| No. | Data set code [a] | Number of experiments $n$ | Coefficients of the compensation equation | | Correlation coefficient $r_e(a, b)$ |
|---|---|---|---|---|---|
| | | | $\alpha$ | $\beta$ | |
| 1 | A01 | 4 | 0.05635 | 10.29275 | 0.97936 |
| 2 | A02 | 3 | 0.06881 | 4.92009 | 0.98900 |
| 3 | A03 | 5 | 0.03598 | 30.12202 | 0.98416 |
| 4 | A04 | 6 | −0.12108 | 9.11486 | −0.79922 |
| 5 | A05 | 6 | 0.09077 | 2.06758 | 0.97841 |
| 6 | A06 | 5 | 0.04921 | 32.09453 | 0.83524 |
| 7 | A07 | 4 | 0.06764 | 3.88541 | 0.99438 |
| 8 | A08 | 8 | 0.06269 | 8.09927 | 0.88162 |
| 9 | A09 | 7 | 0.07550 | −13.24393 | 0.99045 |
| 10 | A10 | 8 | 0.03957 | −25.26714 | 0.98099 |
| 11 | A11 | 9 | −0.11060 | 8.63348 | −0.88926 |
| 12 | A12 | 9 | 0.09390 | −0.75857 | 0.99436 |
| 13 | A13 | 8 | 0.05736 | 19.96403 | 0.99448 |
| 14 | A14 | 8 | 0.06517 | 4.94483 | 0.99902 |
| 15 | B01 | 4 | 0.079720 | −4.93260 | 0.98134 |
| 16 | C01 | 7 | 0.07011 | −0.97281 | 0.99996 |
| 17 | C02 | 7 | 0.08414 | −3.82835 | 0.99940 |
| 18 | C03 | 7 | 0.08809 | −3.84667 | 0.99287 |
| 19 | C04 | 7 | 0.07533 | −2.00554 | 0.99950 |
| 20 | D01 | 3 | 0.10660 | −4.22818 | 0.99818 |
| 21 | D02 | 3 | 0.10650 | −5.43015 | 0.99826 |
| 22 | D03 | 3 | 0.07220 | −1.60699 | 0.99035 |
| 23 | D04 | 3 | 0.08730 | −3.79009 | 0.99964 |
| 24 | E01 | 6 | 0.13792 | −5.00813 | 0.99036 |
| 25 | E02 | 6 | 0.21069 | −6.29274 | 0.99605 |
| 26 | F01 | 10 | 0.04934 | 6.27845 | 0.68907 |
| 27 | G01 | 4 | 0.13228 | 1.54588 | 0.92711 |
| 28 | G02 | 7 | 0.10756 | 0.07959 | 0.97078 |
| 29 | H01 | 3 | 0.15666 | −0.28161 | 0.98713 |
| 30 | H02 | 3 | 0.06498 | 12.59886 | 0.96022 |
| 31 | H03 | 3 | 0.07274 | 8.37917 | 0.99178 |
| 32 | I01 | 17 | 0.30971 | −1.97556 | 0.98200 |
| 33 | J01 | 6 | 0.16705 | −3.98699 | 0.99930 |
| 34 | J02 | 11 | 0.15363 | −3.00962 | 0.99990 |
| 35 | J03 | 3 | 0.13994 | −1.88040 | 0.99850 |
| 36 | K01 | 24 | 0.10874 | −2.78569 | 0.99989 |
| 37 | K02 | 28 | 0.10847 | −2.64909 | 0.99989 |
| 38 | K03 | 21 | 0.10924 | −2.77869 | 0.99985 |
| 39 | K04 | 27 | 0.10916 | −2.71646 | 0.99986 |
| 40 | K05 | 24 | 0.10203 | −2.70367 | 0.99983 |
| 41 | K06 | 28 | 0.10269 | −2.71604 | 0.99991 |
| 42 | K07 | 24 | 0.08915 | −2.88884 | 0.99964 |
| 43 | K08 | 27 | 0.08921 | −2.84638 | 0.99961 |
| 44 | K09 | 24 | 0.08936 | −2.89341 | 0.99967 |

TABLE 2 (continued)

| No. | Data set code [a] | Number of experiments $n$ | Coefficients of the compensation equation | | Correlation coefficient $r_e(a, b)$ |
|---|---|---|---|---|---|
| | | | $\alpha$ | $\beta$ | |
| 45 | K10 | 27 | 0.08938 | −2.83002 | 0.99967 |
| 46 | K11 | 24 | 0.08721 | −2.61048 | 0.99929 |
| 47 | K12 | 27 | 0.08766 | −2.78877 | 0.99969 |
| 48 | K13 | 24 | 0.08716 | −2.85372 | 0.99947 |
| 49 | K14 | 27 | 0.08746 | −2.84710 | 0.99960 |
| 50 | L01 | 7 | 0.08891 | 5.57191 | 0.98206 |
| 51 | L02 | 6 | 0.02415 | 13.22803 | 0.21042 |
| 52 | M01 | 4 | 0.25577 | −4.89438 | 0.99681 |
| 53 | N01 | 16 | 0.45164 | −20.52507 | 0.90227 |
| 54 | P01 | 10 | 0.13837 | 1.87422 | 0.99914 |
| 55 | P02 | 7 | 0.11177 | 4.05009 | 0.45292 |
| 56 | Q01 | 3 | 0.16467 | 2.19938 | 0.99364 |
| 57 | R01 | 11 | 0.67312 | −24.53347 | 0.99871 |
| 58 | S01 | 5 | −4.00177 | −6528.95444 | −0.17855 |
| 59 | S02 | 5 | 0.81118 | 528.96247 | 0.93047 |
| 60 | T01 | 4 | −0.45797 | 746.91420 | −0.84613 |
| 61 | T02 | 3 | 2.37461 | 3.29753 | 0.97201 |
| 62 | U01 | 6 | 3.00570 | −17.44498 | 0.99187 |
| 63 | U02 | 3 | 4.23405 | −65.58247 | 0.99231 |
| 64 | U03 | 10 | 3.61687 | −48.97841 | 0.91225 |
| 65 | U04 | 5 | 2.93384 | −34.77024 | 0.99987 |
| 66 | U05 | 5 | 2.81906 | −38.35932 | 0.99773 |
| 67 | U06 | 6 | 1.60187 | −28.46769 | 0.98545 |
| 68 | U07 | 5 | 2.84233 | −37.45431 | 0.99960 |
| 69 | V01 | 4 | 0.00269 | −3.80551 | 0.99862 |
| 70 | V02 | 6 | −0.00004 | 15.25443 | −0.02634 |
| 71 | W01 | 4 | −0.09557 | 0.09320 | 0.98622 |
| 72 | W02 | 9 | −0.01438 | −0.01884 | −0.51956 |

[a] Key as in Table 1.

standard deviation of the coefficients $s(\alpha)$ and $s(\beta)$ as well as the correlation coefficient $r(\alpha,\beta)$ calculated from

$$r(\alpha, \beta) = \operatorname{cov}(\alpha, \beta)/[s(\alpha)s(\beta)] \tag{35}$$

which together give a full description of the covariance matrix of the "compensation" equation coefficients. In addition, the mean values of the variables $a$ and $b$ have been given.

Table 4 lists the mean temperature values and their standard deviations, estimated from the data describing the measurement conditions, available from the individual papers. They are usually very rough, based on the little information in the texts, on the descriptions of figures or given as certain values, e.g. temperatures characterizing some stages of the experiment: start

TABLE 3

Statistical properties of the compensation equation, $b = \alpha a + \beta$ coefficients sets

| No. | Data set code [a] | Statistical properties | | | | |
|---|---|---|---|---|---|---|
| | | Standard deviation | | Correlation coefficient | Mean value | |
| | | $s(\alpha)$ | $s(\beta)$ | $r(\alpha, \beta)$ | $\bar{b}$ | $\bar{a}$ |
| 1 | A01 | 0.00819 | 3.29303 | −0.99566 | 32.83500 | 400.00000 |
| 2 | A02 | 0.01024 | 5.99876 | −0.96925 | 43.98666 | 567.66666 |
| 3 | A03 | 0.00373 | 2.99285 | −0.96709 | 57.99600 | 774.60000 |
| 4 | A04 | 0.04488 | 1.80383 | −0.99521 | 4.27166 | 40.00000 |
| 5 | A05 | 0.00950 | 4.30076 | −0.99254 | 42.82333 | 449.00000 |
| 6 | A06 | 0.01865 | 19.92829 | −0.99682 | 84.48400 | 1064.60000 |
| 7 | A07 | 0.00506 | 6.06283 | −0.97985 | 83.16500 | 1172.00000 |
| 8 | A08 | 0.01364 | 5.77023 | −0.99672 | 34.51875 | 421.37500 |
| 9 | A09 | 0.00467 | 2.50074 | −0.97418 | 40.53000 | 521.28571 |
| 10 | A10 | 0.00319 | 2.63043 | −0.97863 | 60.38500 | 806.75000 |
| 11 | A11 | 0.02124 | 0.86661 | −0.99420 | 4.14777 | 40.55555 |
| 12 | A12 | 0.00375 | 1.81566 | −0.99489 | 44.46222 | 481.55555 |
| 13 | A13 | 0.00246 | 2.82895 | −0.99714 | 85.67000 | 1145.50000 |
| 14 | A14 | 0.00117 | 1.39724 | −0.97012 | 80.43875 | 1158.25000 |
| 15 | B01 | 0.01097 | 2.27096 | −0.99969 | 11.55950 | 206.87500 |
| 16 | C01 | 0.00027 | 0.06709 | −0.98892 | 15.76560 | 238.71428 |
| 17 | C02 | 0.00128 | 0.30618 | −0.98196 | 15.80178 | 233.28571 |
| 18 | C03 | 0.00469 | 0.99331 | −0.98219 | 14.47658 | 208.00000 |
| 19 | C04 | 0.00105 | 0.17835 | −0.99601 | 10.67171 | 168.28571 |
| 20 | D01 | 0.00635 | 0.60150 | −0.99677 | 5.82816 | 94.33333 |
| 21 | D02 | 0.00621 | 0.54317 | −0.99598 | 3.84666 | 87.10000 |
| 22 | D03 | 0.01005 | 0.76555 | −0.99777 | 3.88090 | 76.00000 |
| 23 | D04 | 0.00231 | 0.25813 | −0.99862 | 5.94476 | 111.50000 |
| 24 | E01 | 0.00946 | 1.17789 | −0.99566 | 12.08586 | 123.93333 |
| 25 | E02 | 0.00899 | 0.18255 | −0.85360 | −2.64145 | 17.33000 |
| 26 | F01 | 0.01830 | 1.20096 | −0.98329 | 9.46215 | 64.52000 |
| 27 | G01 | 0.03716 | 2.26794 | −0.98458 | 9.49287 | 60.07500 |
| 28 | G02 | 0.01175 | 1.97350 | −0.96807 | 17.56331 | 162.54285 |
| 29 | H01 | 0.02477 | 3.46275 | −0.95046 | 20.53333 | 132.86666 |
| 30 | H02 | 0.01881 | 3.30047 | −0.98279 | 23.80000 | 172.36666 |
| 31 | H03 | 0.00933 | 2.15451 | −0.97615 | 24.76666 | 225.26666 |
| 32 | I01 | 0.01410 | 0.77398 | −0.94709 | 14.12228 | 51.97647 |
| 33 | J01 | 0.00303 | 0.24549 | −0.99823 | 9.50000 | 80.73333 |
| 34 | J02 | 0.00067 | 0.16468 | −0.88256 | 30.06272 | 215.26363 |
| 35 | J03 | 0.00750 | 0.61190 | −0.99996 | 9.52333 | 81.49000 |
| 36 | K01 | 0.00033 | 0.13200 | −0.75987 | 29.50208 | 296.91875 |
| 37 | K02 | 0.00030 | 0.10900 | −0.74561 | 26.41392 | 267.92500 |
| 38 | K03 | 0.00041 | 0.15413 | −0.79646 | 29.33571 | 293.96095 |
| 39 | K04 | 0.00035 | 0.11070 | −0.74342 | 22.78851 | 233.63777 |
| 40 | K05 | 0.00038 | 0.18229 | −0.76673 | 33.97583 | 359.48791 |
| 41 | K06 | 0.00025 | 0.12305 | −0.77809 | 35.12071 | 368.42142 |
| 42 | K07 | 0.00050 | 0.13944 | −0.78501 | 16.61333 | 218.75458 |
| 43 | K08 | 0.00049 | 0.13399 | −0.78716 | 16.33000 | 214.95074 |
| 44 | K09 | 0.00048 | 0.14276 | −0.78815 | 17.88875 | 232.56291 |

TABLE 3 (continued)

| No. | Data set code [a] | Statistical properties | | | | |
|---|---|---|---|---|---|---|
| | | Standard deviation | | Correlation coefficient | Mean value | |
| | | $s(\alpha)$ | $s(\beta)$ | $r(\alpha, \beta)$ | $\bar{b}$ | $\bar{a}$ |
| 45 | K10 | 0.00045 | 0.12888 | −0.78213 | 16.98962 | 221.74481 |
| 46 | K11 | 0.00069 | 0.21621 | −0.77882 | 18.62875 | 243.54083 |
| 47 | K12 | 0.00043 | 0.13354 | −0.78866 | 18.63370 | 244.37370 |
| 48 | K13 | 0.00059 | 0.16204 | −0.78297 | 15.68000 | 212.63500 |
| 49 | K14 | 0.00048 | 0.13249 | −0.79520 | 16.08259 | 216.43000 |
| 50 | L01 | 0.00757 | 1.52963 | −0.95459 | 22.71420 | 192.80000 |
| 51 | L02 | 0.05606 | 0.80437 | −0.99488 | 16.67511 | 142.73333 |
| 52 | M01 | 0.01360 | 2.97527 | −0.99004 | 50.50025 | 216.57500 |
| 53 | N01 | 0.04918 | 0.52137 | −0.80630 | 18.07925 | 85.47500 |
| 54 | P01 | 0.00198 | 0.33903 | −0.92863 | 23.77968 | 158.30000 |
| 55 | P02 | 0.09723 | 11.48787 | −0.99275 | 17.15930 | 117.28571 |
| 56 | Q01 | 0.01817 | 0.71946 | −0.97670 | 8.56666 | 38.66666 |
| 57 | R01 | 0.00858 | 0.86251 | −0.99954 | 43.04181 | 100.39000 |
| 58 | S01 | 12.35311 | 507.38122 | −0.99999 | 222.04000 | −1687.00000 |
| 59 | S02 | 0.13523 | 77.67447 | −0.99933 | 63.34000 | −574.00000 |
| 60 | T01 | 0.17404 | 60.12864 | −0.94436 | 597.50000 | 326.25000 |
| 61 | T02 | 0.49568 | 2.16675 | −0.99895 | 13.66666 | 4.36666 |
| 62 | U01 | 0.17460 | 1.84475 | −0.86841 | 10.13333 | 9.17533 |
| 63 | U02 | 0.50098 | 13.01826 | −0.99132 | 43.48666 | 25.76000 |
| 64 | U03 | 0.53550 | 6.30651 | −0.96512 | −7.86900 | 11.36600 |
| 65 | U04 | 0.02385 | 0.36959 | −0.95010 | 8.41600 | 14.72000 |
| 66 | U05 | 0.09827 | 0.78044 | −0.88852 | −18.46800 | 7.05600 |
| 67 | U06 | 0.10688 | 1.46551 | −0.73590 | −12.30533 | 10.08966 |
| 68 | U07 | 0.04143 | 0.51226 | −0.96737 | −3.46000 | 11.96000 |
| 69 | V01 | 0.00010 | 0.71498 | −0.99983 | 15.42750 | 7130.25000 |
| 70 | V02 | 0.00075 | 6.06375 | −0.99937 | 14.93500 | 7975.83333 |
| 71 | W01 | 0.01123 | 0.00798 | −0.54181 | 0.13000 | −0.38500 |
| 72 | W02 | 0.00893 | 0.13863 | −0.47295 | 0.08666 | −7.33444 |

of the reaction, peak temperature, etc. They are usually inaccurate, which is proven by the high standard temperature deviation values. They have been compared with the values of the mean temperature calculated from the values of the α coefficients of the "compensation" equations. In addition, the standard deviations for the temperature are given. For the last two sets, the mean concentration values are given instead of temperature, as in these cases concentrations, not temperature, were the independent variables.

## CHARACTERISTICS OF THE EXPERIMENTAL RESULTS

Brief characteristics of the groups of results are given below.

TABLE 4

Comparison between the values calculated from the "compensation" equation and the "experimental" values

| No. | Data set code [a] | Temperature (K) | | | |
|---|---|---|---|---|---|
| | | Calculated | | Experimental | |
| | | Value | Standard deviation | Value | Standard deviation |
| 1 | A01 | 927 | 135 | 584 | 126 |
| 2 | A02 | 759 | 113 | 584 | 126 |
| 3 | A03 | 1452 | 151 | 584 | 126 |
| 4 | A04 | −431 | 160 | 584 | 126 |
| 5 | A05 | 575 | 60 | 584 | 126 |
| 6 | A06 | 1061 | 402 | 584 | 126 |
| 7 | A07 | 772 | 58 | 584 | 126 |
| 8 | A08 | 833 | 181 | no data | |
| 9 | A09 | 692 | 43 | no data | |
| 10 | A10 | 1320 | 106 | no data | |
| 11 | A11 | −472 | 91 | no data | |
| 12 | A12 | 556 | 22 | no data | |
| 13 | A13 | 911 | 39 | no data | |
| 14 | A14 | 801 | 14 | no data | |
| 15 | B01 | 655 | 90 | 749 | 28 |
| 16 | C01 | 745 | 3 | 648 | 48 |
| 17 | C02 | 621 | 10 | 633 | 38 |
| 18 | C03 | 593 | 32 | 611 | 42 |
| 19 | C04 | 693 | 10 | 622 | 44 |
| 20 | D01 | 490 | 29 | 583 | 137 |
| 21 | D02 | 490 | 29 | 667 | 156 |
| 22 | D03 | 723 | 101 | 583 | 137 |
| 23 | D04 | 598 | 16 | 600 | 169 |
| 24 | E01 | 379 | 26 | 384 | 64 |
| 25 | E02 | 248 | 11 | 506 | 59 |
| 26 | F01 | 1059 | 393 | 363 | 25 |
| 27 | G01 | 395 | 111 | 367 | 79 |
| 28 | G02 | 486 | 53 | 529 | 129 |
| 29 | H01 | 333 | 53 | 660 | 42 |
| 30 | H02 | 804 | 233 | 741 | 94 |
| 31 | H03 | 718 | 92 | 950 | 81 |
| 32 | I01 | 706 | 32 | 730 | 175 |
| 33 | J01 | 313 | 6 | 318 | 10 |
| 34 | J02 | 340 | 2 | 336 | 4 |
| 35 | J03 | 373 | 20 | 335 | 4 |
| 36 | K01 | 480 | 2 | 467 | 6 |
| 37 | K02 | 482 | 1 | 467 | 6 |
| 38 | K03 | 478 | 2 | 462 | 7 |
| 39 | K04 | 478 | 2 | 462 | 7 |
| 40 | K05 | 512 | 2 | 496 | 8 |
| 41 | K06 | 509 | 1 | 496 | 8 |
| 42 | K07 | 586 | 3 | 558 | 19 |
| 43 | K08 | 585 | 3 | 558 | 19 |

TABLE 4 (continued)

| No. | Data set code[a] | Temperature (K) | | | |
|---|---|---|---|---|---|
| | | Calculated | | Experimental | |
| | | Value | Standard deviation | Value | Standard deviation |
| 44 | K09 | 585 | 3 | 557 | 18 |
| 45 | K10 | 584 | 3 | 557 | 18 |
| 46 | K11 | 599 | 5 | 571 | 14 |
| 47 | K12 | 596 | 3 | 571 | 14 |
| 48 | K13 | 599 | 4 | 571 | 16 |
| 49 | K14 | 597 | 3 | 571 | 16 |
| 50 | L01 | 587 | 50 | 434 | 52 |
| 51 | L02 | 2163 | 5021 | 430 | 40 |
| 52 | M01 | 470 | 25 | 492 | 18 |
| 53 | N01 | 116 | 13 | 126 | 198 |
| 54 | P01 | 377 | 5 | 377 | 10 |
| 55 | P02 | 467 | 407 | 403 | 35 |
| 56 | Q01 | 317 | 35 | 289 | 860 |
| 57 | R01 | 1485 | 19 | 1465 | no data |
| 58 | S01 | −250 | 771 | no data | |
| 59 | S02 | 1233 | 206 | no data | |
| 60 | T01 | −2184 | 830 | 317 | 8 |
| 61 | T02 | 421 | 88 | 315 | 7 |
| 62 | U01 | 333 | 19 | 305 | 6 |
| 63 | U02 | 236 | 28 | 305 | 6 |
| 64 | U03 | 276 | 41 | 305 | 6 |
| 65 | U04 | 341 | 3 | 305 | 6 |
| 66 | U05 | 355 | 12 | 305 | 6 |
| 67 | U06 | 624 | 42 | 305 | 6 |
| 68 | U07 | 352 | 5 | 305 | 6 |
| 69 | V01 | 371 | 14 | 405 | 13 |
| 70 | V02 | −24969 | 473684 | 463 | 19 |
| 71 | W01 | 0.0955 | 0.0112 | 0.0413 | 0.0254 |
| 72 | W02 | 0.0143 | 0.0089 | no data | |

[a] Key as in Table 1.

### *Group A*

The individual "compensation" equations are characterized by a high correlation coefficient $r_e(a, b)$ value, which proves the significance of these relationships. Temperature values, calculated on the basis of available data on the experimental conditions are in agreement as regards the order of values for the individual mean temperatures calculated for the given "compensation" equations according to eqn. (28). In only two cases were the calculated mean temperatures negative (sets A04 and A11). The results of calculations regarding the same reactions, but calculated for the experimental values obtained under isothermal conditions and the linear temperature increase, are very similar (1 and 8, 2 and 9, etc.). The high values of the $\alpha$ coefficient of the "compensation" equation, calculated for the isothermal method, correspond with the high values of this coefficient determined for the data obtained by the non-isothermal method. This indicates that the $CO_2$ pressure changes affect the kinetics of the individual reactions. This effect, however, is relatively small. The problem of the agreement of two corresponding sets of results, A04 (isothermic measurements) and A11 (non-isothermic measurements), is ambiguous. In both cases the calculated mean temperature values are negative, but their absolute value approximates the appropriate value estimated for the experimental results analysed.

### *Group B*

The high value of the correlation coefficient $r_e(a, b)$ indicates the significance of the "compensation" relationship. The difference between the mean temperature value calculated for the given "compensation" equation and the value estimated from the available experimental values indicates that the oxygen pressure change has a very weak effect on the "$NbS_2$" oxidation kinetics. The difference is of the order of 14%, which can be acknowledged as a relatively small difference in comparison to the calculated standard deviation value.

### *Group C*

The mean temperature values determined are close to the experimental values estimated from the data available in the article. The difference is particularly small for the C01 set. All differences in the corresponding temperatures, the calculated and "experimental", are statistically insignificant. This good agreement of the values calculated for the "compensation" equations with the experimental values indicates that the experimental error is the principal element affecting the change in the Arrhenius equation coefficient values. It is difficult to explain the connections between the differences observed and the effect of metal concentration changes in the copolymer tested.

### *Group D*

The calculated mean temperature values are generally lower than the "experimental" values. It should be stressed, however, that the experimental values for the mean temperature have been calculated based on the temperature boundary values determining the DTG peak boundaries. Statistically, the differences observed are insignificant.

### *Group E*

The high value of the correlation coefficient $r_e(a, b)$ indicates the significance of the "compensation" equations determined for the first dehydration stage. The calculated mean temperature value is close to the value estimated based on the experimental results. This indicates that the experimental error is the only factor causing the change in the Arrhenius equation coefficients. This is particularly clear for the results regarding the first stage of the dehydration process. Here it can be presumed that the course of this process runs independently of the initial number of $H_2O$ or $D_2O$ molecules joined with the sulphate.

In the second stage of the dehydration process, the calculated mean temperature value differs from the "experimental" one. This result becomes even more striking after repeated calculations of the "compensation" equation coefficients, rejecting the last two points, which are so distinctly different from the rest. In this case the calculated mean temperature value is considerably higher than the experimental value. It seems that the "compensation" effect observed is a result of the random error overlapping the effect connected with the second stage dehydration reaction course. In this case, the course of the reaction is different for different substances, characterized by different initial numbers of $H_2O$ or $D_2O$ molecules.

### *Group F*

The mean temperature value determined is different from the "experimental" value. The "compensation" relationship stated is characterized by a relatively low correlation coefficient $r_e(a, b) = 0.68907$. Nevertheless, this relationship is statistically significant. It has been obtained despite the great variety in chemical composition of the substances tested. An overlapping of the experimental error effect with the actual effect, resulting from the differences in chemical properties, has occurred here. It is also interesting that the "compensation" effect has been observed although different models of chemical reactions have been attributed to the dehydration processes of various compounds.

### *Group G*

In this case, there is good agreement between the mean temperature values calculated for the given "compensation" equation and the "experimental" values. The observed effect has occurred although the tests were made for a large group of chemical substances and the description assumed different values of reaction order. It is clear, that the actual differences between the dehydration processes of the individual substances are comparable with the error of the experimental method applied.

### *Group H*

It is not clear from the text whether natural or decimal logarithms from the Arrhenius equation pre-exponential constant are given. In these calculations, it is assumed that these are decimal logarithms. In this case, a good agreement between the calculated and experimental mean temperature values was found. The high value of the correlation coefficient for the "compensation" equations indicates that the relationships observed are significant. It seems that in the cases observed the experimental error has an effect comparable to the effect of the variable factors. In a case when the pre-exponential constant value would be expressed in form of the natural logarithm, the coefficient values given should be multiplied by 2.3025 ($\log_e(10)$). Thus, a closer agreement for the H01 set would be achieved, but the agreement between the remaining two sets would be worsened. However, this would not change, in principal, the opinion regarding the significance of the measurements made.

### *Group I*

A good agreement between the mean temperature value, calculated based on the "compensation" equation, and the "experimental" value is observed. It seems that the effect of the changing properties of the individual substances is low in comparison with the experimental error.

### *Group J*

The calculations made indicate a good agreement between the calculated mean temperature value and the "experimental" one. The effect of grain size and selection of a specific kinetic model are insignificant as regards the calculated values of the activation energy and pre-exponential constant. The data presented do not allow for an explicit selection of the best kinetic model describing the tested chemical reaction kinetics. All pairs of values describe the process tested equally well.

### *Group K*

The re-calculation of the experimental results, taking into account various kinetic models, has only revealed the effect of experimental error on the results of the estimation of the Arrhenius equation constants. Despite the enormous spread of the activation energy and pre-exponential constant values, the mean temperature determined, based on the "compensation" equation, is very close to the "experimental" value. The agreement is strengthened by the simultaneous increase in both calculated and "experimental" temperatures obtained with subsequent pairs of values of the Arrhenius equation coefficients. It seems that selecting one of the several kinetic equations analysed, based only on the experimental results presented, would not be justified.

### *Group L*

Of two sets presented by the authors, the first, L01, shows a typical agreement of the mean temperature calculated from the "compensation" equation and the "experimental" value.

The second set, L02, is characterized by a large discrepancy between the values. However, in this case the low correlation coefficient value explains the reason; the calculated mean temperature value is rather random.

### *Group M*

It is not clear whether natural or decimal logarithms of the pre-exponential constant are given. Preliminary calculations indicate that these are natural logarithm values. The "compensation" equation coefficient has been calculated in the "standard" form (eqn. (26)), taking into account the decimal logarithm. The mean temperature value was 470 K, which is close to the "experimental" one (492 K) calculated as the geometrical mean of the peaks on the DSC curve. This indicates that the methodology applied does not allow for a differentiation of the Arrhenius equation coefficients due to the type of material tested within the range of the variability investigated.

### *Group N*

As in the case of set K, it can also be seen here that the bases for a selection of the form of the kinetic equation are very weak if they are determined using the presented results only. A good agreement between the value calculated from the "compensation" equation and the "experimental" value of the mean measurement temperature is confirmation of this.

### *Group P*

There is good agreement between the value calculated from the "compensation" equation and the "experimental" value. The maximum difference does not exceed 64 K at the mean temperature of approximately 467 K. This difference is statistically insignificant.

### *Group Q*

This is the last group of data concerning the determination of the Arrhenius equation coefficient based on the kinetics test results. In this case good agreement between the calculated and "experimental" values of the mean measurement temperature is observed. This indicates that the methodology applied does not allow the determination of the Arrhenius equation constant values with an accuracy permitting differentiation of the properties of the individual pyrotechnic mixtures.

### *Group R*

The very good agreement between the mean temperature value calculated from the "compensation" equation (1485 K) and the mean temperature value given by the authors (1465 K) indicates that the effect of changed measurement conditions, i.e. the type of crucible material and form of the substance (powder, solid) is not significant. In contrast to the cases discussed above, the estimation problem (free-enthalpy measurements) is here of greater importance. In previous cases (Arrhenuis equation), the values of both coefficients, i.e. the pre-exponential constant and the activation energy, were used in only one further calculation procedure to estimate the kinetic equation constants for a given temperature, but the enthalpy or entropy values are often used separately in subsequent practical calculations. Selection of the wrong pair of Arrhenius equation constants is of less significance as all pairs describe the experimental values set more or less accurately, and the Arrhenius equation is used merely to interpolate the temperatures of intermediate results, which are not measured directly. Selection of the wrong pair of enthalpy and entropy values is of much greater importance. Although all the pairs describe the free enthalpy changes equally well, the calculation of the enthalpy change in the subsequent reaction using the wrong enthalpy values may lead to large calculation errors or even to wrong conclusions regarding the character of the reaction analysed. This indicates a new aspect of the thermodynamic data agreement problem. The existing correlative relationships between the enthalpy and entropy values determined indirectly by measurement of the free enthalpy changes, i.e. a change in equilibrium constant in the temperature function, may be weakened by using a different type of experimental data. For example, it becomes necessary to take into account additionally the calorimetric data, i.e. the results of the direct enthalpy measurements. In such a case, however, the estimation procedure becomes more complex and cannot be reduced to the problem of the estimation of the straight line coefficient. But this is quite a different problem [2].

### *Group S*

The authors list the enthalpy and entropy values for the formation of telluric fluorides of alkali metals, S01, and alkali metal fluorides, S02. In the first case the individual values originated from different sources or were the results of the authors' assessment; in the second case, all the data were taken from one source, i.e. one of the well-known thermodynamic data sets. In the first case no relationship between the enthalpy and entropy values for the individual compounds were stated and the correlation coefficient $r_e(a, b)$ was very low $(-0.17855)$. Such a relationship exists in the second case. The correlation coefficient was very high $r_e(a, b) = 0.93047$. The calculated value of the mean measurement temperature for this set was 1234 K. The data regarding the types of reactions and experimental conditions are insufficient to allow any conclusions to be drawn. It can be added that the determined temperature value does not seem unreasonable. In relation to the comments made regarding the previous group of results (Group R), this problem seems to be more relevant. The enthalpy and entropy values for the formation of alkali metal fluorides are, it seems, merely a mean estimation of this group of chemical compounds. The problem of determining accurate values of the thermodynamic functions, differentiating the individual fluorides, is still open. The values of the presented thermodynamic functions are certainly consistent, but are they correct?

### *Group T*

After analysis of the data listed by the author, certain doubts have arisen. Despite the footnotes, both tables listing the results are presented in the same manner yet contain differences: the symbols used in the tables' description, the unit dimensions and the number of columns. Due to these uncertainties, it has been assumed that the corresponding enthalpy and entropy values are those listed in the first two columns of the subsequent tables. The existence of a relationship between the appropriate enthalpy and entropy values has been stated in both cases. However, in the first case, regarding the transformation of the DNA analogs, the mean temperature value, calculated from the "compensation" equation, is significantly different from the "experimental" value. In the second case, regarding the data on RNA analog transformation, there is an agreement between the values.

### *Group U*

In all cases the temperature calculated from the "compensation" equation is very close to the "experimental" values (estimated highly tentatively).

Only in the case of U06 is there a more visible difference between these values.

### *Group V*

Both sets refer to the measurement of the pressure changes with temperature. In principle, these measurements are analogous to those determining the free enthalpy equation coefficients. However, this case is different due to a difference in the form of the model equation applied. There was good agreement between the calculated and "experimental" temperatures for the first data set. For the second, the difference is large, but the low correlation coefficient of the "compensation" equation, $r_e(a, b) = 0.0264$, indicates that the calculated value of the mean measurement temperature is a completely random value.

### *Group W*

This last group of experimental data describes a process which is completely different from the others and, therefore, the model equation is different from all the cases discussed so far. However, there is the existence of the "compensation" relationship between the straight line equation coefficients, determined by means of the least-squares method. In this case the directivity coefficient of the "compensation" equation is directly equal to the negative value of the mean polymer concentration in the solution. This results directly from the form of the model equation (33) assumed. The value determined in this way is in agreement with the "experimental" one as regards in the sign and twice as high. It should be added that this apparently large difference is statistically irrelevant in relation to the standard deviation of the "compensation" equation directivity coefficient.

Similarly, for the second data set, the directivity coefficient value does not differ very much from the value determined for the previous set. Nevertheless, in this case it cannot be compared to the "experimental" value due to the lack of information allowing for such an estimation. However, it does seem that the relationship presented mainly discloses the effect of the experimental error and does not allow for a differentiation of the individual measurements.

## CONCLUSIONS

Among the 72 sets of data analysed, only in 4 cases has a relationship between the straight line equation coefficients utilized as model equations not been stated.

In the remaining cases, very strong correlations have been found, with correlation coefficients usually exceeding 0.9. Among these 68 sets, in only three cases was a significant difference stated between the calculated value of the mean measurement temperature and the corresponding "experimental" value estimated for a given experiment. In two cases the calculated value of the mean temperature approximates the absolute temperature value for the given "compensation" equation.

In general, it is striking that the "compensation" type of relationship is observed particularly frequently for data obtained by the dynamic method. It seems that this results from the ease of "production" of large data sets in relatively short time periods. Among the data sets analysed, a majority concerned determination of the Arrhenius equation coefficients (56 cases, i.e. 83% of the total), while 42 cases (i.e. 75%) used dynamic methods. This does not mean that isothermal methods are free of them; they are just more laborious and time-consuming to analyse.

The "compensation" problem also occurs in the case of thermodynamic tests which are most frequently carried out under isothermal conditions. Here, the problem of estimation is more significant and a more detailed analysis of the thermodynamic function values estimation methods should be done and more complex estimation procedures applied to allow for a numerous and varied (in the methodological sense) experimental data set. Special attention should be paid to the utilization of the calorimetric test results to reduce the correlation relationship occurring between the enthalpy and entropy values.

In summary, it should be stated that in the opinion of the present authors, no existence of a true compensation equation has been stated; it has only been revealed that the experimental errors were greater than expected by the authors of the works under discussion.

It can be stated that only the results of the most hard-working teams could be utilized in our analysis; an exposure of this error would not be possible in the case of results from one substance analysed by means of one method. The data chosen were from approximately the last two years from papers published recently. In practice, all the experimental data available have been used: no preliminary data selection was made to find those which would indicate the relationship suggested. The common occurrence of such "pseudo-relationships" would suggest that the instrumental methods used at present very frequently do not allow for the differentiation of the properties of individual substances. The values given are mean values for entire groups of similar substances. It can be stated that the effect of the property change of the individual substances on the model equation coefficient values; the pre-exponential constant and activation energy, or enthalpy and entropy, is comparable to the value of the experimental error.

## REFERENCES

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