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# Dialectic Functions for Description and Prediction of Proton Affinity and Basicity in Gas Phase

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**Abstract**—Functions with discontinuity, jumps and partial repetition are modified and applied to description of proton affinity and basicity in gas phase for  $EIR_n$  where  $EI$  is any  $s$ - or  $p$ -element of the Periodic Table. As independent variables are used the overall number of  $s$ - and  $p$ -electrons in the element  $EI$  and electronic constants of the substituent  $R$ . To account for the change in the basicity along a period for derivatives with a lone electron pair ( $Be$ ,  $BR$ ,  $CR_2$ ,  $NR_3$ ,  $OR_2$ ,  $RF$ ,  $Ne$  and their analogs in the III–IV periods) is suggested and confirmed that the donor substituents  $R$ , also alkyls, provide an appearance of a basicity maximum on the Va (15) group. A surface in a three-dimensional space is considered that describes a function accounting for the overall number of  $s$ - and  $p$ -electrons in  $EI$ , the number of substituents  $R$ , and the electronic parameters of the latter.

The electron and proton affinities ( $EA$ ,  $PA$ ), acidity and basicity in gas phase are fundamental characteristics of elements and compounds indispensable for description of their reactivity. They characterize the simplest reactions that on the one hand are good objects for investigation, and on the other hand compose the elementary stages of the chemical transformations. The results obtained at measuring the acid-base characteristics of organic compounds resulted in radical transformation of concepts on the origin of these properties [1].

Considerable advances have been made in experimental measurement of  $EA$  and  $PA$ , gas-phase acidity and basicity [2, 3]. Yet the data available concern a small part of compounds that are of interest for fundamental research and technology. Therefore it would be feasible to reveal the laws governing the change in these properties and thus be able to calculate the necessary values. These laws are also important to solve the fundamental problems of the reactivity.

It was shown earlier [4] that acidity and basicity in the gas phase of the hydrogen compounds of the  $sp$  elements may be described by “dialectic” functions.

$$y = ae^{bx} \operatorname{tg} \left( \frac{\pi}{8} x + \frac{3}{16} \right) + cx + d, \quad (1)$$

$$y = ae^{bx} \left\{ \frac{x-3}{8} \right\} + cx + d, \quad (2)$$

where  $x$  is the sum of all  $s$ - and  $p$ -electrons in an element,  $\{ \}$  means that from the figure within these curly brackets should be taken a fraction.

These functions are nominated dialectic since they are characterized by discontinuity and jumps at going from one to another period of the Periodic Table and by repetition on the new level [4]. In equations (1) and (2)  $a$  characterizes the initial range of alteration of  $y$ ,  $b$  means the increase or decrease in this range at the change of  $x$ ,  $c$  and  $d$  are displacements of  $y$  in keeping with linear equation,  $8$  fixes the size of the cycle,  $+3\pi/16$  and  $-3$  is the shift of the function sought along the  $x$  axis as compared with the initial function [4].

These studies are outside the framework of the common correlations (with pure calculations) for they may provide a base for development a mathematical expression of the Periodic Law in contrast and in supplement to the existing tables. All the fundamental natural laws but the Periodic one are formulated just in the form of equations [5].

The main application of equations (1) and (2) consists in description of the properties of elements  $EI$ . In going to compounds  $EIR_n$  these equations cannot take into account the electronic properties of substituents  $R$  and their number  $n$ .

These problems are solved in the present study for description and prediction of proton affinity and basicity in the gas phase of various compounds of  $s$ -

and  $p$ -elements of general form  $EIR_n$ . Nontrivial relations were revealed.

#### Initial data and performance of calculations.

The values of basicities in the gas phase and  $PA$  data were taken from review [2]. Note that the data in the review published in the Internet [3] before the appearance of the issue of the journal [2] in many instances are not the same as in [2], although the difference is small.

The compounds in question were carefully selected for in measuring the proton affinity it should add just to the atom whose basicity was considered. For instance, with phosphorus among compounds  $PF_3$ ,  $P(NMe_2)_3$  and  $P(OMe)_3$  the affinity of the former was taken (with correction) from the original article [6] and not from the review [2] where as it turned out was given the energy of addition to fluorine.  $P(NMe_2)_3$  was excluded from consideration because the addition of proton to phosphorus was not unambiguously proved [7]. Only the data on the third compound,  $P(OMe)_3$ , were included in calculations direct from [2] since the data indicated that proton addition occurred definitely to phosphorus and not to oxygen [8–10].

The place of proton addition to  $AsF_3$  and  $SbF_3$  also seemed ambiguous in the light of the above reasoning concerning  $NF_3$ .

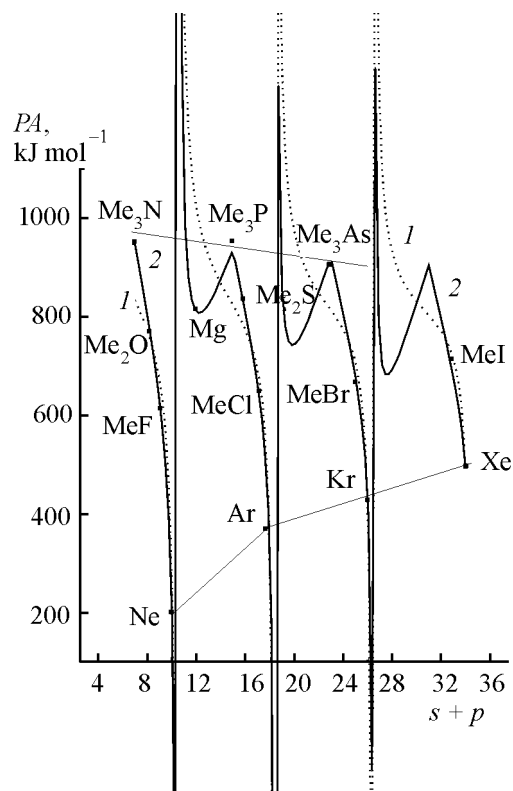
The basicities of halides in phenyl halides were not taken into account since the proton in these compounds adds to benzene ring [11]. The data on vinylamines where the proton reacts with a carbon of the double bond [12] cannot characterize the influence of vinyl substituents on the basicity of nitrogen.

Carbenes  $CF_2$  [13],  $CCl_2$  [13] and  $SiH_2$  [14, 15] were included into the calculations only after we checked in the original publications that the data regarded the species with the paired electrons.

If a data available contained a large number of similar compounds, only some of them were used. For instance, as  $NR_3$  were included  $NH_3$ ,  $NMe_3$ , and  $NEt_3$  but not  $NH_2Me$  or  $NMeEt_2$ .

The values of the constants of the electronic effects for the substituents  $\sigma_I$ ,  $\sigma_d$  and  $\sigma_e$  [16],  $\sigma_\alpha$ ,  $\sigma_F$ , and  $\sigma_R$  [17] were taken from reviews.

The calculations were carried out on PC with the use of common software of Microcal Origin type (Microcal Software, Inc). The selection of coefficients was carried out by the nonlinear least-squares procedure, as  $\{x\}$  was taken  $x - \text{int}(x)$ , where  $\text{int}(x)$



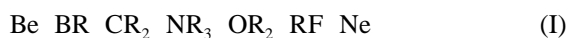
**Fig. 1.** Proton affinity ( $PA$ ) of methyl derivatives of elements  $Me_nEI$ : (1) as a function of the overall number of  $s$ - and  $p$ -electrons in  $EI$  [equation (1), series 2.1]; (2) as a function of the overall number of  $s$ - and  $p$ -electrons with accounting for the number of methyl groups  $n$  [equation (5), series 2.2].

was a function existing in the program equal to the integer part of the  $x$  figure. The level of the confidence probability in significance estimation was taken equal to 0.95. The program gave a possibility to determine the correlation  $\eta$  only for a function of a single independent variable.

The free energy of interaction of a compound with proton that characterizes the basicity in the gas phase, and the proton affinity differ by the entropy term and alter nearly in parallel. The main investigation concerned the  $PA$  values; for the resulting equations the coefficients were also determined with respect to the basicity in the gas phase. All the initial and calculated values are given in  $\text{kJ mol}^{-1}$ .

## RESULTS AND DISCUSSION

The derivatives of the elements from the second period of the Mendeleev Periodic Table that have basicity (i.e., possessing a lone electron pair) may be represented as



NR<sub>2</sub> and OR<sub>2</sub> are commonly regarded as bases, RF is seldom considered as such. The basicity of Ne may seem unexpected but the noble gases are known to show definite and fairly large proton affinity [2, 3].

Be, BR, and CR<sub>2</sub> are introduced into series I in keeping with the necessity to conserve an electron pair to ensure basicity. The data concerning the corresponding three groups are limited to Mg, CF<sub>2</sub>, CCl<sub>2</sub>, and SiH<sub>2</sub> [2, 3]. With CR<sub>2</sub> and SiH<sub>2</sub> the carbenes considered have paired free electrons [13–15].

At the first stage was considered the influence of the element nature. Therewith going from one group of the Periodic System to another was accompanied with a changing number of substituents. Further after constructing the general equations the role played only by an element will be demonstrated (Fig. 2,  $n = 0$ ).

**Effect of Element El.** The data available [2] were sufficient to build three sets of compounds EIR<sub>*n*</sub>; within each sets R were the same, and El varied in wide limits. The set of hydrogen compounds included:

		NH <sub>3</sub>	H <sub>2</sub> O	HF	Ne	
Mg	SiH <sub>2</sub>	PH <sub>3</sub>	H <sub>2</sub> S	HCl	Ar	(II)
		AsH <sub>3</sub>	H <sub>2</sub> Se	HBr	Kr	
			H <sub>2</sub> Te	HI	Xe	

Methyl compounds (set III) are presented in Fig. 1. For R = Et the set was as follows:

Mg, Et<sub>3</sub>N, Et<sub>3</sub>P, Et<sub>2</sub>O, Et<sub>2</sub>S, EtF, EtCl, EtBr, EtI, Ne, Ar, Kr, Xe (IV)

The comparison of the values of proton affinity and basicity in the gas phase revealed the following trends in the sets II–IV for groups 15(Va)–18(VIIIa) of the Periodic System:

- Along the periods from the left to the right is observed a monotonous and parallel decrease in the energy of affinity (Fig. 1, Me<sub>3</sub>N, Me<sub>2</sub>O, MeF, Ne; Me<sub>3</sub>P, Me<sub>2</sub>S, MeCl, Ar) and basicity;
- Therewith the range of changes decreases in downward direction in the Periodic Table (from the left to the right in Fig. 1);
- Within the groups the changes are commonly considerably smaller. In going along a group the char-

\*  $n = 0, \dots, 2, 3, 2, 1, 0$ ; for AlH ( $n = 1$ ) and the other missing compounds no data on PA was published in [2, 3].

acter of changes alters: from decrease in the downward direction in group 15 (Fig. 1, Me<sub>3</sub>N, Me<sub>3</sub>P, Me<sub>3</sub>As) to increase in groups 17 and 18 (Fig. 1, MeF, MeCl, MeBr, MeI; Ne, Ar, Kr, Xe). In the intermediate cases the basicity may be constant within a group;

– In group 15 sometimes are observed maxima on phosphorus; however it may be caused by the altered place of proton addition (see the section “Initial data and performance of calculations”). An analogy exists that suggests the presence of a real maximum in the third period: such variation is observed with electronic parameters of ligands EIR<sub>*n*</sub> in the coordination chemistry [18].

The analysis showed that the above relationships (save the latter) can be described with functions (1) and (2). The first of these relations (decrease along the period) is described when *a* coefficient is taken less than zero, and to the second relation corresponds *b* coefficient less than zero. The third rule follows from the second one if *c* is equal to zero or small, and therefore the term *cx* does not change the pattern.

However a quantitative consideration showed that even when R in EIR<sub>*n*</sub> is an “inert” H (set II) the accounting for a number of substituents *n* is useful (see table, series 1.1 and 1.2).

**Effect of substituents number *n*.** Description of changes in the substituents number was carried out with a saw-tooth function  $|\{x/8\}-0.5|$  [4, 18] where 8 is a number of elements in the cycle, *x* is the sum of all *s*- and *p*-electrons in the element,  $|\ |$  means that absolute value should be used.

This function was first displaced along the *x* acid so that one of the maxima (they were equal to 0.5) was located at N ( $x = 7$ ).<sup>\*</sup> The relation obtained  $|\{(x+1)/8\}-0.5|$  was raised along the *y* axis till the value for Be ( $x = 4$ ) was equal to zero<sup>\*</sup> (berillium had no substituents). Finally, the function formed  $|\{(x+1)/8\}-0.5|-0.125$  for B ( $x = 5$ ) was equated to 1 by dividing by its proper value (0.125). As a result was obtained equation (3).<sup>\*\*</sup>

$$n = [|\{\frac{x+1}{8}\}-0.5|-0.125]/0.125 \quad (3)$$

\* The equations  $|\{(x+\alpha)/8\}-0.5| = 0.5$  and  $|\{(x+1)/8\}-0.5| + const = 0$  were solved in succession to give one of solutions as  $\alpha = 1$  and  $const = -0.125$ .

\*\*  $x \neq 1, 3, 11, 19, 27, 43$  (i.e., El does not include H and alkali metals).

Proton affinity and gas-phase basicity of compounds EI<sub>Rn</sub> depending on the overall number of *sp*-electrons in the EI and electronic parameters of R ( $\eta$  is correlation ration)

Series no.	Set of compounds EI <sub>Rn</sub>			Eq. no.	$\eta$	<i>s</i>	<i>a</i> ( <i>s<sub>a</sub></i> )	<i>b</i> ( <i>s<sub>b</sub></i> )	<i>c</i> ( <i>s<sub>c</sub></i> )	<i>d</i> ( <i>s<sub>d</sub></i> )	<i>f</i> ( <i>s<sub>f</sub></i> )	<i>g</i>	<i>h</i> ( <i>s<sub>h</sub></i> )	<i>k</i> ( <i>s<sub>k</sub></i> )	<i>m</i> ( <i>s<sub>m</sub></i> )	<i>p</i> ( <i>s<sub>p</sub></i> )
	R	Notation	Number of points													
Proton affinity																
1.1	H	<b>II</b>	17	1	0.949	62	-149 (25)	-0.0316 (0.0092)	0	751 (19)	-	-	-	-	-	-
1.2	H	<b>II</b>	17	5	0.975	45	-149 (23)	-0.0457 (0.0107)	0	654 (30)	402 (108)	0	-	-	-	-
2.1	Me	<b>III</b>	14	1	0.928	97	-160 (52)	-0.0276 <sup>a</sup> (0.0200)	-1.80 <sup>a</sup> (5.00)	871 (83)	-	-	-	-	-	-
2.2	Me	<b>III</b>	14	5	0.997	20	-172 (18)	-0.0562 (0.0080)	-2.53 (0.97)	710 (20)	741 (49)	0	-	-	-	-
2.3	Me	<b>III</b> , no Mg	13	5	0.998	20	-164 (20)	-0.0594 (0.0095)	-2.01 <sup>a</sup> (1.08)	673 (40)	827 (94)	0	-	-	-	-
2.4	Me	<b>IV</b>	14	6	0.967	70	-962 (388)	-0.0331 <sup>a</sup> (0.0313)	-6.82 <sup>a</sup> (9.37)	988 (146)	1050 (150)	0	-	-	-	-
2.5	Me	<b>III</b>	14	5	0.996	24	-1826 (21)	-0.0555 <sup>b</sup> (0.0086)	-2.53 <sup>b</sup> (1.13)	722 <sup>b</sup> (24)	727 <sup>b</sup> (574)	0	-	-	-	-
3	Et	<b>IV</b>	13	5	0.998	18	-136 (8)	-0.0375 (0.0038)	0	691 (12)	833 (49)	0	-	-	-	-
4.1.1	Various	<b>II-V</b>	43	7	-	44	-207 (35)	-0.0635 (0.0133)	-4.12 (1.18)	756 (31)	-	-	-9416 (1680)	-757 <sup>a</sup> (418)	-243 <sup>a</sup> (388)	361 (87)
4.1.2	Various	<b>II-V</b>	43	7	-	43	-209 (35)	-0.0645 (0.0133)	-4.04 (1.16)	751 (30)	-	-	-10130 (1220)	-522 (184)	0 (184)	378 (82)
4.2	Various	<b>II-V</b>	43	8	-	37	-182 (26)	-0.0555 (0.0108)	-2.53 (1.07)	722 (28)	-	-	-954 (113)	-1306 (282)	-1156 (343)	301 (74)
4.3	Various	<b>II-V</b>	43	10	-	56	-769 (201)	-0.0211 <sup>a</sup> (0.0205)	-4.26 <sup>a</sup> (6.39)	978 (95)	-	-	-1168 (171)	-1010 (420)	-678 <sup>a</sup> (520)	464 (109)
4.4	Various	<b>II-V</b>	47	7	-	50	-205 (38)	-0.0611 (0.0141)	-4.89 (1.21)	788 (33)	-	-	-3584 (657)	-1962 (296)	-1261 (313)	325 (99)
4.5	Various	<b>II-IV<sup>c</sup></b>	28	7	-	34	-186 (64)	-0.0580 (0.0198)	-3.42 (1.19)	737 (30)	-	-	-4643 (767)	-3555 (608)	-2054 (332)	324 (88)

Table (Contd.)

Series no.	Set of compounds EIRn			Eq. no.	$\eta$	$s$	$a (s_a)$	$b (s_b)$	$c (s_c)$	$d (s_d)$	$f (s_f)$	$g$	$h (s_h)$	$k (s_k)$	$m (s_m)$	$p (s_p)$
	R	notation	number of points													
Basicity in gaseous phase																
5	H	<b>II</b>	17	5	0.975	45	-150 (23)	-0.0462 (0.0107)	0	630 (29)	370 (107)	0	-	-	-	-
6	Me	<b>III</b>	14	5	0.997	20	-174 (18)	-0.0570 (0.0080)	-2.60 (0.97)	688 (20)	717 (49)	0	-	-	-	-
7	Et	<b>IV</b>	13	5	0.998	18	-137 (8)	-0.0379 (0.0038)	0	668 (12)	810 (48)	-	-	-	-	-
8.1	Various	<b>II-VI</b>	47	7	-	50	-206 (38)	-0.0617 (0.0141)	-4.93	765 (1.20)	- (33)	-	-3627 (653)	-1990 (294)	-1299 (311)	295 (98)
8.2	Various	<b>II-V</b>	43	8	-	36	-183 (26)	-0.0562 (0.0106)	-2.56 (1.04)	699 (27)	-	-	-965 (110)	-1322 (276)	-1196 (335)	272 (72)
8.3	Various	<b>II-VIc</b>	28	7	-	33	-187 (64)	-0.0587 (0.0198)	-3.41 (1.17)	714 (29)	-	-	-4712 (757)	-3594 (600)	-2096 (328)	291 (87)

<sup>a</sup> The coefficient is insignificant but it was not neglected in order to exclude the assumption that this procedure at least partly provides the differences under discussion.

<sup>b</sup> Coefficients  $a$ ,  $b$ ,  $c$ ,  $d$  are taken from the 4.2 series of this table;  $f$  value is calculated along equation (12) and  $h$ - $p$  from series 4.2.

<sup>c</sup> The derivatives of elements from the second period were not taken into account.

It is easy to show that by substituting the appropriate  $x$  we obtain just the necessary  $n$  values:

	Be	B	C	N	O	F	Ne	P	Te
$x$	4	5	6	7	8	9	10	15	32
$n$ by equation (3)	0	1	2	3	2	1	0	3	2
$n$ by equation (4)	0	1	2	2.4	2	1	0	2.4	2

Equation (3) describes adequately the effect of the variable number of substituents on the basicity of  $\text{ElR}_n$  only when the effect of the substituents is additive. This is the case when the influence of R is not very strong: with the strong effect usually occurs a saturation.

In the case of saturation may be applied a function

$$n = [\sin(\frac{\pi}{4}x + \frac{3\pi}{4}) + \sin \frac{\pi}{4}] / \sin \frac{\pi}{4}, \quad (4)$$

obtained proceeding from  $\sin(2\pi/8)$  by the above described procedure (the values of the corresponding maxima are with sine equal to 1). We give also some values of this function.

The combination of equations (1), (2), and (3) affords functions (5) and (6) taking into account the number of substituents.\*

$$y = (1) + fe^{gx}n \quad (5)$$

$$y = (2) + fe^{gx}n \quad (6)$$

With R = Me the correlations and standard deviations were significantly improved on going from equations (1) and (2) to equations (5) and (6) (Fig. 1; table, series 2.1 and 2.2). The accumulation of methyls considerably increases the basicity of compounds. This is understandable since although the inductive parameters  $\sigma_I$  for H (see above) and Me are close to zero, they are smaller than those of the other substituents save  $\text{Me}_3\text{Si}$  [16]. Consequently, H and Me do not possess acceptor qualities in the system taken for standard, and they should be relatively strong donors with respect to a fragment with a significant positive charge which arises on protonation.

Alongside the inductive effect the alkyl substituents favor the distribution of the charge by polarizability resulting in a strongly enhanced gas-phase basicity [1, 17].

\* The cofactor 1/0.125 from equation (3) in calculations was included into coefficient  $f$  and further in  $h$ ,  $k$ ,  $m$ ,  $p$ .

For description of methyl and hydrogen compounds the equations with a tangent function (1) and (5) always gave better approximation than the equations (2) and (6) based on a set of straight lines (series 2.2 and 2.4).

By estimating the coefficients (see table) in equation (5) was solved a problem of calculation of  $PA$  for any compound of  $sp$ -elements  $\text{ElR}_n$  with R = H, Me, and Et. However for the other substituents were lacking data for building up the initial sets of II type. This problem can be solved as accumulate experimental and calculated data.

Nonetheless, equations (5) and (6) have a fundamental drawback. The characteristics of substituents R (polarizability, inductive effect) are not explicitly expressed in these equations, and therefore they are included into  $f$  values. As a result every substituent requires a separate equations.

**Generalized equations.** The logical approach suggests that R can be characterized by the overall number ( $y$ ) of  $s$ - and  $p$ -electrons in the atom of the substituent (as has been taken above  $x$  to characterize El). Then instead of  $e^{gx}$  in equation (5), similarly to equation (1) should be written  $e^{hy} \text{tg}(y + 3/16\pi) + ky + m$ . The formula obtained is very bulky, and it fits only to monoatomic R. Therefore to build up the universal relationships were used substituent constants characterizing their polarizability, inductive and resonance effects. Two systems of constants were applied:  $\sigma_I - \sigma_d - \sigma_e$  [16] and  $\sigma_\alpha - \sigma_F - \sigma_R$  [17]. The first system is very extensively developed, and the efficiency of the second one has been previously demonstrated just in description of proton transfer reactions in the gas phase (for the sets of  $\text{ElR}_n$  with the constant El and variable R).

Combining functions (1) and (2) with these systems of constant provided four equations.

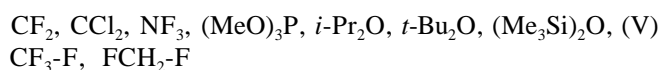
$$y = (1) + (h\sigma_e + k\sigma_I + m\sigma_d + p)_n \quad (7)$$

$$y = (1) + (h\sigma_a + k\sigma_F + m\sigma_R + p)_n \quad (8)$$

$$y = (2) + (h\sigma_e + k\sigma_I + m\sigma_d + p)_n \quad (9)$$

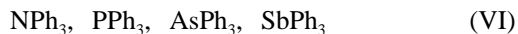
$$y = (2) + (h\sigma_a + k\sigma_F + m\sigma_R + p)_n \quad (10)$$

The sets of compounds **II–IV** were combined and supplemented with set **V** where were included  $\text{ElR}_n$  with R possessing extremal or close to that  $\sigma$  values:



“Compounds” with  $n = 0$ : Mg, Ne–Xe at combining the sets were included only once.

The set obtained II-V (II+ III+ IV+ V) may be treated along any of the equations (7-10), but the initial data and accordingly the results are limited to aliphatic compounds. If were included the compounds with phenyl groups



the set would be more representative but it cannot be described by equations (8) and (10) since the values  $\sigma_\alpha$ ,  $\sigma_F$ , and  $\sigma_R$  for the phenyl group are lacking.

A comparison of results of applying equations (7-10) or (7, 9) to the described two combined sets showed that functions (9) and (10) based on the fragments of straight lines provided less accurate description. The coefficients at the resonance constants in this case were insignificant (series 4.3).

Equation (8) of the functions based on tangent (series 4.1, 4.2) including the substituent constants  $\sigma_\alpha$ - $\sigma_F$ - $\sigma_R$  [17] gave a little more precise results.

The standard deviations  $s$  for individual sets of the methyl and ethyl compounds (series 2.2, 3) are smaller than with the combined sets (series 4.1.2, 4.2), but the second version includes more experimental data. As a result the confidence intervals are virtually identical: 12 and 11 kJ mol<sup>-1</sup> (for series 2.2 and 4.2 respectively). The application of the coefficients from the set 4.2 to the case of R = Me gives a particular set 2.5 close in accuracy of description to the set 2.2 (see table).

All the results cited above were based on the data of *PA*. The next stage consisted in selection of the most adequate among equations obtained, and coefficients were determined for describing the basicity in the gas phase (series 5-8). The calculated values of coefficients  $a$ ,  $b$ , and  $c$  were the same as in equations for the proton affinity;  $d$  for the basicity is smaller by a constant value of 22-24 kJ mol<sup>-1</sup>.

As follows from the above, the calculation of *PA* and the gas-phase basicity for compounds with phenyl groups should be performed with the use of equation (7) with appropriate coefficients (series 4.4, 8.1). For aliphatic compounds a little more accurate results provides equation (8) (series 4.2, 8.2).

The accuracy can be considerably raised by excluding the derivatives of the elements of the second period. These elements are cainosymmetrics, and their properties frequently deviate from general relationships. Therefore in moving along a group may arise extrema on the elements of the third period (see

the above mentioned maxima on the phosphorus derivatives).

The elements of the second period were formerly excluded in description with dialectic functions of the electronic parameters of ligands in the coordination chemistry [18]. In the present report the comparison of series 4.4 and 4.5, 8.1 and 8.3 demonstrates the reduced standard deviations at such exclusion. Equation (7) with the coefficients from series 4.5 and 8.3 should be applied to calculation of proton affinity and gas-phase acidity of derivatives of the elements from III-VII periods.

**Geometry of relationships.** In functions (7-10) are four independent variables, and they are realized in a five-dimensional space. However these equations can be transformed into dependencies (5) and (6) that can be realized in three dimensions.

Comparing equations (5), (6), and (7-10) we see that at  $g = 0$  (in conformity to table)

$$f = h\sigma_e + k\sigma_i + m\sigma_a + p \quad (11)$$

$$f = h\sigma_a + k\sigma_F + m\sigma_R + p \quad (12)$$

Thus the  $f$  values describe the overall electronic effect and unambiguously characterize each substituent. If the  $f$  value were regarded as characteristics of the substituent nature, then equations (5) and (6) would become functions of two independent variables ( $x$  and  $f$ ) that may be displayed in a three-dimensional space.

To show the form of the surface expressed by equation (5) were calculated the  $f$  values according to equation (12) and coefficients  $h$ - $p$  from series 4.2. For H, Me, and F the values were 301, 727, -109. These substituents are located on the  $f$  axis just at these values, The sections of the surface in question with the planes normal to  $f$  axis at the above values provide the curves corresponding to compounds  $\text{ElH}_n$ ,  $\text{ElMe}_n$  (series 2.5), and  $\text{ElF}_n$ .

It is seen in Fig. 2 as with decreasing  $f$  from 727 (Me) to -109 (F) the secondary "mountain ridge" ( $\text{ElMe}_n$ ) on the slope of the "main ridge" (general trend of decrease along a period) through a smooth descent ( $n = 0$ ) comes to a slight "valley" ( $\text{ElF}_n$ ).

[In discussion of the curves 2 on Fig. 2 corresponding to curves  $\text{Me}_n$  on Fig. 1 it seems presumable that the maximum is due to an experimental error in determination of proton affinity for magnesium or by the  $s$ -character of  $\text{Mg}^0$ . However on excluding magnesium (series 2.3) the maximum does

not disappear, even becomes more pronounced (Fig. 3)]

The curves corresponding to  $n = 0$  (Fig. 2) describe the effect of replacing element "in pure state", unaffected by the character and number of substituents.

The maxima and minima on the curves arising from changes in the number of substituents (Fig. 2) are not consistent with the common viewpoint [19, 20] which assumes that the basicity of compounds with the same substituents  $EIR_n$  diminishes from the left to the right in the period due to the growing charge of the nucleus of the element EI.

In the past the effect of the number of substituents was not revealed because the basicity was considered within limited sets (the right parts of curves on Fig. 2) of compounds from 15–17 groups (see also above, the section "Effect of element EI"). Besides in going from group 15 to 17 the charge on the nucleus grows, and the number of substituents is reduced; with donor substituents both factors decrease the basicity, and it is difficult to separate individual contributions.

Although the relationships presented on Fig. 2 seem logically confirmed it is necessary to obtain as proofs experimental data on proton affinity of metallic Be and Ca and (or) of monomethyl (monoethyl) compounds of B, Al, and Ga, also dimethyl (diethyl) compounds of C, Si, and Ge. The calculation of electronic effects of substituents with the use of equations (11, 12) provides an understanding of some strange from the first sight data. Thus the substituents H and Cl turned out to have close  $f$  values (301 and 320 respectively: the polarizability and the resonance effect of chlorine were neutralized by its inductive effect. Consequently, the carbenes  $CH_2$  and  $CCl_2$  have nearly identical values of proton affinity (206.3 and 206.5 kcal mol<sup>-1</sup> respectively [13]).

It should be noted in conclusion that since the famous works of D.I. Mendeleev interpolation and extrapolation along the groups and (or) periods of the Periodic Table served as important source of data on the properties of elements and compounds. However these operations require availability of a fairly large set of data.

The relationships developed in this study are suitable for all  $s$ - and  $p$ -elements and therefore they allow to use significantly less initial data. It is important that the data may be incomplete within the groups and periods of elements, may be stray within types and number with respect to the substituents at

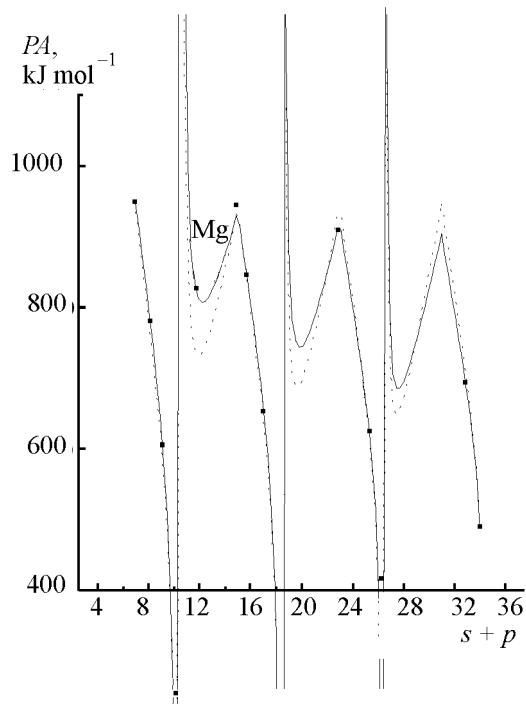


Fig. 2. Functions describing proton affinity of compounds for any elements  $EIR_n$  with  $R = H, Me$  and  $F$ , and also with no substituents ( $n = 0$ ) [Equation (5), series 2.5, 4.2].

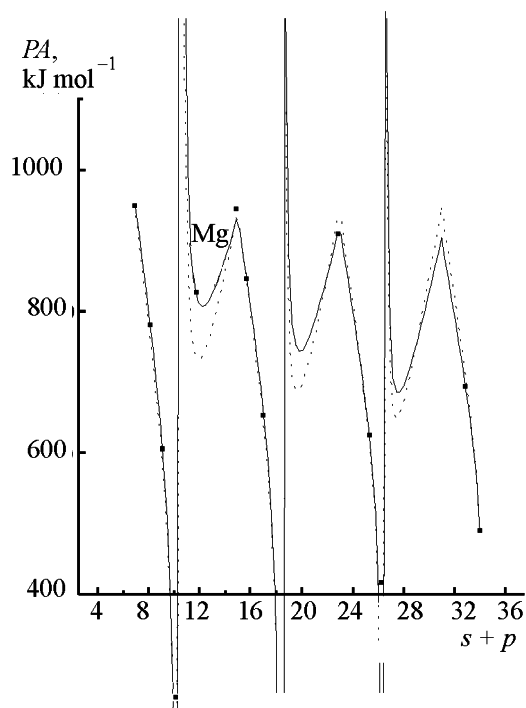


Fig. 3. Variation in the curves describing proton affinity in set III on excluding magnesium [Equation (5), series 2.2, 2.3].



the elements. If it is possible to calculate by traditional methods the properties of  $\text{SbH}_3$  in set II, the basicity in the gas phase and  $PA$  of chlorine derivatives  $\text{EICl}_n$  cannot be reckoned: the initial data are limited to a single compound ( $\text{CCl}_2$ ).

The calculations are especially valuable when the experimental data cannot be obtained. For instance, the gas-phase basicity of nitrogen and oxygen in vinyl compounds cannot be measured directly since the proton adds to the double bond. This and the other cases were considered in the section "Initial data and performance of calculations".

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