Molecular interpretation of the linear relationship between the entropy and the enthalpy of activation of charge transfer reactions in polar liquids

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MS received 6 September 1991

Abstract. The well-known linear relationship \( T \Delta S^\ddagger = \alpha \Delta H^\ddagger + \beta \), where \( 1 > \alpha > 0, \beta > 0 \) between the entropy \( \Delta S^\ddagger \) and the enthalpy \( \Delta H^\ddagger \) of activation for reactions in polar liquids is investigated by using a molecular theory. An explicit derivation of this linear relation from first principles is presented for an outer sphere charge transfer reaction. The derivation offers microscopic interpretation for the quantities \( \alpha \) and \( \beta \). It has also been possible to make connection with and justify the arguments of Bell put forward many years ago.

Keywords. Molecular interpretation; linear relationship; entropy; enthalpy of activation; polar liquids; charge transfer reactions.

1. Introduction

The study of the effects of solvent on chemical reactions in solution has been a subject of great importance in chemistry (Glasstone et al. 1941; Amis 1966; Entelis and Tiger 1976; Reichardt 1979). It was recognized quite early that the solvent can significantly affect the reaction potential energy surface, especially if the reaction involves polar species in a dipolar liquid which is most often the case. The following expression for the rate constant, \( k \),

\[
k = \left( k_B T / h \right) \exp(\Delta S^\ddagger / k_B) \exp(-\Delta H^\ddagger / k_B T)
\]

has been used widely to rationalize the solvent effects on chemical reactions (Wynne-Jones and Eyring 1935). In (1), \( \Delta S^\ddagger \) and \( \Delta H^\ddagger \) are the entropy and the enthalpy of activation per molecule, respectively, \( k_B \) is the Boltzmann constant, \( h \) is Planck’s constant and \( T \) is the temperature.

Recently great attention has been focussed on understanding the dynamic solvent effects on various ultra-fast chemical reactions (Hynes 1985; Kosower and Huppert 1986; Barbara and Jarzeba 1988, 1990; Simon 1988; Bagchi 1989; Marroncelli et al. 1989; Fleming and Wolynes 1990; Bagchi and Chandra 1991) and a better understanding of both the equilibrium and the dynamic solvent effects is beginning to emerge. Several

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microscopic studies are now available which can be used to address some of the long-standing problems in chemical dynamics.

One such problem is the often observed linear relationship between the enthalpy and the entropy of activation given by (Evans and Polanyi 1936; Bell 1937; Amis 1966)

\[ T\Delta S^\# = \alpha \Delta H^\# + \beta. \tag{2} \]

It is known experimentally that \( \alpha \) is positive and less than unity. The intercept \( \beta \) also appears to be positive (Evans and Polanyi 1936; Bell 1937; Amis 1966). Equation 2 is interesting (and also important) for the following reasons. Firstly, if solvent effects are not important, then there is no \textit{a priori} reason that (2) should hold and no such constraint seems possible. If solvent effects are important, then such an equation is possible because both \( \Delta H^\# \) and \( \Delta S^\# \) may partly have the same origin. Even then (2) is non-trivial because \( \Delta S^\# \) and \( \Delta H^\# \) are rather different thermodynamic quantities. Secondly, if a relation like (2) is truly valid, then it would have serious implications for the experimental determination of the activation energy of the reaction. For example, if \( \beta \) is small, then a determination of the enthalpy of activation by the usual temperature variation method would actually measure \( (1 - \alpha) \Delta H^\# \), instead of \( \Delta H^\# \).

There have been attempts in the past to explain (2). Evans and Polanyi (1936) noted that a relation of the form of (2) also holds for enthalpy and entropy of solution of the same solute in a series of different solvents

\[ T\Delta S = \alpha \Delta H + \beta, \tag{3} \]

where \( \Delta S \) and \( \Delta H \) now refer to the entropy and the enthalpy of solution. Therefore, if one assumes that the equilibrium relation (3), holds, not only for the reactant, but also for the activated complex, then one naturally recovers (2).

Many years ago Bell (1937) investigated the reason for the existence of a linear relation between \( T\Delta S \) and \( \Delta H \) by using the basic statistical thermodynamics. He arrived at the conclusion that a relation like (3) is possible only when the interaction between the solute and the solvent molecules is small and also when the solute molecule is considerably smaller than the solvent molecules. The argument of Bell was based on qualitative grounds. It fails to account satisfactorily, as recognized by Bell himself, for the relation given by (2) and (3) which exist for a large solute in different solvents.

A \textit{limited} explanation for these relations can be given for the solvation of a large dipolar solute in a dipolar liquid, if one assumes that the main source of \( \Delta H \) and \( \Delta S \) is the electrical interaction between the solute and the solvent and also if the solvent can be replaced by a dielectric continuum. Under these assumptions, the free energy of solute–solvent interaction can be given by (Onsager 1935; Frohlich 1958)

\[ \Delta A = -\mu \cdot \mathbf{R} + \gamma R^2, \tag{4} \]

where \( \mu \) is the dipole moment of the solute and \( \mathbf{R} \) is the reaction field at the solute cavity. If one minimizes the free energy with respect to \( \mathbf{R} \), then one obtains

\[ \Delta A = -\frac{1}{2}\mu \cdot \mathbf{R}. \tag{5} \]

Under the same conditions the change in the energy of the system (\( \Delta \mathcal{E} \)) and the change in the enthalpy (\( \Delta H \)) are both equal to \( -\mu \cdot \mathbf{R} \). Next, the use of the thermodynamic relation \( \Delta A = \Delta H - T\Delta S \) gives the following relation between \( \Delta H \) and \( T\Delta S \),

\[ T\Delta S = \frac{1}{2}\Delta H, \tag{6} \]