

TABLE II  
The functional constants for 0.3 mole fraction ethanol

Function	Constants		
	A	B	C
[4]	-11.620	$4.779 \times 10^{-4} \text{ atm}^{-1}$	
[5]		$5.379 \times 10^{-4} \text{ atm}^{-1}$	
[6]	-11.743	$8.615 \times 10^{-4} \text{ atm}^{-1}$	$-1.366 \times 10^{-7} \text{ atm}^{-2}$
[7]		$8.503 \times 10^{-4} \text{ atm}^{-1}$	$-1.334 \times 10^{-7} \text{ atm}^{-2}$
[8]	$9.742 \times 10^{-4} \text{ atm}^{-1}$	$-5.155 \times 10^{-7} \text{ atm}^{-1.523}$	
[9]	$8.284 \times 10^{-4} \text{ atm}^{-1}$	$-2.544 \times 10^{-7} \text{ atm}^{-2}$	

TABLE III  
Volumes of activation for benzyl chloride solvolysis at 50.25 °C in aqueous ethanol†

Mole fraction ethanol	$\Delta V^*$ (ml/mole) for function					
	[4]	[5]	[6]	[7]	[8]	[9]
0.000	-10.9	-10.0	-8.3	-7.2	-0.4	-7.0
0.100	-10.8	-12.0	-17.0	-17.6	-21.9	-18.0
0.200	-13.4	-14.4	-20.3	-20.0	-21.6	-19.6
0.300	-12.7	-14.3	-22.9	-22.6	-25.9	-22.0
0.400	-11.3	-12.3	-17.6	-17.7	-19.0	-17.7

†The values reported for functions [6], [7], [8], and [9] are those evaluated at atmospheric pressure.

well with those from [6] and [7]. This is not surprising since all three allow for the pressure dependence of  $\Delta V^*$ , i.e.  $(\partial \Delta V^* / \partial p)_T \neq 0$ . For this study we consequently can restrict further consideration to eqs. [4], [6], [8], and [9].

It is readily apparent that the general shapes of the curves in Fig. 1 are similar (viz. they all show a minimum in the region between 0.2 and 0.3 mole fraction alcohol). It can therefore be concluded, from a qualitative viewpoint, that the different functions give similar results. However, from a quantitative viewpoint, there are striking differences. The depth of the minimum, as measured with respect to pure water, ranges from 2 ml/mole for the linear analysis to 26 ml/mole for the Benson-Berson equation (4). Evidently for our interest, namely the effect of solvent composition on  $\Delta V^*$ , it is necessary to ascertain which analysis is the most reliable. As the measure of reliability we chose to use the ability of the functions to reproduce the experimental data.

After the constants of eqs. [4], [6], and [8] were obtained, the value of  $\ln k$  at each of the experimental pressures was calculated, giving  $\ln k_{\text{calcd}}$ . We then used the deviation,  $\Delta$  (eq. [10])

$$[10] \quad \Delta = \ln k_{\text{obs}} - \ln k_{\text{calcd}},$$

as a measure of the functional reproducibility (the subscript "obs" refers to the experimental value). For the Benson-Berson equation (eq. [8]) the experimental value of  $\ln k_0$  was used in these calculations.

Equation [9] has two unknowns,  $k_{n+1}$  and  $k_n$ , prohibiting the determination of  $\ln k_{\text{calcd}}$ . Therefore only the values of  $\ln(k_{n+1}/k_n)_{\text{calcd}}$  can be calculated and compared with the observed value. In this case the deviation is given by eq. [11].

$$[11] \quad \Delta = \ln (k_{n+1}/k_n)_{\text{obs}} - \ln (k_{n+1}/k_n)_{\text{calcd}}$$

The  $\Delta$  values for the four equations are shown in Fig. 2 as a function of pressure for each of the solvents.

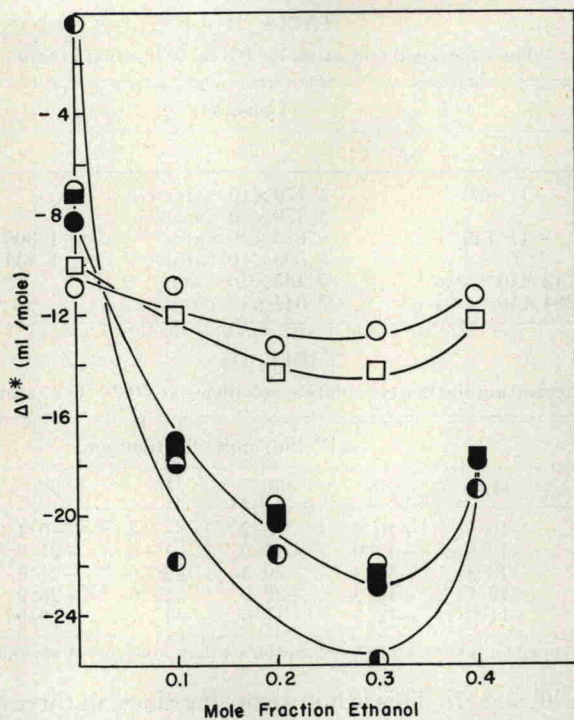


FIG. 1. The variation of  $\Delta V^*$  with solvent composition: (○) eq. [2]; (□) eq. [3]; (●) eq. [4]; (■) eq. [5]; (◐) eq. [6]; (◑) eq. [7].

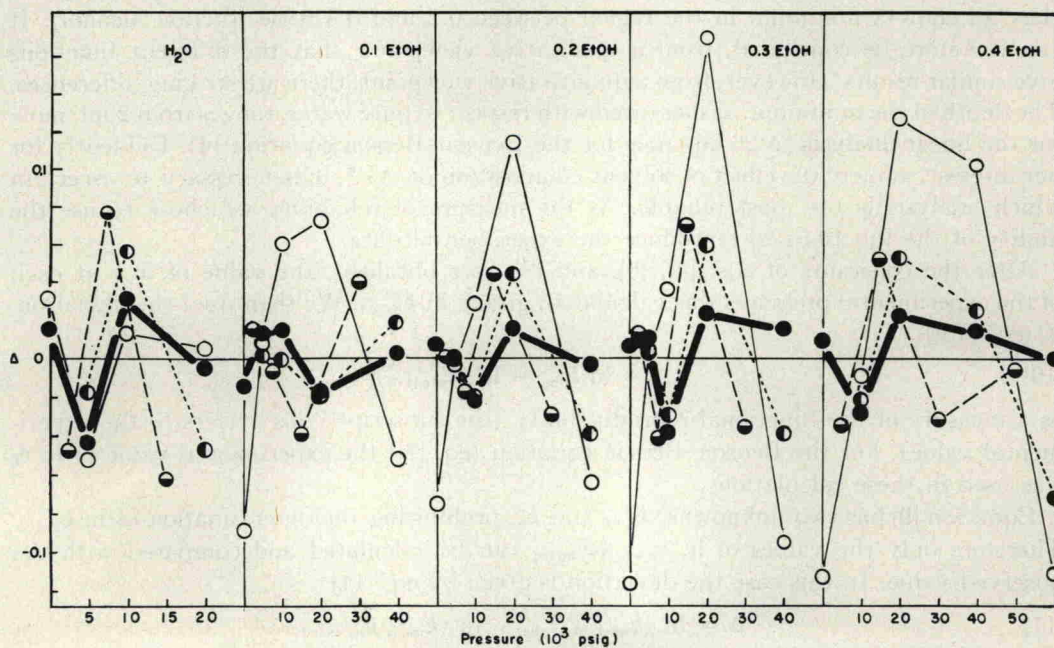


FIG. 2. Variation of the deviation of  $\ln k$  with pressure for each solvent: (○) linear analysis (eq. [2]); (●) quadratic analysis (eq. [4]); (◐) Benson-Benson analysis (eq. [6]); (◑) incremental slope analysis (eq. [7]).