

## Pressure dependence of rate and equilibrium constants in solution. A guide to analytical equations

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*Abstract* - Most of the equations proposed since 1940 to express the isothermal pressure dependence of rate and equilibrium constants in solution are critically reviewed. Purely empirical, mechanical compression and model-based approaches are identified for constructing analytical equations. The original equations are rewritten in the form  $-[RT / (p-p_0)] \ln (K_p / K_{p_0}) = \varphi(p)$ , so that  $\Delta V_{p_0} = \varphi(p_0)$  and  $\Delta V_{\infty} = \varphi(\infty)$ . This analysis, highlighting similarities and differences, revealed that mathematically equivalent equations have been derived in the past by different authors using different approaches. Special attention is paid to equations predicting finite values for  $\Delta V_{\infty}$ . It is concluded that in general  $\varphi(p)$  should contain at least three independent parameters related to volume changes arising respectively, from intramolecular rearrangements, activation or reaction solvating power, and the nature of the solvent. If one of these volume changes is inoperative (as the intramolecular term in some ionization equilibria), then the number of adjustable parameters may be reduced accordingly. Finally, it is shown that most of the equations can be represented by  $\ln K = a_0 + a_1 p + a_2 f(p) + a_3 p f(p)$  which comprises three distinct classes corresponding to  $f(p) = p^2$ ,  $f(p) = 1/(1+a_4 p)$  and  $f(p) = \ln(1+a_4 p)$ .

### INTRODUCTION

The kinetic and equilibrium approaches to elucidate the mechanism of chemical reactions in solution involve the measurement of rate and equilibrium constants as functions of different chemical and physical variables. Temperature-dependence studies tell us something about the energetics of the process, whereas pressure-dependence studies reveal information on the volume profile of the process. Therefore, the volume change accompanying reactions and activated rate processes at constant temperature and pressure is an important quantity in solution chemistry. Reaction or activation volumes for ionization equilibria and for a variety of organic and inorganic reactions have been extensively tabulated (1-3). Volume changes are thermodynamically related to the isothermal pressure dependence of chemical constants. Because this relationship is generally nonlinear, analytical equations in pressure have been in use for a long time.

Formalisms for equilibrium constants and for rate constants of single-step reactions are analogous. Thus, for the sake of simplicity, we denote by the common symbol  $K$  rate and equilibrium constants not referred to a standard pressure. We use the notation  $\Delta V$  for the standard volume of reaction  $\Delta_r V^0$  and the volume of activation  $\Delta^\ddagger V$ , and the notation  $\Delta K_T$  for the standard isothermal compression of reaction  $\Delta_r K_T^0$  and the isothermal compression of activation  $\Delta^\ddagger K_T$ . In short,

$$-\Delta K_T = \left( \frac{\partial \Delta V}{\partial p} \right)_T = -RT \left( \frac{\partial^2 \ln (K / \text{units})}{\partial p^2} \right)_T$$

It is therefore a matter of convenience to express rate and equilibrium constants in pressure-independent units (4), a procedure implicitly assumed in the following arguments.

### FORMS OF ANALYTICAL EQUATIONS

More than a dozen analytical equations have been proposed over the years to express the isothermal pressure dependence of rate and equilibrium constants in solution. Many more could have been counted if the various forms for each pressure function employed had been taken into account. We may describe these forms as *indefinite*, *indefinite with reference* and *definite*. Consider the following hypothetical equation:

$$\ln K = a_0 + a_1 p + \frac{a_2}{1 + a_4 p} + a_3 \ln (1 + a_4 p)$$

It exemplifies an *indefinite* function of the pressure. If the difference  $p - p_0$  is used from the outset then we have the corresponding *indefinite form with reference*:

$$\ln K = a_0 + a_1(p - p_0) + \frac{a_2}{1 + a_4(p - p_0)} + a_3 \ln [1 + a_4(p - p_0)]$$

The *definite form* usually results from integrating a model equation for volume changes. In our example it reads:

$$\ln K_p = \ln K_{p_0} + a_1(p - p_0) + \frac{a_2(p - p_0)}{1 + a_4(p - p_0)} + a_3 \ln \frac{1 + a_4 p}{1 + a_4 p_0}$$

These forms are easily convertible from one to another, as partially exemplified by the transformation:

$$\ln \frac{1 + a_4 p}{1 + a_4 p_0} = \ln \left[ 1 + \frac{a_4(p - p_0)}{1 + a_4 p_0} \right] = -\ln (1 + a_4 p_0) + \ln (1 + a_4 p)$$

This equivalence is clearly warranted in the case of zero pressure as reference. Otherwise, it should be checked. For instance, for the incomplete cubic equation proposed by Asano and le Noble (2), but apparently never tested, the indefinite and the indefinite with reference forms are not interchangeable.

From a theoretical point of view, our preference is for the *definite form* because it leads to expressions of the type

$$-\frac{RT}{p - p_0} \ln \frac{K_p}{K_{p_0}} = \varphi(p)$$

which has the following important advantages:

- The number of adjustable parameters is one less than in the corresponding indefinite forms.
- The logarithmic function is rendered dimensionless so that there is no need to specify units.
- The dependent variable has the proper dimensions of activation or reaction volumes so that least squares analysis is directly referred to these quantities.
- Application of L'Hospital's rule for derivatives with indeterminate forms shows that  $\Delta V_{p_0} = \varphi(p_0)$  and  $\Delta V_\infty = \varphi(\infty)$ .
- It provides a good scaling when applying a given equation to different experimental data.

### APPROACHES TO ANALYTICAL EQUATIONS

Recently, Blandamer (5) characterized two approaches for establishing analytical equations as follows:

- *Purely empirical* equations based on the geometrical features of the measured dependence of constants on pressure, if the aim is to use reaction and activation volumes to get insights into the reaction and its mechanism.
- *Model-based* equations, if "we speculate about the chemistry and hence formulate an equation for the dependence of constants on pressure".

To these we add a third approach:

- *Mechanical compression*, if species in solution are considered as solvated ions or as molecular liquids as far as their volume—pressure relations are concerned.

According to its graphical representation, most of the equations in this field can be classified as *polynomial*, *hyperbolic* and *logarithmic equations* in pressure. These three types are well represented in purely empirical equations. In addition, there is an instance of *exponential equation* in pressure. Model-based and mechanical compression approaches have led to logarithmic equations in pressure but with a single exception in each approach. It is therefore convenient to organize our guide of analytical equations according to their graphical representation.

TABLE 1. A guide of reduced polynomial equations in pressure

Case	Simplification	$\phi(p)$	$f^a$	$\Delta V_{p_0}$	Ref.
General, cubic	None	$\Delta V_{p_0} - \Delta K_{T_{p_0}} \frac{p-p_0}{2} - \left( \frac{\partial \Delta K_T}{\partial p} \right)_T \frac{(p-p_0)^2}{6}$	3	$\pm \infty$	(6)
a) Incomplete cubic	$\left( \frac{\partial \Delta K_T}{\partial p} \right)_T = \frac{\Delta K_{T_{p_0}}}{p_0}$	$\Delta V_{p_0} - \Delta K_{T_{p_0}} \left[ \frac{p-p_0}{2} + \frac{(p-p_0)^2}{6p_0} \right]$	2	$\pm \infty$	(2)
b) Quadratic	$\left( \frac{\partial \Delta K_T}{\partial p} \right)_T = 0$	$\Delta V_{p_0} - \Delta K_{T_{p_0}} \frac{p-p_0}{2}$	2	$\pm \infty$	(7,8)
c) Constrained quadratic	$\left( \frac{\partial \Delta K_T}{\partial p} \right)_T = 0,$ $\frac{\Delta V_{p_0}}{\Delta K_{T_{p_0}}}$ is a solvent property	$\Delta V_{p_0} [1 - \Delta K_{T_{p_0}} (p-p_0) / 2\Delta V_{p_0}]$	1	$\pm \infty$	(9)
d) Linear	$\Delta K_{T_{p_0}} = 0,$ $\left( \frac{\partial \Delta K_T}{\partial p} \right)_T = 0$	$\Delta V_{p_0}$	1	$\Delta V_{p_0}$	(10)

<sup>a</sup> Number of fitting parameters.

### A GUIDE OF REDUCED POLYNOMIAL EQUATIONS IN PRESSURE

*Polynomials* are the prototype of purely empirical equations. The *reduced cubic polynomial* in pressure represents a general case encompassing four particular cases (Table 1). Except for the linear case, infinite volume changes are predicted for infinite pressure, and extremes may occur in calculated rate and equilibrium constants within or near the experimental range of pressure. The third degree polynomial may also introduce a change of curvature from concave to convex in this range. This inflexion is at zero pressure for the *incomplete cubic equation* of Asano and le Noble (2). These difficulties are illustrated in Fig. 1-3.

It is well known that the *quadratic equation* in pressure systematically underestimates volume changes at ambient pressure (12-14). This is also the case with the incomplete cubic polynomial because its curvature also increases with increasing pressure (Fig. 3), which is usually the opposite of that experimentally observed. Hence it cannot be the more flexible equation surmised by Asano and le Noble (2). Despite these limitations, the quadratic in pressure, first employed by Owen and Brinkley in 1941 (7), is certainly the most popular equation in this field. However, its application should be confined within a pressure range corresponding to a 10 per cent change in solvent density, as recommended by Eckert (15).

### A GUIDE OF EXPONENTIAL EQUATIONS IN PRESSURE

An *exponential function* of pressure was considered by Heydtmann and Stiegger (16). This purely empirical equation (Table 2) with only two adjustable parameters has not stood up favourably in the comparative study of Kelm and Palmer (12). We believe that this is because the high-order derivatives of this equation with respect to pressure are never zero, even in their limit of very high pressures.

TABLE 2. A guide of exponential equations in pressure

Case	Simplification	$\varphi(p)$	$f^a$	$\Delta V_{\infty}$	Ref.
Single	None	$\frac{\Delta V_{p_0} [\exp c (p - p_0) - 1]}{c (p - p_0)}$	2	$\pm \infty$	(16)

<sup>a</sup> Number of fitting parameters.

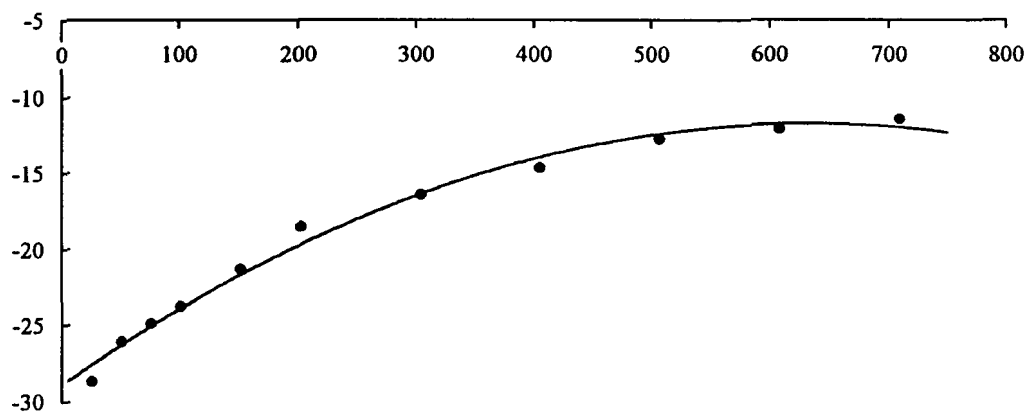


Fig. 1 Plot of  $\varphi(p) / \text{cm}^3 \text{mol}^{-1}$  vs  $(p-p_0) / \text{MPa}$  for the reaction of tri-*n*-propylamine with iodomethane in acetone at 30 °C. The curve drawn is for the reduced cubic polynomial and has an extreme for  $p = 633 \text{ MPa}$ . Data from Ref. (11).

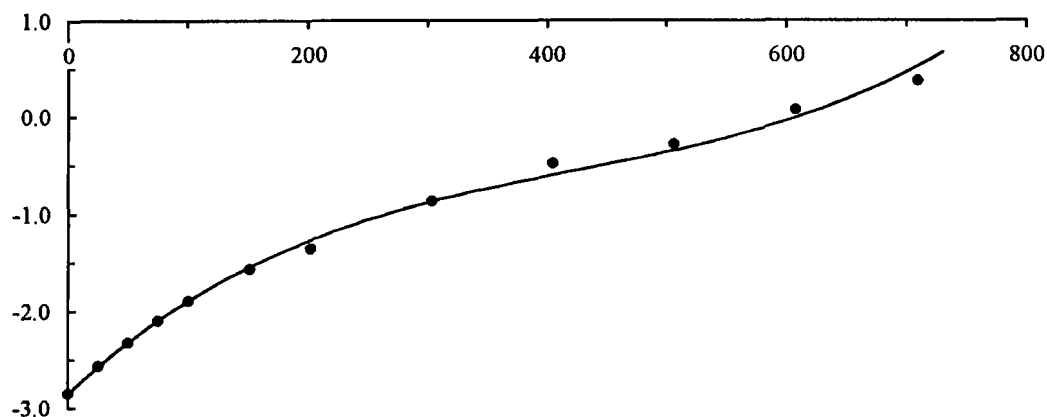


Fig. 2 Plot of  $\ln(k/s^{-1})$  vs  $p/\text{MPa}$  for the reaction in Fig. 1. The curve drawn is for the cubic polynomial and has an inflexion for  $p = 422 \text{ MPa}$ .

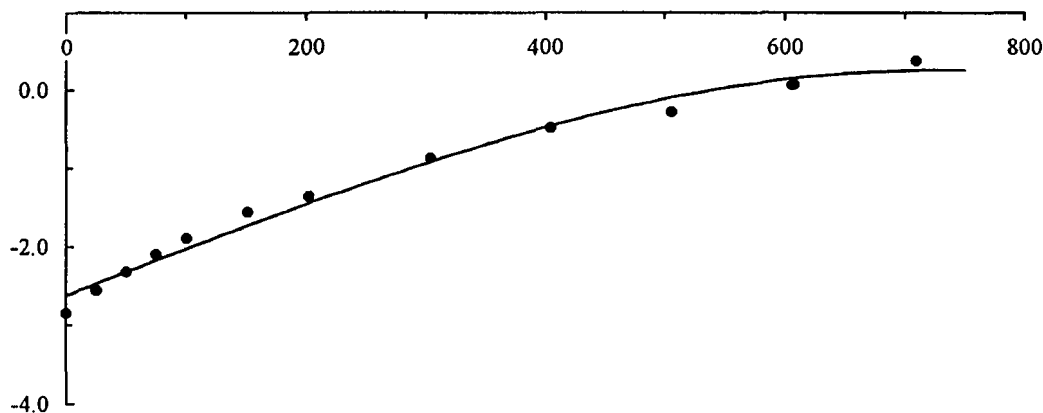


Fig. 3 Plot of  $\ln(k/s^{-1})$  vs  $p/\text{MPa}$  for the reaction in Fig. 1. The curve drawn is for the incomplete cubic polynomial of Asano and le Noble (2) and has an inflexion for  $p = 0$ .

## A GUIDE OF HYPERBOLIC EQUATIONS IN PRESSURE

*Hyperbolic functions* of pressure have been introduced in purely empirical equations (Table 3). Heydtmann and Stiegger (16) were the first to propose this function and it was accepted much better than these authors' exponential equation. In fact, Baliga and Whalley (17) and El'yanov and Hamann (18), apparently unaware of previous similar works, presented equivalent expressions. Nakahara (19) was able to confer theoretical meaning to this empirical equation by using an electrostatic solvation model together with the equation of Dunn and Stokes (20) for the effect of pressure on the solvent dielectric constant.

The attractiveness of the hyperbolic function appears to reside in predicting a finite volume change in the limit of very high pressures, which is zero with the Heydtmann and Stiegger two-parameter equation (Table 3, case b). However, by introducing a third parameter, Asano and Okada (13) obtained a hyperbolic equation (Table 3, general case) leading to finite non-zero limiting volume changes. Nonetheless, this feature can also be incorporated in two-parameter hyperbolic equations by imposing a special parameter combination, as shown in Table 3, case a. Finally, analysis of Nakahara's version (Table 3, case c) reveals that for ionization equilibria the ratio  $\Delta V_{p_0} / \Delta K_{T,p_0}$  is a solvent property in agreement with the empirical finding that led to the constrained quadratic of Lown *et al.* (9) (Table 1, case c).

TABLE 3. A guide of hyperbolic equations in pressure

Case	Simplification	$\varphi(p)$	$f^a$	$\Delta V_\infty$	Ref.
General	None	$\Delta V_{p_0} + \frac{b(p-p_0)}{1+c(p-p_0)}$	3	$\Delta V_{p_0} + b/c$	(13)
a)	$b = \frac{(1+cp_0)c^2\Delta V_{p_0}}{1-c(1-cp_0)}$	$\Delta V_{p_0} \left[ 1 + \frac{c(p-p_0)}{1-c(1-cp_0)} \right] / [1+c(p-p_0)]$	2	$\Delta V_{p_0} / [1-c(1-cp_0)]$	this work
b)	$b = -c \Delta V_{p_0}$	$\frac{\Delta V_{p_0}}{1+c(p-p_0)}$	2	0	(16-18)
c)	$b = -c \Delta V_{p_0}$ , $c = \beta$ (solv.)	$\frac{\Delta V_{p_0}}{1+\beta(p-p_0)}$	1	0	(19)

<sup>a</sup> Number of fitting parameters.

## A GUIDE OF LOGARITHMIC EQUATIONS IN PRESSURE

The *logarithmic function* is used in the largest number of analytical equations. Under this heading we find equations developed by means of purely empirical, model-based and mechanical compression approaches. We now present the fundamentals of these latter approaches.

*Mechanical compression approach*

The thermodynamic definition of standard volume of reaction is  $\Delta_r V^0 = \sum_i \nu_i V_i^0$ . Here  $\nu_i$  is the stoichiometric coefficient of reactant or product  $i$  and for solutes  $V_i^0$  is the partial molar volume of the chemical species  $i$  at infinite dilution. Now, if a reliable empirical relationship is employed to describe the compression properties of species in solution, then an equation for the effect of pressure on equilibrium constants should be obtained upon integration. This is the basis of the mechanical compression approach. At this point two slightly different treatments were developed, one for ions in solution and the other for non-ionic solutes.

Owen and Brinkley (7) pioneered the application of this approach to ionic equilibria. These authors used the Gibson equation (21) for the isothermal compression of salt solutions which in turn is an extension of the century-old *Tait equation* (22). Hence we see the first appearance of a *logarithmic function* of pressure in this field. It is also of interest to note that the Owen-Brinkley equation was rederived three decades later by researchers using model-based approaches (23-25).

The other treatment originated in the idea presented by Benson and Berson (26) to consider non-ionic species in solution as having isothermal volume—pressure relations similar to ordinary liquids. These

authors chose the Tait equation to express the compressibility of the activated complex as well as of the reactants. Facing an excessive number of unknowns, Benson and Berson (26) resorted to a numerical approximation. As a consequence, their working equation is  $\ln K = a_0 + a_1 p + a_2 p^{1.523}$  and hence it is not truly a logarithmic equation in pressure. Nearly 15 years later, two research groups (27-29) improved on the Benson-Berson analysis to obtain a better equation. Less known is the fact that this equation is mathematically equivalent to a model-based equation arrived at a few years earlier by others (30,31).

#### *Model-based approach*

The origin of the model-based approach can be traced to the proposal by Evans and Polanyi (32) of dissecting activation volumes in solution into two contributions. The first arising from an essentially pressure-independent intramolecular or intrinsic volume change,  $\Delta_1 V$ , and the second from pressure-dependent solvent-reorganization volume changes,  $\Delta_2 V$ . These concepts also apply to reaction volumes. Now, by modelling the intermolecular or solvation contribution, an analytical equation should follow upon integration with respect to pressure. Two not very different treatments have emerged from this approach, one focussing on the solvating-solvent density and the other on electrostatic solvation theories.

The most useful molecular model for  $\Delta_2 V$  was advanced independently in the 1960s by Kondo *et al.* (33) and by Hills and Viana (34,35). According to this model the intermolecular term is given by

$$\Delta_2 V = n (V_{m,s} - V_{m,A})$$

where  $n$  represents the extra number of solvent molecules involved in an activation or reaction event, and  $V_{m,s}$  and  $V_{m,A}$  are the molar volumes of the solvent in its solvating (s) and pure (A) states. To progress additional assumptions are necessary. Thus the extra solvation number  $n$  along with  $\Delta_1 V$  are generally considered pressure-independent. However, different treatments were adopted for the change in solvent density with pressure.

Hills and Viana (34,35) treated the solvating solvent as being in a glassy state and much less compressible than the bulk solvent. By describing the effect of pressure on  $V_{m,A}$  with the help of the *Tait equation*, Jones *et al.* (30) for rate constants, and North (31) for equilibrium constants, independently of each other and of Hills and Viana, obtained an analytical equation from which the extra solvation number can be estimated. Except for using the constant  $B$  of the Tait isotherm for the solvent as a solvent parameter this equation was obtained a few years later from the mechanical compression approach by Országh *et al.* (27), and by El'yanov and Gonikberg (28,29).

Kondo *et al.* (33) approximated the solvent density change due to solvation with the quantity  $-\delta p V_{m,A} \kappa_{T,A}$  where  $\kappa_{T,A}$  is the pure solvent isothermal compressibility and  $\delta p$  is a constant that can be interpreted as the extra pressure required to bring the solvent to the density of its solvating state. Based on this treatment, Asano (24), resorting once more to the Tait isotherm for the solvent, derived an analytical equation incorporating Kondo and coworkers' approximation, as recently shown by Viana *et al.* (14). However, only the product  $n \cdot \delta p$  can be estimated from this equation. It should be no surprise by now to note that the Asano equation (24,25) is mathematically identical to the much older equation developed by Owen and Brinkley (7) in terms of the mechanical compression approach.

The latest development using the model-based approach is being introduced at this Conference by Reis and Segurado (36). Let us recall the approximate treatments applied to the intermolecular term in this quest for better analytical equations. Following Hills and Viana (34,35), only the bulk solvent would contribute significantly to volume changes with pressure. On the other hand, Kondo *et al.* (33), while recognizing that the compressibility of the solvating solvent should not be disregarded, made a simplification from the outset. In a more rigorous treatment, albeit at the cost of one extra adjustable parameter, Reis and Segurado (36) circumvented these limitations and obtained an equation where both bulk and solvating solvent densities are described by related Tait isotherms. Hence the pressure-independent quantities are reduced to the intramolecular volume change and the extra solvation number.

To complete this overview of the approach based on models, it remains to consider treatments using the *Born equation* for the solvation energy. From its application, the intermolecular contribution to volume changes can be related to the pressure derivative of the solvent dielectric constant. This variation has been expressed by means of two equations. While employing the *Dunn-Stokes relationship* (20), Nakahara (19)

obtained the hyperbolic equation in pressure first proposed by Heydtmann and Stiegger (16). If the effect of pressure upon the solvent dielectric constant is described by the *Owen-Brinkley equation* (37), which is formally analogous to the Tait equation, then the Owen-Brinkley equation for ionic equilibria (7) is obtained (23) as well as its variant for no intramolecular volume contribution (19).

It is interesting to note that we have found several instances in which equivalent equations were constructed on the basis of distinct approaches.

Let us now review briefly the various *logarithmic equations* in pressure. Our analysis of these equations suggested a four-parameter general expression (Table 4, first general case) encompassing most of the previously proposed equations (Table 4, cases a-f). However, we make it clear that we do not recommend its use except for the purpose of systematization. We observe that a model-based equation may appear as purely empirical if a solvent-related parameter is set free, as was done by Asano and Okada (13) and by

TABLE 4. A guide of logarithmic equations in pressure

Case	Simplification	$\phi(p)$	$f^a \Delta V_{\infty}$	Ref.
First general	None	$\Delta V_{p_0} + \frac{b+dp_0}{1/c+p_0} \left[ \frac{(1/c+p_0)(b+dp)}{(b+dp_0)(p-p_0)} \ln \frac{1+cp}{1+cp_0} - 1 \right]$	4 $\pm \infty$	this work
a)	$d = bc$	$\Delta V_{p_0} + bc \left( \frac{1/c+p}{p-p_0} \ln \frac{1+cp}{1+cp_0} - 1 \right)$	3 $\pm \infty$	(27-29)
b)	$d = bc,$ $c = 1/B(\text{solv.})$	$\Delta V_{p_0} + \frac{b}{B} \left( \frac{B+p}{p-p_0} \ln \frac{B+p}{B+p_0} - 1 \right)$	2 $\pm \infty$	(30-31)
c)	$b = 0$	$\Delta V_{p_0} + \frac{dp_0}{1/c+p_0} \left( \frac{(1/c+p_0)p}{p_0(p-p_0)} \ln \frac{1+cp}{1+cp_0} - 1 \right)$	3 $\pm \infty$	(38)
d)	$d = 0$	$\Delta V_{p_0} + \frac{b}{1/c+p_0} \left( \frac{1/c+p_0}{p-p_0} \ln \frac{1+cp}{1+cp_0} - 1 \right)$	3 $\Delta V_{p_0} - \frac{b}{1/c+p_0}$	(13,39)
e)	$d = 0,$ $c = 1/B(\text{solv.})$	$\Delta V_{p_0} + \frac{b}{B+p_0} \left( \frac{B+p_0}{p-p_0} \ln \frac{B+p}{B+p_0} - 1 \right)$	2 $\Delta V_{p_0} - \frac{b}{B+p_0}$	(7,23-25)
f)	$d = 0,$ $b = (1/c+p_0) \Delta V_{p_0},$ $c = 1/B(\text{solv.})$	$\frac{\Delta V_{p_0}(B+p_0)}{p-p_0} \ln \frac{B+p}{B+p_0}$	1 0	(19)
Second general	none	$\Delta V_{p_0} + b \left( \frac{B+p}{p-p_0} \ln \frac{B+p}{B+p_0} - \frac{B'+p}{p-p_0} \ln \frac{B'+p}{B'+p_0} \right)$	3 $\Delta V_{p_0} + b \ln \frac{B'+p_0}{B+p_0}$	(36)
a')	$\Delta V_{p_0} = b \ln \frac{B+p_0}{B'+p_0}$	$b \left( \ln \frac{B+p_0}{B'+p_0} + \frac{B+p}{p-p_0} \ln \frac{B+p}{B+p_0} - \frac{B'+p}{p-p_0} \ln \frac{B'+p}{B'+p_0} \right)$	2 0	(36)
Third	use of the Tait equation	$-\frac{b}{p-p_0} \ln \left( 1 - a \ln \frac{B+p}{B+p_0} \right)$	1 0	(40-42)

<sup>a</sup> Number of fitting parameters.

Gavish (39) (Table 4, case d) with respect to the Owen-Brinkley equation (7) (Table 4, case e). We note further that no theoretical derivation has been advanced for the purely empirical equation suggested by an anonymous author (38) (Table 4, case c). It is also interesting to note that the equations corresponding to the first general and a-e cases in Table 4 differ only in the form of the pre-logarithmic factor. A second class of logarithmic equations in pressure is due to Reis and Segurado (36). These equations (Table 4, second general and a' cases) differ in the value for the limiting volume change at very high pressures. Finally, mention should be made of an empirical equation which assumes a linear relationship between Gibbs energy changes and the solvent density. Based on earlier work by Franck (40), this equation has been applied to ionization equilibria by Marshall and coworkers (41,42). Inserting the by now ubiquitous Tait isotherm for the solvent, it can be transformed into a logarithmic equation in pressure (Table 4, last case). Figures 4-6 illustrate the fitting capability of some logarithmic equations.

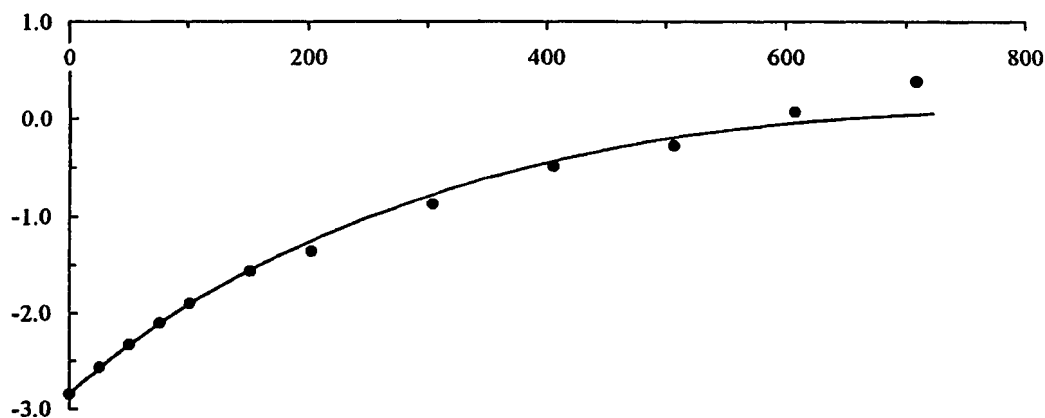


Fig. 4 Plot of  $\ln(k/s^{-1})$  vs  $p/MPa$  for the reaction of tri-*n*-propylamine with iodomethane in acetone at 30 °C. The curve drawn is for the equation with pre-logarithmic factor  $(B+p)/(p-p_0)$  (Table 4, case b). Kinetic data from Ref. (11) and  $B = 72.83$  MPa from Ref. (43).

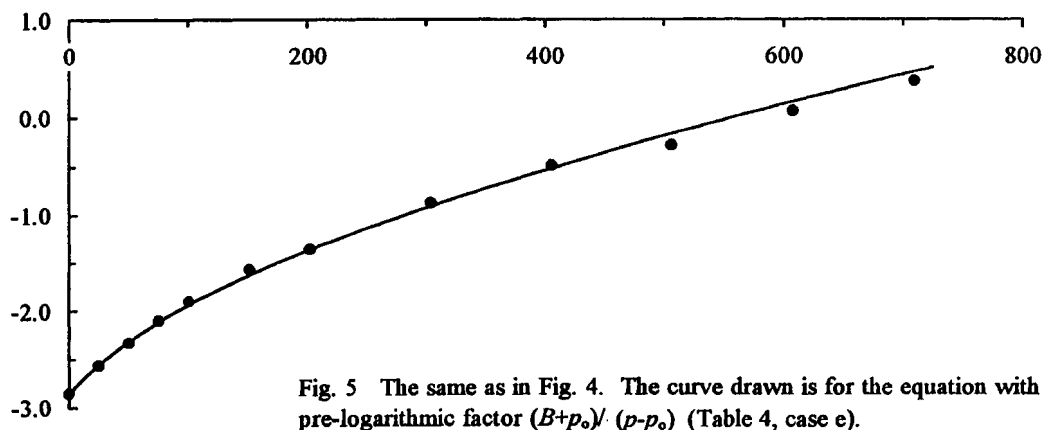


Fig. 5 The same as in Fig. 4. The curve drawn is for the equation with pre-logarithmic factor  $(B+p_0)/(p-p_0)$  (Table 4, case e).

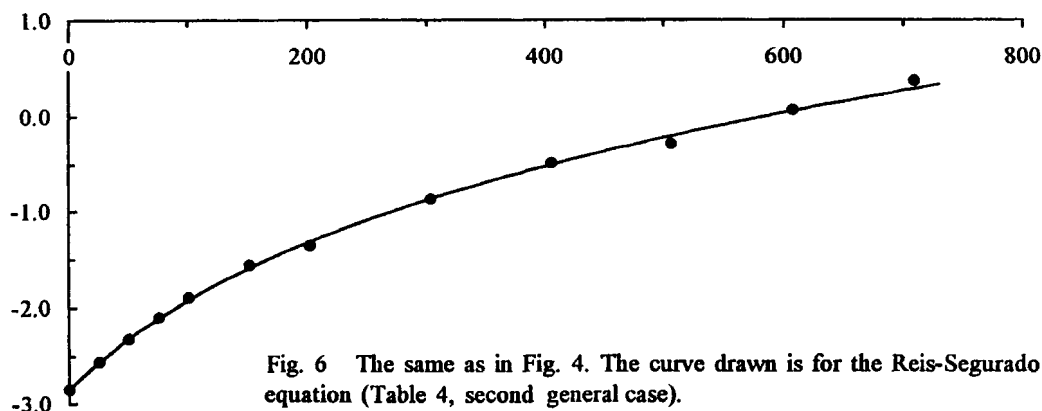


Fig. 6 The same as in Fig. 4. The curve drawn is for the Reis-Segurado equation (Table 4, second general case).



## COMPARATIVE ANALYSIS

We have highlighted the fact that hyperbolic equations predict finite volume changes at very high pressures. Except for the linear case, polynomial and exponential equations in pressure cannot represent this feature. However, some, but not all, of the logarithmic equations yield finite values for  $\Delta V_\infty$ . This dual consequence of employing the logarithmic function can be ascribed to the varied use of the Tait equation. It is well known that the Tait isotherm predicts negative densities at finite pressures outside the experimentally accessible range (44). This awkward situation can be transmitted to equations resorting to the Tait isotherm. Fortunately, it can also be avoided. This is most clearly seen in Reis-Segurado's treatment. In fact, the difference between two molar volumes expressed by Tait isotherms goes to zero as the pressure becomes indefinitely large.

We emphasize the importance of an analytical equation predicting finite volume changes at very high pressures. This feature is considered by Asano and Okada (13) to be one that a good function should satisfy. Let us return to the basic dissecting model for the interpretation of activation and reaction volumes. It is generally assumed that the intramolecular term is pressure-independent. On the other hand, both electrostatic and density treatments of changes in solvation volume agree in that the intermolecular term should vanish at very high pressures. Moreover, we are primarily interested in gaining information about the reacting system at ambient pressure from meaningful extrapolated quantities, and *not* in describing the system at inaccessible pressures. Therefore, within the framework of this model, good analytical equations are expected to yield finite values for  $\Delta V_\infty$ . This quantity was identified by Asano (24) as the intramolecular term. Noticeably, some of the equations specifically developed for ionization equilibria (18,19,41) predict no intramolecular contribution to the volume of ionization. Even the dissenting view of Inoue *et al.* (23) was severely criticized by El'yanov and Vasylytskaya (45).

## CONCLUSIONS

We are firmly persuaded that a good analytical equation should predict finite activation or reaction volumes at very high pressures. This limiting value, interpreted as the intramolecular or intrinsic volume change, should appear in the equation as, or linked to, a pressure-independent parameter. It can safely be assumed constant in different solvents and in a series of similar reactions. A second parameter is required to express the solvating power of an activation or reaction event. It has been measured by the extra solvation number and varies with the solvent and within a reaction series. The remaining parameters in a good analytical equation should reflect the nature of the solvent. Until recently, only one such parameter was considered necessary. However, in addition to a parameter linked to the pure solvent, Reis and Segurado (36) introduced a parameter related to the properties of the solvating solvent. It is not yet clear whether or not this additional parameter depends on the reaction. Summing up, a good analytical equation in pressure should contain at least three adjustable parameters. The assumption of no intramolecular volume change, as in ionic reactions, allows elimination of one parameter. Another parameter may be eliminated by using an appropriate quantity for the pure solvent.

To close, we present a practical guide to analytical equations in pressure. Most of the equations reviewed in this lecture comply to the general indefinite form

$$\ln K = a_0 + a_1 p + a_2 f(p) + a_3 p f(p)$$

*Polynomial equations* correspond to  $f(p) = p^2$ , *hyperbolic equations* to  $f(p) = 1/(1+a_4 p)$ , and *logarithmic equations* to  $f(p) = \ln(1+a_4 p)$ . General expressions for  $\ln K$  and  $\Delta V$  are shown in Table 5 and expressions for  $\Delta V_0$  and  $\Delta V_\infty$  in the various particular cases are in Table 6. The exceptions are the exponential in pressure (Table 2), and the Reis-Segurado and the linear in density equations (Table 4, last three cases).

TABLE 5. A practical guide of equations of the form  $\ln K = a_0 + a_1 p + a_2 f(p) + a_3 p f(p)$ : general expressions for  $\ln K$  and  $\Delta V$

$f(p)$	$\ln K$	$-\Delta V / RT$
$p^2$	$a_0 + a_1 p + a_2 p^2 + a_3 p^3$	$a_1 + 2a_2 p + 3a_3 p^2$
$1/(1+a_4 p)$	$a_0 + a_1 p + (a_2 + a_3 p) / (1 + a_4 p)$	$a_1 + (a_3 - a_2 a_4) / (1 - a_4 p)^2$
$\ln(1+a_4 p)$	$a_0 + a_1 p + (a_2 + a_3 p) \ln(1 + a_4 p)$	$a_1 + a_4 (a_2 + a_3 p) / (1 + a_4 p) + a_3 \ln(1 + a_4 p)$

TABLE 6. A practical guide of equations of the form  $\ln K = a_0 + a_1 p + a_2 f(p) + a_3 p f(p)$ : expressions for  $\Delta V_0$  and  $\Delta V_\infty$

$f(p)$	Simplification	$-\frac{\Delta V_0}{RT}$	$-\frac{\Delta V_\infty}{RT}$	Ref.
$p^2$	$a_2 = a_3 = 0$	$a_1$	$a_1$	(10)
	$a_3 = 0, a_1 / a_2 = c(\text{solv.})$	$a_1$	$\pm \infty$	(9)
	$a_3 = 0$	$a_1$	$\pm \infty$	(7,8)
	$a_2 = 0$	$a_1$	$\pm \infty$	(2)
	none	$a_1$	$\pm \infty$	(6)
$\frac{1}{1+a_4 p}$	$a_1 = 0, {}^a a_4 = \beta(\text{solv.})$	$a_3 - a_2 a_4$	0	(19)
	$a_1 = 0 {}^a$	$a_3 - a_2 a_4$	0	(16-18)
	$a_2 = 0, a_3 = -a_1 a_4$	$a_1 (1 - a_4)$	$a_1$	this work
	none <sup>b</sup>	$a_1 + a_3 - a_2 a_4$	$a_1$	(13)
$\ln(1+a_4 p)$	$a_1 = a_3 = 0, a_4 = 1/B(\text{solv.})$	$a_2 a_4$	0	(19)
	$a_3 = 0, a_4 = 1/B(\text{solv.})$	$a_1 + a_2 a_4$	$a_1$	(7,23-25)
	$a_3 = 0$	$a_1 + a_2 a_4$	$a_1$	(13,39)
	$a_2 = 0$	$a_1$	$\pm \infty$	(38)
	$a_3 = a_2 a_4,$ $(1+1/a_4 p) \ln(1+a_4 p) =$ $1.018 + 0.461 (a_4 p)^{0.523}$	$a_1 + 1.018 a_2 a_4$	$\pm \infty$	(26)
	$a_3 = a_2 a_4, a_4 = 1/B(\text{solv.})$	$a_1 + a_2 a_4$	$\pm \infty$	(30,31)
	$a_3 = -a_2 a_4$	$a_1 + a_2 a_4$	$\pm \infty$	(27-29)
none	$a_1 + a_2 a_4$	$\pm \infty$	this work	

<sup>a</sup> Equivalent equations result from  $a_1 = a_2 = 0$  or  $a_1 = a_3 = 0$ .

<sup>b</sup> Equivalent equations result from  $a_2 = 0$  or  $a_3 = 0$  or  $a_3 = -a_1 a_4$ .

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