Saturated vapor pressure of individual substance. Supplement to interpretations and procedures for processing experimental polythermal data

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Abstract A universal (that is, actual for any reaction) interconnection between enthalpy ($\Delta_r H$), entropy ($\Delta_r S$), and Gibbs energy ($\Delta_r G$) was applied to the analysis of the formation of saturated vapor of individual condensed (liquid and solid) substances. This allowed us to specify the conceptual and metrological sense of thermodynamic parameters available for estimation within the framework of tensimetric investigations. Proposals for the procedures of experimental data processing were made. The informativity of the approach was illustrated by the example showing the results of processing two arrays of primary data obtained using the static and the flow methods for crystal hafnium(IV) dipivaloylmethanate.

Keywords: Saturated vapor · Tensimetric data · Processing procedure · Thermodynamic parameters · Hafnium(IV) dipivaloylmethanate

Introduction

Volatile hafnium β-diketonates are of interest because of the possibility to use them as precursors in the processes of formation of HfO_2 films and coatings for various applications by chemical vapor deposition [1–3]. In this aspect, complex investigations of the thermal properties of these compounds are important. Data on the saturated vapor pressure for crystal hafnium(IV) acetylacetonate, trifluoroacetylacetonate, pivaloyltrifluoroacetonate, and dipivaloylmethanate have already been published [4, 5]. However, we had to perform a special analysis for this information to reach the level of conceptually and metrologically substantiated thermodynamic characteristics of vaporization processes.

Problem formulation

The first problem is to demonstrate the necessity and consequences of the correct standardization of the account of the action that the partial pressure of the monomolecular component has on its partial entropy and Gibbs energy within the composition of the saturated vapor of condensed *individual substance* (we borrowed the term "individual substance" from the title and context of the fundamental reference handbook [6, 7]).

The second problem is to demonstrate the existence and consequences of the two types of compensation in the effects of temperature on the enthalpy and entropy contributions into Gibbs energy for the reactions of evaporation of condensed substances under the equilibrium conditions.

The third problem is to apply the results of conceptual analysis to mastering the procedures of processing the tensimetric data, specifying the address of thus obtained thermodynamic characteristics, and illustrating the proposed approach with a part of the data on crystal hafnium(IV) dipivaloylmethanate $Hf(thd)_4$ that have been already published [4, 5].

Theory

The universal equation:

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$$\Delta_r G = \Delta_r H - T\Delta_r S, \tag{1}$$

in which subscript "r" denotes an arbitrary reaction in an arbitrary p, T-state of a homogeneous or heterogeneous system, can be applied to an analysis of the meaning of the thermodynamic data whose correct estimates can be obtained in tensimetric investigations. Without the loss of generality of the sought solutions, we can restrict ourselves to processes:

$$A_{crystal} = A \text{ (gas)}, \tag{2}$$

where we consider the final reagent to be only the monomolecular chemical species A in the composition of the gas phase, independently of the detailed chemical composition of the latter [8, 9]. In this case, a standard linear combination may be brought into correlation with any extensive characteristics X from the row G, H, S, V, C_p:

$$\Delta_r X = \bar{X}_A - \tilde{X}_A, \tag{3}$$

where $\bar{X}_A$ is the partial characteristic of the monomolecular component A in the composition of the gas phase, and $\tilde{X}_A$ is the normalized on mole (molar) characteristic of the corresponding crystalline phase and $\Delta_r X$ is the characteristic of reaction under study (2).

Under the permissibility of the ideal gas approximation (which is almost strictly applicable in the majority of tensimetric studies), the effect of partial pressure of the monomolecular component on its partial entropy and Gibbs energy is described in the standard manner:

$$\begin{aligned} \bar{S}_A(T, p_A) &= \bar{S}_A^\circ(T) - R\ln p_A, \\ \bar{S}_A(T) &= \bar{S}_A^\circ(T) - R\ln p_A(T), \end{aligned} \tag{4}$$

$$\begin{aligned} \bar{G}_A(T, p_A) &= \bar{G}_A^\circ(T) + RT\ln p_A, \\ \bar{G}_A(T) &= \bar{G}_A^\circ(T) + RT\ln p_A(T). \end{aligned} \tag{5}$$

It should be noted that the first equations in each pair (4, 5) relate to the situations of both the absence and presence of the equilibrium between the condensed individual substance under consideration and chemical species A, while the second equation in each pair relates only to the conditions of equilibrium for process (2) for any composition of the gas phase in the system under consideration in any point of the considered interval T. These relations explicitly show also the fact that under the conditions of ideal gas approximation the effect of total pressure ($p_{tot.}$) on $\bar{S}_A$ and $\bar{G}_A$ is possible only in the cases when it is mediated by the effect on p_A. Unlike for $\bar{S}_A$ and $\bar{G}_A$, partial enthalpy ($\bar{H}_A$) is independent not only of $p_{tot.}$, but also on p_A [10, 11]. It should also be noted that the zero superscript in Eqs. 4 and 5 means only relation of the corresponding characteristic of *detailed component* A [8, 9] to its state at the *singular* value of p_A in those units in which it is accepted as the standard value (p°), because it is

meant in $\ln p_A$ on default that the value standing under the logarithm (ln) is in fact the dimensionless ratio p_A/p° under an additional condition: the p_A value should be calculated in the same units. Some effect of total pressure on $\tilde{H}_A$, $\tilde{S}_A$, $\tilde{G}_A$ and therefore on the partial pressure of saturated vapor is possible strictly speaking. However, in the region of tensimetry for the changes of total pressure from extremely low level to 1–2 atm this effect may be neglected because the density of condensed substance is very high. It is not very difficult to estimate the level of such an influence on $\ln p_A$ ($\Delta\ln p_A$) using equation:

$$\Delta(\Delta_r G^\circ) \cong -RT\Delta\ln p_A \cong -\tilde{V}_A \Delta p_{tot.,} \tag{6}$$

deduced taking into account the independence of $\bar{G}_A^\circ$ value on $p_{tot.}$ (including the case, when $p_{tot.} = p_A$ [10, 11]), and low values of compressibility and thermal expansion coefficients of the condensed phase. For instance, for crystals of Hf(dpm)$_4$ $\tilde{V} = 0.74$ l/mol (the density was taken from XRD data [12]). Hence, for $T = 600$ K, for $p_{tot.}$ changing from a value close to zero to 1 atm, $\Delta\ln p_A$ will be only 0.015. Since total pressure in tensimetric experiments either is equal to the sum of partial pressures of the detailed components of vapor formed by the *initial component* A [8, 9] (the static method) or is at a level of 1 atm (e.g., the flow method), we may neglect not only deviations from ideality (that is, we may do without introducing fugacity coefficients), but also the effects of $p_{tot.}$ on all the values $\tilde{X}$ and $\bar{X}$ except $\bar{V}$. Therefore, the entire chain of equations holds true with a very high degree of accuracy (almost strictly) in tensimetric studies of equilibria with respect to transformations (2) for any temperature:

$$\begin{aligned} \Delta_r G(T) &= \Delta_r H(T) - T\Delta_r S(T) \\ &= \Delta_r H(T) - T\Delta_r S^\circ(T) + RT\ln p_A(T) = 0. \end{aligned} \tag{7}$$

The latter of equalities can be easily written in the form:

$$R\ln p_A(T) = \Delta_r S^\circ(T) - \Delta_r H(T)/T. \tag{8}$$

However, in routine practice [13–15] the zero superscript is also given to the $\Delta_r H$ value for some reasons. Maybe, the reason of confusion between standardizations with respect to the account of the effect of total pressure, on the one hand, and partial pressure, on the other hand, is in the use of Clausius–Clapeyron equation [16] to deduce the consequences represented by Eq. 8 obtained by us within the framework of a more general approach.

Thus, under the conditions under consideration, parameters $\ln p_A$, $\Delta_r S^\circ$, and $\Delta_r H$ may significantly depend only and solely on temperature and for any A, and these dependencies cannot contradict Eqs. 7 and 8. Not only the known equation, $\Delta_r G^\circ(T) = -RT\ln p_A$, but also the mutual compensation of the effects of temperature on the enthalpy ($\Delta_r H$) and entropy ($T\Delta_r S$) components follow from this.

Turing to the chain of three equations (7) verified by us in detail we find two types of specific (depending on the nature of component A) compensations. The origination of the first of them is connected with the shift of equilibrium (2), that is, with the change of term $R\ln p_A(T)$ included in $\Delta_r S(T)$ value if $|\Delta_r H(T)| \neq 0$. Symbasis (unidirectional connectedness) of the effects of temperature on $\Delta_r H$ and $\Delta_r S°$ (!) at $|\Delta_r C_p| \neq 0$ is responsible for the second type of compensation. In our opinion, a serious disadvantage of processing and interpretation of the tensimetric data (besides the abovementioned mixing of the effect of p_A with the effect of $p_{tot.}$) is the neglect of an objective possibility of substantial effects of temperature on $\Delta_r S°$ and $\Delta_r H$ not revealed due to almost complete mutual cancelation of their consequences. It should be noted that we did not find any work considering this possibility and its consequences. We will demonstrate the reason of such a possibility below relying on Eqs. 7 and 8.

If phase transitions (both the first and the second types) are absent for $A_{crystal}$ in the temperature range under consideration, then the reflection of possible effects of T on functional relation (8) is reduced to the results of transforming the terms of this equation according to the expression:

$$R \int_{T^*}^{T} d[\ln p_A(T)] = \int_{T^*}^{T} \Delta_r C_p(T) d\ln T \\ - \int_{T^*}^{T} d\left[\frac{1}{T}\left(\Delta_r H^* + \int_{T^*}^{T} \Delta_r C_p(T) dT\right)\right]. \quad (9)$$

Placing the start of integration (T^*) into the neighborhood of the center of initial data array and admitting the possibility to neglect the variability of $\Delta_r C_p$ for replacements from T^* to the ends of the temperature range, we determine:

$$R\ln p_A(T) - R\ln p_A^* \cong \Delta_r H^*(1/T^* - 1/T) \\ + \Delta_r C_p^*(\ln(T/T^*) - \Delta T/T), \quad (10)$$

where

$$-R\ln p_A^* = \Delta_r G^{°*}/T^* = \Delta_r H^*/T^* - \Delta_r S^{°*}. \quad (11)$$

Equation 10 may be easily rewritten as:

$$R\ln p_A(T) \cong \Delta_r S^{°*} - \Delta_r H^*/T + \Delta_r C_p^*(\ln(T/T^*) - \Delta T/T). \quad (12)$$

Expanding the term $\ln(T/T^*)$ in a Taylor series, we obtain:

$$\ln(T/T^*) = \Delta T/T + 1/2(\Delta T/T)^2 + \xi, \quad (13)$$

where ξ is the residual. Usually, temperature ranges in tensimetry are such that:

$$|\Delta T/T| \gg 1/2(\Delta T/T)^2 \gg |\xi|. \quad (14)$$

For this reason, it is possible to expect that for most real situations, in which $|\Delta_r C_p| > 0$, consequences of the temperature effect on $\Delta_r S°$ и $\Delta_r H$ values are almost completely mutually canceled, while this uncompensated part $\Delta_r C_p^* 1/2(\Delta T/T)^2$ is clouded by errors. Here, we can draw two conclusions. First, satisfactory linearity of $\ln p_A$ regression on $1/T$ is an insufficient argument for the conclusion that $\Delta_r S°$ и $\Delta_r H$ values are fairly constant in the investigated temperature interval. Second, in many cases the evaluations of $\Delta_r C_p^*$ will be *statistical zeros* (zero gets into the interval estimate, too) or close to them values, still maintaining certain informativeness [17–20].

Supplements to interpretations and the procedure for processing tensimetric data

Previously [21], experimental dependencies of saturated vapor pressure on temperature were approximated mainly using regressions:

$$\lg p \,(\text{Torr}) \cong a + b/T \text{ (frequently)}, \quad (15)$$

$$\lg p \,(\text{Torr}) \cong \tilde{a} + \tilde{b}/T + \tilde{c}\lg T \text{ (rarely)}, \quad (16)$$

Here, p (Torr) is a numerical (dimensionless) value of p measured in mmHg (Torr). In fact, at present the situation remains the same [22], in particular in the works dealing with the urgent area outlined in the "Introduction" section [13, 14]. If we accept, in addition to the ideal gas approximation, that $p \cong p_A$, then, relying on (12), we may easily establish a correlation between the parameters of Eq. 16 and the conceptual equivalents:

$$\tilde{a} = \Big[(\Delta_r S^{°*}/2.303R + \lg 760) \\ - \left(\Delta_r C_p^* \lg T^*/R + \Delta_r C_p^*/2.303R\right)\Big], \quad (17)$$

$$\tilde{b} = \left[\Delta_r C_p^* T^*/2.303R - 10^3 \Delta_r H^*/2.303R\right], \quad (18)$$

$$\tilde{c} = \left[\Delta_r C_p^*/R\right]. \quad (19)$$

In Eq. 17, the term lg 760 depicts the necessity to recalculate the numerical (dimensionless) pressure value under the sign of logarithm (lg) «from Torr into atm»; factor «10^3» in (18) provides the possibility to obtain $\Delta_r H^*$ in kcal/mol or kJ/mol using R expressed in cal/(mol K) or J/(mol K). Turning to Eqs. 17, 18, and 19, one clearly sees that the application of Eq. 16 in standard [23, 24] least-squares treatment is non-constructive. Indeed, we see that two terms, almost completely compensating each other, in the contribution into the conceptual Eq. 12 (see also 13, 14) which is responsible for the practical possibility to

determine $\Delta_r C_p^*$ are not compensated in Eq. 16 but are separated from each other, and their components are distributed among all the three terms in the right-side part of this equation. The occurrence of the situations of this kind always causes a sharp decrease in the conditionality of matrices of normal equation coefficients, down to almost strict equality to unity of the modules of all pair correlation coefficients (in our case they are: $r_{\tilde{a}\tilde{b}}$, $r_{\tilde{a}\tilde{c}}$, and $r_{\tilde{b}\tilde{c}}$) between the estimations of the corresponding groups of parameters. Because of this, it would be reasonable in many aspects to perform processing using the following equation:

$$\lg p \,(\text{Torr}) \cong a^* + b^*(\Delta T/T) + c^*(\Delta T/T)^2. \qquad (20)$$

This equation excludes the existing compensation and complications connected with it. The conceptual form equivalent to it, which will be applied below, looks like:

$$\begin{aligned} R \ln p_A \,(\text{atm}) = \; & [-1000\Delta_r G^{\circ *}/T^*] \\ & + [1000\Delta_r H^*/T^*](\Delta T/T) \\ & + \left[\Delta_r C_p^*/2\right](\Delta T/T)^2, \end{aligned} \qquad (21)$$

$$\Delta_r S^{\circ *} = [1000\Delta_r H^*/T^*] - [1000\Delta_r G^{\circ *}/T^*]. \qquad (22)$$

For large intervals and/or low T, it may be not very correct to neglect the residue of series (13). These situations can be easily revealed and some action may be taken. And there are two versions: either iteration with the introduction of ξ or rejection of the simple square regression (20) by substituting variable $(\Delta T/T)^2$ for $2(\ln(T/T^*) - \Delta T/T)$. For the first time, the common approach based on fundamental equation (7) has been specifically applied to the analysis of polythermal data on solubility of ferrocene in water [25] and later to the analysis of literature data on saturated vapor pressure of liquid mercury in brief communication [26].

The array of primary data for which the results of conventional processing have already been published [4, 5] is presented in Table 1. In this study, aiming at the problems under solution and the conclusions already made above, we applied a more complete set of interconnected models to the analysis of the data shown in Table 1:

I. $y = a_0 + a_1 \cdot x_1,$

II. $y = a_0^* + a_1 \cdot x_1^*,$

III. $y = a_0 + a_1 \cdot x_1 + a_2 \cdot x_2,$

IV. $y = a_0^* + a_1 \cdot x_1^* + a_2 \cdot x_2,$

V. $y = a + b \cdot x_1 + c \cdot x_2,$

where $y = R\ln p$ (atm), $x_1 = 10^3/T$, $x_1^* = (10^3/T - 10^3/T^*)$, $x_2 = 1/2(\Delta T/T)^2$, $x_2 = \lg T$, $R = 8.31431$ abs. J/(mole K), $T^* = 572$ K.

Turning to Eqs. 12, and 13 and to the mode of change of variables according to the procedure already used above (15–22), one can see that the following equivalences are assumed for the least-squares estimations of parameters of regressions I–V and the desired estimations for specifically standardized by us thermodynamic characteristics of process (2): $\tilde{a}_0$ or $a_0 \sim \Delta_r S^{\circ *}$, a_0^* or $a_0^* \sim (\Delta_r S^{\circ *} - \Delta_r H^* \cdot 10^3/T^*) = -\Delta_r G^{\circ *} \cdot 10^3/T^*$, $\tilde{a}_1$ or $a_1 \sim -\Delta_r H^*$, $a_2 \sim \Delta_r C_p^*$, $a \sim (\Delta_r S^{\circ *} - -\Delta_r C_p^* - \Delta_r C_p^* \ln T^*)$, $b \sim (\Delta_r C_p^* T^*/10^3 - \Delta_r H^*)$, $c \sim 2.303 \, \Delta_r C_p^*$.

Table 1 The array of primary data used in regression analysis

N	Static method		Flow method		N	Static method		Flow method	
	T, K	p, Torr	T, K	p, Torr		T, K	p, Torr	T, K	p, Torr
1	530.55	4.45	473.15	0.199	16	572.45	17.43	588.15	29.87
2	530.70	4.49	473.15	0.204	17	577.65	20.62	592.15	32.74
3	542.35	6.73	503.15	0.955	18	578.75	21.23	592.15	31.48
4	542.95	6.72	523.15	2.533	19	581.55	24.07	598.15	41.79
5	551.55	9.11	543.15	5.784	20	583.15	24.36	598.15	40.51
6	552.25	9.37	543.15	5.733	21	583.15	24.44	603.15	46.48
7	552.30	9.22	553.15	8.813	22	586.15	26.61		
8	558.15	11.10	553.15	8.707	23	588.45	28.83		
9	562.15	12.65	563.15	12.25	24	589.05	29.37		
10	562.30	12.62	563.15	12.16	25	592.65	32.76		
11	566.95	14.92	572.15	16.80	26	592.95	32.65		
12	567.15	14.64	572.15	16.84	27	596.15	36.20		
13	571.45	17.00	578.15	19.94	28	597.65	36.73		
14	571.45	17.15	578.15	20.28	29	600.75	40.73		
15	571.95	17.11	583.15	25.89	30	601.30	41.50		

It was shown in the experiments performed using the static method that the state of the initial component in the gas phase may be considered to be monomolecular, as a good approximation

To illustrate interconnections between models I–V and to choose a more informative one among them, the results of the application of these models to any of the two independent series of experimental data presented in Table 1 are equally suitable. Here, we will limit the consideration to a comparative analysis of the results of standard [23, 24] least-squares processing over all the models only for the data obtained using the static method (see Table 2).

At first, it should be noted that the picture of residues [24, pp. 186–239] (they are also often called discrepancies) is an evidence that models with two parameters are adequate to the array of initial data (sign alternation is random, while scattering corresponds to the mean-square deviation in solitary measurements of p at a level of 1.3%, see $\sigma°$ for I and II). It is known that for one-dimensional linear regressions centering carried out canonically [24, p. 49] does not change the estimation of parameter a_1, but the a_0 parameter gets substituted by a_0^*, the estimation of which is many times more stable and is not correlated with a_1. One can see in Table 2 that, as expected, we obtained a value for r_{01} almost equal to unity in version I, while in version II this value was -0.049, which is an evidence of insignificance of this correlation according to the regression analysis. Hence, though models I and II are mathematically equivalent, only the results of the application of model II directly show that among three universally bound to each other thermodynamic characteristics ($\Delta_r G^{\circ *} = \Delta_r H^* - T^* \Delta_r S^{\circ *}$) the most stable estimation is that for $\Delta_r G^{\circ *}$, what is more, it is almost uncorrelated with the estimation of $\Delta_r H^*$. In turn, one can see in Table 3 that non-linearity in the coordinates $\ln p - \Delta T/T$ may be due only to 1/42 and 1/26 (according to the data for the ends of section) of total influence of T on $\Delta_r S^\circ$ (or $\Delta_r H$). Therefore, the fact of the satisfactory linearity of $\ln p = \varphi(\Delta T/T)$, established on the basis of I–II, is insufficient to evaluate the possible level of influence of T on $\Delta_r S^\circ$ and $\Delta_r H$. Under these conditions, three-parameter models (III and IV) with compensation taken into account explicitly will always give new useful information. Among them, similarly to the cases of I and II, version IV is preferable because it is this version that explicitly shows the reason of the highest stability of

estimation for $\Delta_r G^{\circ *}$ and the absence of its correlation with the estimation for $\Delta_r H^*$. Unsuitability of model V for the same purposes according to the results shown in the fifth row of Table 2 is so clear that there is no need in any additional explanations (see p. 7).

As a result of three-parameter processing the data obtained using the static method, we obtain $\Delta_r C_p^* \cong 82 \pm 26$ J/(mol K), which leads, with the stereotyped use of t-distribution, to the interval estimation $29 \div 135$ J/(mol K). Therefore, with the permissibility of the hypothesis about the normal law of distribution for the random component in measurement errors of $\ln p$ and absence of the systematic component in them, we would accept that the product $\Delta_r C_p^* \cdot |\Delta T/T|$ may fall within the range $7 \div 11$ J/mol at the end of the investigation section of temperature values (with a 5% risk of the error of first kind). Yet, we have got no data on $\Delta_r C_p$ of the sublimation of β-diketonates. However, there are some literature data [27] that the $\Delta_r C_p$ values for organometallic compounds are negative. It point to the possibility of the positive displacement of the estimate found by us because of the presence of a systematic error in measurements carried out by using static method.

The result of the application of model IV to the data obtained using the flow method also turned out to be quite adequate (sign alternation of discrepancies was random, while the mean-square deviation for a solitary measurement of p was at a level of 2.8%). Estimations of the thermodynamic characteristics of process (2) for Hf(thd)$_4$, obtained separately on the basis of two independent series of experimental data, are shown in Table 4. We see that the interval estimation for $\Delta_r C_p$ according to the data obtained

Table 3 Taylor series expansion, example (see Eq. 13)

No	$\ln T/T^*$	$\Delta T/T$	$1/2(\Delta T/T)^2$
1	−0.0752	−0.0781	0.00305
2	−0.0749	−0.0778	0.00303
29	0.0490	0.0479	0.00115
30	0.0500	0.0487	0.00118

Table 2 Parameters of linear regressions I–V ($\sigma°$ is the root-mean-square deviation and r_{ij} are the correlation coefficients between the corresponding parameters) obtained as a result of processing the data of the static method

	$\tilde{a}_0, a_0, a$	$\tilde{a}_1, a_1, b$	a_0^*, a_0^*	a_2, c	$\sigma°$	r_{01}	r_{02}	r_{12}
I	115.4 ± 0.6[a]	−84.0 ± 0.3			0.109	−0.999		
II		−84.0 ± 0.3	−33.34 ± 0.02		0.109	−0.049		
III	116.3 ± 0.6	−84.5 ± 0.3		82 ± 26	0.095	−0.999	−0.521	−0.500
IV		−84.5 ± 0.3	−31.39 ± 0.02	82 ± 26	0.095	0.319	−0.671	−0.521
V	−500 ± 196	36.5 ± 15.1		193 ± 61	0.095	−0.999	−0.999	0.999

[a] Standard deviations are given as errors

Table 4 Thermodynamic characteristics of reaction (2) for Hf(thd)$_4$, the estimations of which were obtained by smoothing the primary data using model IV

Method	Thermodynamic characteristics			
	$\Delta_r G^{\circ *}$, kJ/mole	$\Delta_r H^*$, kJ/mole	$\Delta_r S^{\circ *}$, J/mole K	$\Delta_r C_p^*$, J/mole K
Static	17.96 ± 0.01	84.5 ± 0.3	116.3 ± 0.6	82 ± 26
Flow	18.08 ± 0.03	95.0 ± 0.9	134.5 ± 1.6	-98 ± 18
Static (-0.77 Torr)	18.16 ± 0.01	89.0 ± 0.3	123.8 ± 0.6	-98 ± 27

Standard deviations are given as errors

with the flow method gets into the negative region, which agrees with the expectations on the basis of literature data [27]. The introduction of the correction -0.77 Torr into the data of the static method gives the interval $-153 \div -43$ J/(mol K) (for confidence probability 0,95), which symmetrically covers the corresponding estimation for the flow method ($-136 \div -60$ J/(mol K)). In addition, it should be noted that the estimation of $\Delta_r G^{\circ *}$ value on the basis of the data obtained using the static method (both with correction and without it) almost coincided with the estimation of this value on the basis of the data obtained using the flow method. This means that the point of intersection of regressions is in the neighborhood of 572 K. However, the difference between the estimations of $\Delta_r H^*$ remained significant, which points to the presence of a systematic error linearly varying in the coordinates lg$p$–$1/T$; this error is present in the results of one or both measurement series. It is quite evident that a new experimental investigation is necessary to reveal the reasons and to remove the systematic error the presence of which in one or both of the procedures applied in [4, 5] was allowed to establish with the approach developed by us.

Summary

On the basis of current work material presented, the regression model IV together with its significant interpretation based on Eqs. 12, and 13 and in Eq. 14 can be recommended as most informative (for the accumulation and subsequent comparative analysis of the results of tensimetric investigation). This procedure will allow one to obtain directly not only stable uncorrelated estimations for $\Delta_r G^{\circ *}$ and $\Delta_r H^*$ but also, on this basis, for $\Delta_r S^{\circ *}$, but as a rule unstable for $\Delta_r C_p^*$. The latter, taking into account (13, 14), even if they get into the stage of statistical zero (there is zero inside the interval estimation [17–20]), will not lose definite informativity. In particular, the data on the boundaries of the interval will give the information about possible levels of the conjugated influence of temperature on $\Delta_r H(T)$ and $\Delta_r S^{\circ}(T)$ or/and some grounds for estimations of the occurrence and level of systematic errors in vapor pressure measurements (of course, relying on the entire amount of related independent knowledge). One more recommendation may turn out to be useful: generalizing the literature data on the values of $\Delta_r H$ and $\Delta_r S^{\circ}$, estimated using the parameters of linear regression [lg$p$] versus [$1/T$], one should relate these values to the center of the investigated temperature range, while independent information is to be drawn to the conclusions on the limits of temperature influence on them.

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