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SOME RECENT APPROACHES TO THE QUANTITATIVE DESCRIPTION OF THE EFFECT OF HIGH PRESSURE ON THE THERMODYNAMIC AND KINETIC PARAMETERS OF CHEMICAL REACTIONS

By B. S. El'yanov and E. M. Vasylytskaya

The paper is concerned with dependencies and some quantitative regularities relating to the effect of pressure on the rate and equilibrium of chemical reactions. Consideration is given to the approaches to the calculations of the thermodynamic and kinetic parameters. Some applications of these approaches to chemical problems are presented.

1. Introduction

Organic synthesis at high pressures, whose intensive development is observed at the present time, attempts to look into the future of carrying out reactions at high pressures, quantitative evaluation of change in product composition and to choose the most advantageous conditions for these reactions to occur. All these problems can be solved based on a knowledge of how the rate and equilibrium constants depend quantitatively on pressure and temperature.

Another important and extensive field where high pressure is employed is chemical reaction mechanisms and properties of the transition state. In this case the desired information is borrowed from the values of the activation volumes $\Delta V^\ddagger$ which are obtained when studying the effect of pressure on the reaction rate constants. According to the transition state theory

$$\Delta V^\ddagger = -RT(\partial \ln k / \partial P)_T, \quad (1)$$

and the problem thus amounts to finding the derivative $(\partial \ln k / \partial P)_T$. When calculating k , use is made of concentration units independent of pressure. Note that as the number of problems whose solution requires the use of the numerical values of $\Delta V^\ddagger$ becomes larger, the requirements for the accuracy of this quantity should be necessarily more rigid.

Many investigators have greatly contributed to the development of reliable and precise experimental techniques,¹⁾ but the poor methods of calculating $\Delta V^\ddagger$ detract, to a large extent, from these experimental advances. The problem is essentially that the dependence $\ln k = f(P)$ is not linear and no sufficiently reliable formula for this function has been proposed so far. Therefore there is much trouble in finding the derivative $(\partial \ln k / \partial P)_T$, especially at the boundary of the curve $f(P)$ at $P=0$. When use is made of a comparatively narrow pressure

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region near $P=0$ for determining $\Delta V^\ddagger$ (by graphical or analytical differentiation) the result is getting very sensitive to random errors. In widening the pressure region by using insufficiently reliable formulas there appears a risk of unpredictable systematic errors.

The present paper discusses some results stemming from our approach to the quantitative description of the effect of pressure on the thermodynamic and kinetic parameters of chemical reactions. This approach involves the following elements:

1) The establishment and use of regularities characterizing the effect of pressure and temperature on the parameters of related reactions (linear free energy relationship, *etc.*); 2) The search for theoretically and/or experimentally reliable formulas for $\ln k = f(P)$; 3) The use of successive approximations that are adequate to the amount and accuracy of the experimental data for refining the coefficients in $f(P)$ and other dependences; 4) The development and application of tests of goodness of fit for the formulas used.

This complex approach seems to permit a successive and more reliable descriptive approximation of the dependence of thermodynamic and kinetic parameters of chemical reactions on pressure, which, apart from a purely academic value, is of a practical significance to the solution of the above problems.

We shall turn now to the application of this approach to the basic thermodynamic and kinetic parameters of chemical reactions.

2. Rate and Equilibrium Constants: Volume Change on Activation and Reaction

2-1. Linear free energy relationships

It was found²⁾ in 1961 that the effect of pressure on the rate and equilibrium constants of a large number of chemical reactions can be described by an equation that some time later³⁾ was given in the form:

$$\log(K_p/K_0) = -(\Delta V_0^\ddagger/T) \times \phi. \quad (2)$$

Here K_p and K_0 are the rate and equilibrium constants expressed in concentration units independent of pressure; $\Delta V_0^\ddagger$ is the volume change on activation or reaction at atmospheric pressure and ϕ is the pressure function common to related reactions (or reactions of the same type). The values of ϕ for different pressures were calculated by Eq. (2) with the aid of the available experimental values of K_p , K_0 and $\Delta V_0^\ddagger$ for one or several standard reactions and then they were averaged. Equation (2) is a linear free energy relationship (LFER) on pressure variation. It has been shown⁴⁾ that the necessary and sufficient condition for Eq. (2) to exist is the requirement of $\Delta V^\ddagger$ being presented as the product

$$\Delta V^\ddagger = \psi_1(\chi_A) \psi_2(P). \quad (3)$$

Here $\psi_1(\chi_A)$ is the function depending on the parameters that characterizes the reaction only, and $\psi_2(P)$ is the function of the pressure only (within a class of related reactions). By

taking logarithm and differentiating Eq. (3) we shall have

$$\frac{1}{JV_A} \frac{\partial JV_A}{\partial P} = \frac{\partial \ln \phi_2}{\partial P} \quad (4)$$

For any two reactions of the same type (A and B) we shall have⁵⁾

$$\frac{1}{JV_A} \frac{\partial JV_A}{\partial P} = \frac{1}{JV_B} \frac{\partial JV_B}{\partial P} \quad (5)$$

An approximate observance of equality (5) can be really expected, especially for reactions characterized by the same structural changes and occurring in the same conditions. In these conditions even the volume changes in the reactions are close to one another. However, as our concern is the application of equations of the general form (2) to practical calculations it will be more or less important, depending on the nature of the problems to be solved, to evaluate their applicability and accuracy of the results obtained. In some instances rough evaluations are sufficient, for example, to foresee the effect of pressure on organic synthesis. Thus in 1967, at the early stage of high pressure organic synthesis, its future was appraised theoretically by using equations of the form (2) for ionic reactions.³⁾ High pressure is shown to offer great advantages to carrying out the reactions that do not practically occur at atmospheric pressure. Conditions were stated, the most favourable to a specific synthesis. Recently,⁶⁾ based on an equation for nonionic reactions (see below), the effects of temperature and pressure on the reaction rate have been correlated. This permits a meaningful approach to be exercised to the choice of the synthesis conditions, which acquires a special interest to the reactions where labile reagents or products are involved. The above consideration appears to be most realistic, so there is hardly any sense now in using for the same purposes a rougher assumption of JV^* being independent of pressure.⁷⁾

For reliable calculations of the rate and equilibrium constants, as well as the activation and reaction volumes, requirements for calculation accuracy should be more rigid. It can be noted that equations of the general form (2) belong to the most accurate LFER's. Thus, for example, out of 58 ionization reactions of different types of weak electrolytes in water⁸⁾ 56 reactions had the correlation coefficients r within 0.9938-0.9999. For the totality of the kinetic data for 56 Diels-Alder reactions the minimum value of r turned out to be 0.9934. One example of the high accuracy of the values of K_p , calculated *a priori* starting from K_0 and JV_0 obtained at atmospheric pressure by independent measurements is a calculation for the ionization of water²⁰⁾ (Table 1). Recently it has been shown by Kryukov *et al.*^{9a)} that the

Table 1. Effect of pressure on ionization of water (25°C)

$P(\text{bar})$	981	1961	2942	3923	4903	5884	6865	7846
K_p/K_0	calculation ^{a)}	2.20	4.19	7.21	11.8	18.3	26.3	37.2
	experiment ^{a)}	2.19	4.18	7.25	12.00	18.62	27.55	38.91

a) $JV_0 = 21.3 \text{ cm}^3 \text{ mol}^{-1}$. b) Ref. (9a).

calculation fits the experiment to 150°C. Using equations of the general form (2) to calculate ΔV^* and ΔV offers important advantages as compared with graphical methods and analytical equations containing empirical parameters. These advantages consist in the standard calculation procedure and lesser effect of random errors on the quantity to be found by calculation. Owing to this it will be possible to trace the influence of minor effects on ΔV^* and ΔV in a series of reactions. Examples of this kind will be discussed in what follows. Moreover, it is possible, in principle, to find the value of volume change by two points only, which has been done for the first time by le Noble.¹⁰ Zhulin has used this equation to determine k_0 in a reaction occurring at a noticeable rate at high pressures only.¹¹ Finally, other linear dependences of thermodynamic and kinetic parameters on ϕ have been derived by using the thermodynamic approach.

At present the disadvantages of the dependences of the form (2) lie in the fact that the concept "reactions of the same type" is not sufficiently definite. It is not improbable that the desire to have the maximum possible general equation for calculational purposes results in the excessively liberal interpretation of the limits of this concept thus detracting from the accuracy of calculation. However, the gradual appearance of the effective tests of the goodness of fit, indices of the accuracy of calculation and higher accuracy of experimental data will permit a more strenuous attribution and reliable approximations to be made.

A number of tests and indices based on statistical and other considerations have been already introduced.¹²⁾

The term "test of goodness of fit" implies a characteristic possessing the properties of a necessary and/or sufficient condition as distinct from the index of accuracy that is not so unequivocal although it can be used in some cases for the same purpose. The following tests and indices have been introduced:

1. Test and index of accuracy;
2. Test of linearity for the dependence " $\lg K - \phi$ ";
3. Test of error randomness;
4. Index of accuracy for ΔV_0 .

The use of these characteristics ensures a greater confidence in the applicability of a given equation. They enable one to discard the equations not fit for describing the experimental data or to isolate the data that are not, for some reason or other, described by the equation. Thus, in particular, it has been possible to show that the function ϕ introduced initially for calculating the Diels-Alder reactions does not meet one of the tests of feasibility. This function has been refined by an improved method.¹²⁾

Higher accuracy in the determination of ϕ and check on the fulfilment of Eq. (2) increases the theoretical significance of LFER. Condition (3) is of a most general nature and can correspond to different theoretical models. At the same time it sets limits on their selection. But as soon as a model is adopted, it can be used to theoretically calculate the function ϕ and to correlate the latter with the experimental and most accurate values obtained by the

statistical treatment of a large body of data. Such an application of LFER takes place partially in the consideration of ionization reactions (see below).

2-2. *Analytical formulas and calculation procedure*

Nonionic reactions. Until recently the following dependencies have been used to calculate $\Delta V_p^\ddagger$ most often

$$\ln k_p = \ln k_0 + ap + bP^2, \quad (6)^{1,14}$$

$$\ln k_p = \ln k_0 + ap + bP^{1.523}, \quad (7)^{15}$$

and

$$\ln k_p = \ln k_0 + ap/(1 + bP). \quad (8)^{13,16}$$

Here $a = -\Delta V_0^\ddagger/RT$. The calculation has been performed by either the least-squares method (LSM) or, for Eqs. (6) and (7), by graphically constructing the straight lines in the coordinates " $\ln(k_p/k_0)/P - P$ " and " $\ln(k_p/k_0)/P - P^{0.523}$ ". The practice of the use of these dependencies was not sound enough to either reject or accept any one of them.^{1,14-17} This is primarily due to the fact that even a high accuracy of experimental data is not sufficient for the purposes of selection. At the same time, the form of the function adopted produces a considerable effect on the calculated value of $\Delta V_p^\ddagger$. It is shown¹² that all these dependences are not met even at fairly small pressures. An increase in sensitivity in the verification of these functions is attained through a study of derivative functions which, according to Eqs. (6)-(8), have the forms

$$\Delta V_p^\ddagger = \Delta V_0^\ddagger - b'P, \quad (9)$$

$$\Delta V_p^\ddagger = \Delta V_0^\ddagger - b'P^{0.523}, \quad (10)$$

and

$$\Delta V_p^\ddagger = \Delta V_0^\ddagger/(1 + bP)^2. \quad (11)$$

According to the basic assumption, $\Delta V = \varphi(P)$ provides a model for a similar dependence of $\Delta V^\ddagger$. To verify these equations their molar volumes V were calculated by using the published values of density and compression and then the values of ΔV for 23 reactions (both real and hypothetical). Graphical verification reveals a deviation from the straight lines in the corresponding coordinates: for Eqs. (9) and (11) as early as in the region under 1 kbar, for Eq. (10) above 1.5 kbar. Thus it is desirable to eliminate Eqs. (6)-(8) from calculative practice as they lead to the admissible pressure region becoming unduly narrow, which results in a growing role of random errors and higher requirements for the accuracy of experimental data.

In the same paper,¹²¹ assuming Tait's equation being valid for all the reaction components the following equation has been derived:

$$\Delta V_p^\ddagger = \Delta V_0^\ddagger [1 - \alpha \ln(1 + \beta P)] \quad (12)$$

It was shown to be fulfilled in rather general conditions, and verification, similar to that of

Eqs. (9)-(11) showed its excellent applicability within the entire pressure region up to 12 kbar.

Optimization of data for all the 23 reactions under consideration by Eq. (12) yielded the "average" values $\alpha=0.170$ and $\beta=3.91 \times 10^{-3} \text{ bar}^{-1}$. When using these values, the average error in the IV_0 calculation of these 23 reactions was 3.8% and the maximum deviation as small as 8.7%.

Eq. (12) is matched with the following formula describing the effect of pressure on the reaction rate constants:

$$RT \ln(k_p/k_0) = -IV_0^*[(1+\alpha)P - (\alpha/\beta)(1+\beta P) \times \ln(1+\beta P)] \quad (13)$$

It is wise to use α and β as empirical parameters in the treatment of kinetic quantities for very accurate experimental data only. In the other cases $\alpha=0.170$ and $\beta=3.91 \times 10^{-3} \text{ bar}^{-1}$ can be used as a first approximation. A second approximation for α and β can be found when using LFER. It will be obtained from Eqs. (2) and (13)

$$\phi = [(1+\alpha)P - (\alpha/\beta)(1+\beta P) \ln(1+\beta P)] / R \ln 10. \quad (14)$$

It follows hence that α and β have the same values for reactions of the same type. They can be found based on the accurate data for the standard reaction or by statistical treatment of data for many reactions. The two calculation methods have been applied¹²⁾ to the Diels-Alder reactions. For a very precise standard reaction of isoprene with maleic anhydride in ethylacetate¹⁸⁾ it was found that $\alpha=0.170$ and $\beta=4.94 \times 10^{-3} \text{ bar}^{-1}$ which, as one can see, is fairly close to the first approximation obtained earlier by the independent method. Statistical calculation of data for 56 reactions yielded the values $\alpha=0.236$ and $\beta=2.52 \times 10^{-3} \text{ bar}^{-1}$. Although these values differ from the corresponding values for the standard reaction, the values of ϕ calculated from the values of the two pairs of these parameters differ by as small as 2.6% up to 4 kbar.

Two disadvantages of the statistical calculation procedure¹²⁾ should be noted. One of them is conditioned by a strong correlation of empirical parameters so that at insufficiently accurate starting data the values of α and β in different reactions vary in nonrealistic limits (3-4 orders of magnitude). This leads to extremely large deviations of IV^* from reasonable values. Therefore the values of β are intentionally confined to the interval $0.6 \leq \beta \times 10^3 \text{ bar}^{-1} \leq 15$. The second disadvantage is neglect of the nonequal accuracy of the data employed. Inaccuracies arising from these disadvantages are smoothed down, to some extent, due to a large body of data, and still a more correct procedure is desirable.

Our intention is to propose an improved and simplified method of the statistical data treatment. First of all, as seen from the consideration of the values of α obtained by the optimization of the functions $IV=\varphi(P)$ ¹²⁾ the standard deviation of this quantity from its average value is about 20%, i.e. comparatively small. Moreover, as already stated, the optimization of data for the Diels-Alder reaction, taken as the standard, yields a value of α equal to 0.170 that coincided with the one derived earlier from nonkinetic data. Therefore we attempted to look into the possibility of performing calculations at a fixed value $\alpha=0.170$

Optimization by LSM according to Eq. (12) for each of the same 23 reactions, as in Ref. (12), shows that the calculated values of $\Delta V_0^\ddagger$ do not practically differ from the "experimental" ones, the maximum deviation being 1.6%. Thus we have adopted this value of α for further calculations, which simplifies the calculation procedure and reduces parameter correlation.

To account for the nonequal accuracy of the data used it is proposed that the parameters should be optimized by finding a minimum of the function M :

$$M = \sum_{i=1}^n (g_i - 2.5) \ln S_{0i}. \quad (15)$$

Here i is the reaction number, S_{0i} and g_i are the standard error and the number of experimental points in the i -th reaction, respectively. The optimization procedure involves the following stages:

- 1) a particular value of β is specified;
- 2) values of ϕ are calculated for each reaction, data are optimized by Eq. (2) and S_{0i} is determined;
- 3) a value of M is found;
- 4) by varying β its value is found to be such that M will be minimum. Some comments should be made on Eq. (15).

In the point where M is minimum conditions $\frac{\partial M}{\partial \pi_k} = 0$ are fulfilled, where π^* is the optimized parameter ($\pi^* = \ln k_{01}, \dots, \ln k_{0n}, \Delta V_{01}^\ddagger, \dots, \Delta V_{0n}^\ddagger, \beta$). Then from Eq. (15) it follows:

$$\frac{\partial S_{0i}}{\partial \pi_i} = 0, \quad (16)$$

and

$$\sum_{i=1}^n (g_i - 2.5) \frac{1}{S_{0i}^2} \frac{\partial S_{0i}^2}{\partial \beta} = 0. \quad (17)$$

Here Eq. (16) is the normal LSM condition for all the parameters, except for β and Eq. (17) is the estimate of the maximum likelihood condition¹⁹ for parameter β :

$$\sum_{i=1}^n \frac{1}{\sigma_i^2} - \frac{\partial}{\partial \beta} \sum_{j=1}^{g_i} (\ln k_{i, \text{exp}} - \ln k_{i, \text{theor}})^2_{ij} = 0. \quad (18)$$

In this case $\ln k_{i, \text{theor}}$ are the values of the function $\ln k = F(\beta)$ that are obtained after inserting the real values of π_i and p_j into the theoretical expression. The values $(g_i - 2.5)$ are the "effective" values adopted by us for the number of degrees of freedom $f_i (g_i - 3 \leq f_i \leq g_i - 2)$. It can be readily seen here that for measurements of equal accuracy (17) converts into a normal LSM condition.

Based on this procedure we again performed a statistical treatment of the same 56 Diels-Alder reactions as in Ref. (12). A value of $\beta = 5.07 \times 10^{-3} \text{ bar}^{-1}$ was obtained, that fits well to the earlier obtained value $\beta = 4.94 \times 10^{-3} \text{ bar}^{-1}$ for the only standard reaction. The values of $\Delta V_0^\ddagger$ as calculated at the two values of β differ by as small as 0.4%. Therefore, in order

to maintain the stability of the calculated parameters for the Diels-Alder reaction, the values $\alpha=0.170$ and $\beta=4.94 \times 10^{-3} \text{ bar}^{-1}$ are retained.

Ionization reactions. It has been found elsewhere^{3,20)} that the effect of pressure up to 3 kbar on dissociation in water of a large number of different weak electrolytes can be described by the equation of the form (2). This equation has been also shown to describe well the ionization of water²⁰⁾ and some organic acids⁴⁾ up to 8 kbar, and then a simple formula has been proposed²¹⁾ with one parameter characterizing the dependence of ϕ on pressure:

$$\phi = p / (1 + bP) R \ln 10, \quad (19)$$

where $b=9.2 \times 10^{-5} \text{ bar}^{-1}$. This formula, together with Eq. (2), more accurately, and in a wider pressure interval, describes the effect of pressure on ionization constants as compared with other relationships. As has been stated above, the calculations are characterized by high correlation coefficients and small standard deviations. Thus out of 58 reactions 44 have an excellent, 7- good and 7- satisfactory accuracy. And only one reaction, *viz.*, ionization of 3- chlorophenylacetic acid, did not withstand the test of linearity.

It should be noted that the indications of the LFER applicability, most approximately though, follow from the works by other authors as well. For example, Lown *et al.*²²⁾ report on an approximate proportionality between ΔV and $(\partial \Delta V / \partial P)_T$ for a number of ionization reactions, which is equivalent to condition (5). In a wider temperature interval a similar regularity was observed by Ryzhenko and Chernushevich.²³⁾ North²⁴⁾ proposed an equation of the general form (2) which describes the values of ϕ within 2% up to 10 kbar, as compared with our Eq. (19), but at higher pressure the difference becomes greater.

The applicability of LFER (2) and Eq. (19) were explained by using Born's electrostatic model on the assumption that volume change on ionization is governed primarily by electrostriction and the ion is practically incompressible.²¹⁾ Hence the following equation has been derived:

$$1/\epsilon_p = 1/\epsilon_0 + k\phi = 1/\epsilon_0 + (\partial \epsilon_{-1} / \partial P) \times P / (1 + bP), \quad (20)$$

Its validity is confirmed by the agreement between the experimental and calculated values up to 10 kbar for water at 25°C.

Nakahara²⁵⁾ has made reasoning in the opposite direction. Starting with the Dunn-Stokes empirical equation which is equivalent to Eq. (20) and under the same assumptions he derived an expression as a combination of Eqs. (2) and (19). The value of b calculated from the parameters of the Dunn-Stokes equation turned out to be equal to $9.46 \times 10^{-5} \text{ bar}^{-1}$ for water at 25°C, which is fairly close to our value $9.2 \times 10^{-5} \text{ bar}^{-1}$. It was also noted that the value of b thus calculated depends on temperature. Therefore the function ϕ should depend on temperature too.

However such a dependence has not been established as yet. Thus it is shown²¹⁾ that ionization of acetic acid in water at pressures up to 3 kbar is described well by Eqs. (2) and

(19), at $b = 9.2 \times 10^{-5} \text{ bar}^{-1}$ and temperatures up to 225°C . The effect of pressures up to 8 kbar on ionization of water at temperatures up to 150°C is also described well by the same function ϕ .⁹⁾ Moreover, as shown below, the independence of ϕ on temperature results, as a consequence, in the linear dependences of ΔH and ΔS on ϕ , which is actually observed. It seems likely that more data and higher accuracy of experimental data are required to solve this problem.

In the same paper,²⁵⁾ based on the Owen-Brinkley equation describing the dependence of ϵ on p , another equation of the form (2) was derived in the similar way:

$$\lg(K_p/K_0) = -\frac{\Delta V_0}{T} \times \frac{B}{R \ln 10} \ln(1 + P/B). \quad (21)$$

It has been shown comparatively that the numerical values of ϕ calculated by this equation are only slightly different from ours at low pressures but at 12 kbar the difference amounts up to 4% and then it increases rapidly.

Table 2. Verification of formula (23)

		$-\Delta V(\text{cm}^3 \text{mol}^{-1}) \left(\frac{\partial \epsilon^{-1}}{\partial p} \right) \times 10^6$			$\left(\frac{\Delta V_T}{\Delta V_{T_0}} - 1 \right) / (T - T_0)$		$\left(\frac{\partial \epsilon^{-1}}{\partial p} \right)_T / \left(\frac{\partial \epsilon^{-1}}{\partial p} \right)_{T_0} - 1$
		el.	Σ		el.	Σ	
Triethylamine (in methanol)	25°	36.2	47.7	3.76	5.15	15.8	14.7×10^{-3}
	40°	39.0	59.0	4.59	$\times 10^{-3}$	$\times 10^{-3}$	
Ammonium hydroxide (in water)	25°	29.0	28.7	0.600	1.55	5.57	8.78×10^{-3}
	45°	29.9	31.9	0.679 ^a	$\times 10^{-3}$	$\times 10^{-3}$	

^a40°C.

Inoue *et al.*²⁶⁾ decided to apply Eq. (21) to the description of the ionization reaction of triethylamine in methanol by using a value B derived from the measurements of ϵ but with no success. This has led them to assume additionally the existence of a nonelectrostrictive term ΔV_{intr} which is taken to be independent of pressure. The results of their calculation are listed in Table 2 together with the data for ionization of ammonium hydroxide in water. One can see here a significant difference between ΔV_{el} and ΔV_{t} , *i.e.* between the electrostrictive term and the total volume change in the ionization reaction of $(\text{C}_2\text{H}_5)_3\text{N}$ in methanol. However a closer examination casts doubts on this conclusion.

As it is assumed that the electrostrictive term is described by the equation

$$\Delta V_{\text{el}} = f_1(p) \times \frac{\partial \epsilon^{-1}}{\partial p}, \quad (22)$$

where $f_1(p)$ is independent of p , it would be logical to believe that $f_1(p)$ is independent of T either, and then we shall have for ΔV_{el} :

$$\left(\frac{\Delta V_T}{\Delta V_{T_0}} - 1 \right) / (T - T_0) = \left[\left(\frac{\partial \epsilon^{-1}}{\partial p} \right)_T / \left(\frac{\partial \epsilon^{-1}}{\partial p} \right)_{T_0} - 1 \right] / (T - T_0). \quad (23)$$

It can be seen from Table 2 that in the two reactions the right and left hand sides of Eq. (23) differ most heavily for ΔV_d but if one takes the corresponding expression for ΔV_s , a much more closeness will be observed. This result may suggest that the initial considerations for the calculation of ΔV_d are imperfect and the assumption that $\Delta V_s \simeq \Delta V_d$ is valid in this case too.

3. Dependence of Volume Change on Activation and Reaction on Temperature

The regularities and quantitative characteristics of the temperature dependence of volume changes on activation and reaction have thus far received little study. This is explained, to a large measure, by an insufficient accuracy of the values of $\Delta V^\ddagger$ and ΔV and laborious experimental procedure. Apart from the intrinsic value, the information of this type is essential to practical solutions, e. g. to the calculations of the kinetic effects of pressure at various temperatures and comparison of the values of $\Delta V^\ddagger$ for the several reactions studied at different temperatures. It will be shown in what follows that such an information permits certain quantitative evaluations and calculations of the effect of pressure on the enthalpy and entropy of activation and reaction.

3-1. *Nonionic reactions*

The starting point for our study¹²⁾ was an important finding by Marani and Talamini.¹⁷⁾ It has been shown by these authors that over the range to which Arrhenius' equation is applicable the linear dependence of $\Delta V^\ddagger$ on T is to be observed. A wide-scale verification of this dependence for $\Delta V^\ddagger$ is practically impossible at present because of an insufficient accuracy of these values. Therefore it is assumed that the temperature dependence of $\Delta V^\ddagger$ can be simulated by the corresponding dependence of ΔV . This assumption offers strong possibilities for calculations as a large body of information available in the literature on the densities of substances at various temperatures can be used to calculate ΔV for a variety of reactions. We made such calculations for 34 reactions of 8 different types.¹²⁾ In all instances no significant deviations from the straight lines were observed (for the temperature intervals up to 90°C).

Despite a noticeable multiplicity of these reaction types distinguished by different values of ΔV and straight line slopes, it is found that the value of $\kappa = \frac{1}{\Delta V} \frac{\partial \Delta V}{\partial T}$ features a substantial constancy. Thus the standard deviation of the mean value $\kappa_{20} = 4.4 \times 10^{-3} \text{ K}^{-1}$ is 11%.

The results obtained permit a simple rule to be formulated, *viz.* a temperature increase by 1° increases the absolute value of ΔV by $(0.5 \pm 0.1)\%$ (at temperatures close to room temperature).

For more accurate calculations the following formulas should be used:

$$\Delta V_T = \Delta V_0 [1 + \kappa_0 (T - T_0)], \quad (24)$$

$$\kappa_T = \kappa_0 / [1 + \kappa_0 (T - T_0)]. \quad (25)$$

and

$$\kappa_0 = \kappa_T / [1 - \kappa_T(T - T_0)], \quad (26)$$

In practical calculations $\kappa_{20} = 4.4 \times 10^{-3} \text{K}^{-1}$ can be taken as a first approximation. A very narrow interval of κ variations for different reactions permits κ to be regarded as constant for reactions of the same type. This will be a second approximation. It can be probably assumed that the values of κ for the activation process and equilibrium in the same reaction are equal. Such estimates are most useful and can be utilized for a priori calculations. The validity of these assumptions will be demonstrated in the discussion of activation enthalpies and entropies.

3-2. Ionization reactions

As follows from the consideration of ionization reactions, the temperature dependence of ΔV for these reactions is not described by a linear function.^{28a)} Thus the value of

$$\kappa_0^{(T)} = \left(\frac{\Delta V_T}{\Delta V_{T_0}} - 1 \right) / (T - T_0),$$

as distinct from nonionic reactions, is a function of temperature. However, as stated above, if $\Delta V \simeq \Delta V_{el}$, and formula (23) is valid, $\kappa_0^{(T)}$ will be a universal function of temperature. Table 3 gives the values of $\kappa_{25}^{(T)}$ calculated by us for some electrolytes. They are fairly close to one another, except for the value of $\kappa_{25}^{(T)}$ for water. It seems likely that the available model does not describe comprehensively the features of the ionization of water. The theoretical value of $\kappa_{25}^{(T)}$ in Table 2 is equal to $8.78 \times 10^{-3} \text{K}^{-1}$ which is fairly close to the experimental values. However this problem should be investigated in more detail.

Table 3. The Values of $\kappa_{25}^{(T)}$ for some of ionization reactions

Electrolyte	$T(^{\circ}\text{C})$	$\kappa_{25}^{(T)} \cdot 10^3$	Reference
Acetic acid	75	6.31	28a
Hydrogen sulfide	75	4.94	28b
Water	75	2.12	9
Ammonium hydroxide	45	5.57	26

4. Activation and Reaction Enthalpies and Entropies. ρ -Constants of Hammett's Equation and Related Dependences

A number of corollaries can be derived from LFER.⁴⁾ Let us present Eq. (2) in the form

$$\Delta G_p = \Delta G_0 + R \ln 10 \times \Delta V_0 \Phi. \quad (27)$$

Here ΔG is the Gibbs standard free energy. Let χ_A be one of the parameters characterizing a reaction. If χ_A and Φ are independent variables and ΔG_p can be differentiated with respect to these parameters, we shall obtain a new linear dependence on Φ :

$$\frac{\partial \Delta G_p}{\partial \chi_A} = \frac{\partial \Delta G_0}{\partial \chi_A} + m\phi, \quad (28)$$

where

$$m = R \ln 10 \frac{\partial \Delta V_0}{\partial \chi_A}. \quad (29)$$

The most interesting specific cases of Eq. (28) take place at $\chi_A = T$ and $\chi_A = \sigma$, where σ is the substituent constant in Hammett's equation or its analogues.

Let us consider the case of $\chi_A = T$. As has been stated above, up to now no violations of Eq. (2) have been observed at temperature variations within fairly wide regions. This means that ϕ is independent of T . Then Eq. (28) yields the following equations:

$$\Delta S_p = \Delta S_0 - m\phi, \quad (30)$$

and

$$\Delta H_p = \Delta H_0 + n\phi. \quad (31)$$

Here,

$$m = R \ln 10 \times \frac{\partial \Delta V_0}{\partial T}, \quad (32)$$

and

$$n = R \ln 10 \left(\Delta V_0 - T \frac{\partial \Delta V_0}{\partial T} \right). \quad (33)$$

It follows from Eqs. (30) and (31) that

$$(\Delta H_p - \Delta H_0) = \beta (\Delta S_p - \Delta S_0), \quad (34)$$

where $\beta = -n/m$ is the isokinetic (isoequilibrium) temperature. One can show readily a reverse relation in that the observance of Eq. (34) means that ϕ is independent of T . The dependence of Eq. (34) for ionization reactions was first observed by Laidler.²⁹ Linear dependences (30) and (31) were demonstrated in the discussion of data for the ionization of acetic and sulphanilic acids⁴¹ and isoprene dimerization³⁰; all these reactions were studied at pressures up to 8 kbar. The values of m and n calculated by Eqs. (32) and (33) did not differ markedly from those obtained from the straight line slopes by Eqs. (30) and (31). It is most important that calculation by Eqs. (32) and (33) can be, in principle, performed from the independent values found experimentally at atmospheric pressure or estimated otherwise, so that Eqs. (30) and (31) can be used for the *a priori* calculations of ΔH_p and ΔS_p . Let us write down Eqs. (32) and (33) as

$$m = R \ln 10 \times \Delta V_0 \kappa_0, \quad (35)$$

and

$$n = R \ln 10 \times \Delta V_0 (1 - T \kappa_0), \quad (36)$$

where $\kappa_0 = \frac{1}{\Delta V_0} \frac{\partial \Delta V_0}{\partial T}$. We have considered above various approximations for the values of κ_0 in nonionic reactions, which can be applied to calculations by Eqs. (35) and (36). It is wise

to discuss one more approach¹²⁾ to the calculation of the effect of pressure on activation or reaction enthalpies and entropies. It follows from Eqs. (27) and (30), and also (27) and (31) with consideration for Eqs. (35) and (36) that

$$(\Delta S_p - \Delta S_0) = -\kappa_0(\Delta G_p - \Delta G_0), \quad (37)$$

and

$$(\Delta H_p - \Delta H_0) = (1 - \kappa_0/T)(\Delta G_p - \Delta G_0). \quad (38)$$

Examples of these linear dependences for isoprene and cyclopentadiene dimerization are reported elsewhere.¹²⁾ As one would expect, the values of κ_0 calculated from the straight line slopes turned out to be close to one another for the two Diels-Alder reactions and they did not differ markedly from those obtained by other approximate estimations.

We shall discuss now another specific case of using Eq. (28) at $\chi_A = \sigma$. Fisher *et al.*^{31a)} have found that Hammett's equation can be applied to the values of ionization constant of substituted benzoic and phenylacetic acids under pressure. As the values of Φ for this group of reactions do not depend on σ , and σ does not depend on pressure, Φ and σ will be independent variables. It follows⁴⁾ then from Eq. (28) with consideration for Hammett's equation that

$$\rho_p = \rho_0 + r\Phi, \quad (39)$$

where

$$r = -\frac{1}{T} \frac{\partial \Delta V_0}{\partial \sigma}. \quad (40)$$

It follows from the applicability of Hammett's equation to the constants under pressure^{31b)} that

$$\Delta V^{(R)} = \Delta V^{(H)} + \alpha\sigma \quad (41)$$

Superscripts (R) and (H) relate to the reactions of the substituted and unsubstituted compound, respectively; $\alpha = -RT \ln 10 (\partial \rho / \partial P)$. Hence, from Eqs. (40) and (41) we have

$$\alpha_0 = -rT. \quad (42)$$

Thus equality (42) relates the angular coefficients of the linear dependences by Eqs. (39) and (41). Dependence (41) has been found by Fisher *et al.*^{31a)} for the ionization reactions of substituted benzoic and phenylacetic acids. We have shown⁴⁾ for the same species a good observance of Eq. (39) and fulfillment of Eq. (42) within the accuracy of the experimental data. The applicability of these dependences to nonionic reactions is exemplified in what follows.

5. Some More Examples of Application to Chemical Problems

Zhulin *et al.*³²⁾ have used Eq. (2) to standardize a calculation procedure for $\Delta V^\ddagger$ in various radical reactions. A study of radical hydrogen transfer reactions has given good linear dependences between the values of $\Delta V_0^\ddagger$ and $\lg k$ for these reactions. For substituted

aromatic substrates it has been possible to find^{32b)} linear dependences between $JV_0^\ddagger$ and Hammett's σ -constants of the type (41) and good " $\rho-\phi$ " linear relationships of the type (39).

Table 4. $JV_0^\ddagger$ for the reaction of 2,2-diphenyl-1-picrylhydrazyl with substituted phenols at 25°C

Phenol	$-JV^\ddagger$ (cm ³ mol ⁻¹)	
	Palmer and Kelm ³¹⁾	This paper
2,4,6-Trimethylphenol	18.1	17.1 $\pm$ 0.3
2,6-Di- <i>t</i> -butyl-phenol	17.9	18.0 $\pm$ 0.2
2,6-Di- <i>t</i> -butyl-4-methyl-phenol	17.7	18.8 $\pm$ 0.6
2,4,6-Tri- <i>t</i> -butyl-phenol	18.3	20.4 $\pm$ 0.4

³¹⁾ Palmer and Kelm have made a mistake in the sign of the correction for the solvent compressibility. This table gives the rectified values.

The values of α calculated by Eq. (42) and determined from the straight line slopes by Eq. (41) turned out to be in excellent agreement. Palmer and Kelm³³⁾ have studied the effect of pressure on the hydrogen atom abstraction rate for 2,2-diphenyl-1-picrylhydrazyl from sterically hindered phenols. However they failed to detect the effect of steric hindrances on the values of $JV^\ddagger$. We have calculated the same kinetic data by Eq. (2). First, in collaboration with V. M. Zhulin, the statistical treatment of data for 36 reactions of radical substitution was made by the above procedure to give a value of β in Eq. (19), equal to 4.31×10^{-3} bar⁻¹. The values of $(-JV_0^\ddagger)$ calculated by us and listed in Table 4 show a distinct increase with the steric hindrance, which agrees with the up-to-day conceptions.

The diene condensation of 1-methoxy-1,3-butadiene with acetaldehyde has been carried out at a high pressure only.³⁴⁾ Nevertheless, the isomeric composition of adducts at atmospheric pressure has been calculated by extrapolating the straight line constructed in the coordinates " $\lg(C_{\text{cis}}/C_{\text{trans}})-\phi$ " up to $\phi=0$.

The study of the effect of pressure on the regio- and stereoselectivity of the diene condensations of 1-substituted-1,3-dienes with acrylates involved the calculation of the small values of $JJV_0^\ddagger$, characterizing the selectivity, by Eq. (2). Owing to the standardized calculation procedure used it has been possible to establish a regular change of these quantities under the action of minor factors.³⁵⁾ This has made it possible to define the delicate details of the steric structure of the transition state and detect its shift along the reaction coordinate towards the adduct as the radical becomes larger in the diene.

The foregoing examples illustrate the utility of the approaches dealt with in the present paper.

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*N. D. Zelinsky Institute of Organic Chemistry
U. S. S. R. Academy of Sciences. Leninsky Prospect
47, Moscow, U. S. S. R.*