

TABLE 7. The relative signs of $\partial\Delta V_0^*/\partial T$, $\partial\Delta S^*/\partial P$, $(\Delta V_0^* - T\partial\Delta V_0^*/\partial T)$ and $\partial\Delta H^*/\partial P$ at 50.25 °C and atmospheric pressure

Mol fraction <i>t</i> -BuOH	ΔV_0^*	$-T\partial\Delta V_0^*/\partial T$	$\partial\Delta S^*/\partial P$	$\partial\Delta H^*/\partial P$	$(\Delta V_0^* - T\partial\Delta V_0^*/\partial T)$
0	-9.9	+20	+	+	+10
0.025	-13.0	+75	+	+	+60
0.05	-24.7	?	+	0	?
0.10	-24.0	-25	-	-	-50
0.20	-20.2	+50	+	+	+30
0.30	-19.5	?	+	0	?

$\underbrace{\hspace{10em}}$
Maxwell
relationship

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ently equal "compressibility" of the transition state and initial state solvent shells is particularly interesting since it implies that the *electrostricted* solvent shell around the strongly dipolar transition state is no "harder" than the solvation shell around the initial state which presumably is primarily the result of *hydrophobic* type interactions.

Until experimental techniques are developed to enable the transition and initial state contributions to $\partial\Delta V^*/\partial P$ to be determined, any interpretation of the solvent dependence of this parameter is perhaps premature. It is nonetheless interesting to note that the compression of aqueous *t*-butyl alcohol passes through a minimum at 0.03 mol fraction alcohol (28), close to the composition possessing a maximum in $\partial\Delta V^*/\partial P$. This must surely be yet a further indication that the extremum behavior of these activation parameters primarily reflects changes in solvent structure.

The sharp extremum behavior of $\partial\Delta V^*/\partial P$, a *second pressure derivative* of the rate, for the solvolysis of benzyl chloride in aqueous *t*-butyl alcohol, is remarkably similar to the solvent dependence of the second temperature derivative of the rate, ΔC_p^* , for the solvolysis of *t*-butyl chloride in the same solvent mixtures as reported by Robertson and Sugamori (7). It would appear that the extremum behavior of such second derivative pseudo thermodynamic parameters of activation is both more pronounced and more complex than is the case for the corresponding first derivative parameters (ΔH^* , ΔS^* , ΔV^*) where single extrema of modest amplitude are more characteristic.

Mixed Temperature and Pressure Derivatives,

$$\partial\Delta S^*/\partial P, \partial\Delta H^*/\partial P, \text{ and } \partial\Delta V_0^*/\partial T$$

It should be recognized at once that the pa-

rameters under consideration in this section are second derivatives of the measured rate and are subject to the accumulated errors of rate, pressure, and temperature measurements. It is, therefore, hardly surprising that the errors associated with such mixed second derivatives are sizeable. The values shown in Table 7 should therefore be viewed primarily as indications of the sign of the parameter (*i.e.* the slope, positive or negative, of the plots in Figs. 10 and 11) with little significance being attached to the numerical values where these are shown.

The entropy and enthalpy of activation are plotted against pressure in Figs. 10 and 11. The plots indicate that both these activation parameters are pressure dependent and at some compositions the dependence is non-linear. This non-linearity presents difficulties in obtaining numerical values of the pressure dependence of the entropy, $\partial\Delta S^*/\partial P$, and the enthalpy, $\partial\Delta H^*/\partial P$. Because of these difficulties the signs, as obtained from the *initial* slopes of Figs. 10 and 11, but not the magnitudes of $\partial\Delta S^*/\partial P$ and $\partial\Delta H^*/\partial P$ are reported in Table 7.

Examination of Figs. 10 and 11 and also the signs in Table 7 reveals that the solvent dependence of $\partial\Delta S^*/\partial P$ and $\partial\Delta H^*/\partial P$ are very similar. This would tend to suggest that the well known compensatory behavior of ΔH^* and ΔS^* (27) is still in evidence when the second derivatives are compared. This is in fact to be expected. The differences in the intermolecular interactions, of the initial state and the transition state with the solvent environment, that resulted in the compensatory behavior of the first derivative parameters are still operative in the second derivatives.

The volumes of activation for the solvolysis of benzyl chloride in aqueous *t*-butyl alcohol mixtures were determined at 40.00, 50.25, and

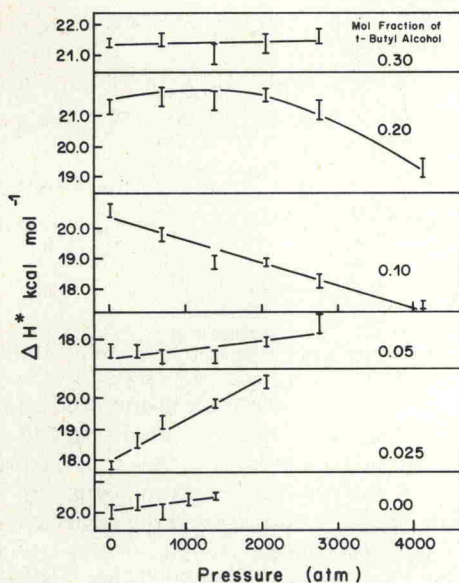


FIG. 10. Pressure dependence of activation enthalpy at various *t*-butyl alcohol mol fractions.

60.50 °C (Table 5). The temperature dependence, $\partial\Delta V_0^*/\partial T$, can thus be evaluated. Values of $\partial\Delta V_0^*/\partial T$ are not reported for 0.05 or 0.30 mol fraction of *t*-butyl alcohol since it appears that at these solvent compositions the dependence of ΔV_0^* on temperature is markedly non-linear. The values of $\partial\Delta V_0^*/\partial T$ obtained at other solvent compositions are listed in Table 7, and it is apparent that this second derivative of the rate is extremely sensitive to solvent composition changes.

The solvent dependence of $\partial\Delta V_0^*/\partial T$ is due to the different responses of the temperature dependence of the volume of the component initial and transition states to solvent changes. The solvent dependence of the initial and transition state contributions, and hence of the activation parameter itself, may well be a reflection of the changing structural stability of the solvent medium as cosolvent is added to water.

Maxwell Type Pseudo Thermodynamic Relationships

The availability of a large number of temperature and pressure derived pseudo thermodynamic parameters of activation for the single system examined in this work permits the application of classical thermodynamic identity tests to these "kinetic" parameters. In particular the following well established thermodynamic relationships

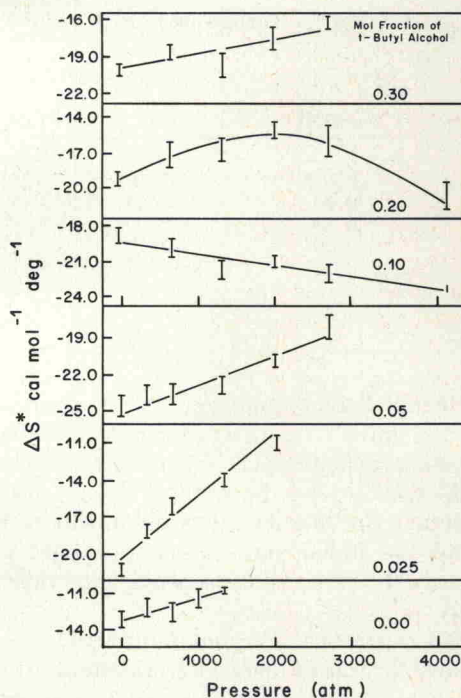


FIG. 11. Pressure dependence of activation entropy at various *t*-butyl alcohol mol fractions.

may be tested using the pseudo thermodynamic parameters obtained in this work.

$$[19] \quad (\partial\Delta S^*/\partial P)_T = -(\partial\Delta V^*/\partial T)_P$$

$$[20] \quad (\partial\Delta H^*/\partial P)_T = \Delta V^* - T(\partial\Delta V^*/\partial T)_P$$

The high experimental accuracy required to obtain meaningful values of the mixed second derivative parameters in eq. 19 has limited the testing of this identity to establishing that the parameters have indeed opposite signs in the case of the Menshutkin reaction (29) and some hydrolyses (30).

The present work offers the opportunity of examining this Maxwell relationship as a function of solvent composition. Unfortunately, as was noted above, the determination of a numerical value of $\partial\Delta S^*/\partial P$ was not possible. It was possible, however, to determine the sign of $\partial\Delta S^*/\partial P$. The signs of both $\partial\Delta S^*/\partial P$ and $\partial\Delta V_0^*/\partial T$ are shown in Table 7 and demonstrate again that these parameters have opposite signs as required by eq. 19.

The present data also enables eq. 20 to be tested. The numerical evaluation of $\Delta V_0^* - T\partial\Delta V_0^*/\partial T$ is shown in Table 7. Numerical values of $\partial\Delta H^*/\partial P$ could not be obtained but again its