

## A thermodynamic approach to analyzing relative permittivity and solvent mole fraction models, and application to SN1 reactions

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### Supplemental Section

#### *Replacement of the Chemical Potential Terms with the Mole Fraction Term*

The chemical potential expression for a binary system,  $\mu_1 dn_1 + \mu_2 dn_2$ , can be recast with implicit differential terms as:

$$\mu_1 dn_1 + \mu_2 dn_2 = \left(\frac{\partial G}{\partial X_1}\right)_{P,T} \left(\frac{\partial X_1}{\partial n_1}\right)_{P,T,n_2} dn_1 + \left(\frac{\partial G}{\partial X_2}\right)_{P,T} \left(\frac{\partial X_2}{\partial n_2}\right)_{P,T,n_1} dn_2 \quad (\text{S1})$$

in which  $\mu_i = \left(\frac{\partial \Delta G}{\partial n_i}\right)_{P,T,n_{j \neq i}}$ . Since  $X_1$  and  $X_2$  vary with each other in a complementary fashion, they are not included as constant variables for  $\left(\frac{\partial G}{\partial X_1}\right)_{P,T}$  and  $\left(\frac{\partial G}{\partial X_2}\right)_{P,T}$ . Using the general definition,  $X_i = \frac{n_i}{\sum n_j}$ , it can be shown that for a binary system:

$$\left(\frac{\partial X_1}{\partial n_1}\right)_{P,T,n_2} = \frac{X_2}{n_1+n_2} \quad (\text{S2})$$

$$\left(\frac{\partial X_2}{\partial n_2}\right)_{P,T,n_1} = \frac{X_1}{n_1+n_2} \quad (\text{S3})$$

Combining Equations (S1) - (S3) yields:

$$\mu_1 dn_1 + \mu_2 dn_2 = \left(\frac{\partial G}{\partial X_1}\right)_{P,T} \frac{X_2 dn_1}{n_1+n_2} + \left(\frac{\partial G}{\partial X_2}\right)_{P,T} \frac{X_1 dn_2}{n_1+n_2} \quad (\text{S4})$$

Noting that  $dX_1 = -dX_2$  for a binary system, Equation (S4) reduces to:

$$\mu_1 dn_1 + \mu_2 dn_2 = \left( \frac{\partial G}{\partial X_1} \right)_{P,T} \frac{X_2 dn_1 - X_1 dn_2}{n_1 + n_2} \quad (\text{S5})$$

It can be shown that  $dX_1 = \frac{X_2 dn_1 - X_1 dn_2}{n_1 + n_2}$ , so Equation (S5) finally becomes:

$$\mu_1 dn_1 + \mu_2 dn_2 = \left( \frac{\partial G}{\partial X_i} \right)_{P,T} dX_i \quad (\text{S6})$$

Since  $\left( \frac{\partial G}{\partial X_1} \right)_{P,T} dX_1 = \left( \frac{\partial G}{\partial X_2} \right)_{P,T} dX_2$ , the subscript “i” can be dropped. For an activation process, this expression is redressed as  $\mu_1^\ddagger dn_1 + \mu_2^\ddagger dn_2 = \left( \frac{\partial \Delta G^\ddagger}{\partial X} \right)_{P,T} dX$ , in which  $\mu_i^\ddagger = \left( \frac{\partial \Delta G^\ddagger}{\partial n_i} \right)_{P,T, n_{j \neq i}}$ .

### *Isobaric/Iso-mole Fraction Expression*

The expression for  $\partial \Delta G_{P,X}^\ddagger$  from Equation (2) is:

$$\partial \Delta G_{P,X}^\ddagger = -\Delta S_{P,X,\varepsilon_r}^\ddagger \partial T + \left( \frac{\partial \Delta G^\ddagger}{\partial \varepsilon_r} \right)_{P,T,X} \partial \varepsilon_r \quad (\text{S7})$$

Integrating this expression with  $\Delta S_{P,X,\varepsilon_r}^\ddagger$  constant yields:

$$\int_{\Delta G_{P,X,0}^\ddagger}^{\Delta G_{P,X}^\ddagger} \partial \Delta G_{P,X}^\ddagger = -\Delta S_{P,X,\varepsilon_r}^\ddagger \int_{T_0}^T \partial T + \int_{\varepsilon_{r,0}}^{\varepsilon_r} \partial \Delta G_{P,T,X}^\ddagger$$

$$\Delta G_{P,X}^\ddagger = \Delta G_{P,X,0}^\ddagger - \Delta S_{P,X,\varepsilon_r}^\ddagger (T - T_0) + \Delta G_{P,T,X}^\ddagger - \Delta G_{P,T,X,0}^\ddagger \quad (\text{S8})$$

in which the subscript “0” denotes reference values, and  $\Delta G_{P,T,X}^\ddagger$  is functionally dependent only on  $\varepsilon_r$ . Using the Kirkwood-Onsager model for the term,  $\Delta G_{P,T,X}^\ddagger - \Delta G_{P,T,X,0}^\ddagger$ , yields the following result:

$$\Delta G_{P,X}^{\ddagger} = \Delta G_{P,X,0}^{\ddagger} - \Delta S_{P,X,\varepsilon_r}^{\ddagger} (T - T_0) - \frac{3AQ(\varepsilon_r - \varepsilon_{r,0})}{(2\varepsilon_r + 1)(2\varepsilon_{r,0} + 1)} \quad (\text{S9})$$

The regression parameters are  $\Delta G_{P,X,0}^{\ddagger}$ ,  $\Delta S_{P,X,\varepsilon_r}^{\ddagger}$ , and  $Q$ .

### *Isobaric/Isodielectric Expression*

The expression for  $\partial\Delta G_{P,\varepsilon_r}^{\ddagger}$  from Equation (2) is:

$$\partial\Delta G_{P,\varepsilon_r}^{\ddagger} = -\Delta S_{P,X,\varepsilon_r}^{\ddagger} \partial T + \left(\frac{\partial\Delta G^{\ddagger}}{\partial X}\right)_{P,T,\varepsilon_r} \partial X \quad (\text{S10})$$

Using our empirical mole fraction model for the term,  $\left(\frac{\partial\Delta G^{\ddagger}}{\partial X}\right)_{P,T,\varepsilon_r}$ , yields the following result upon integration:

$$\Delta G_{P,\varepsilon_r}^{\ddagger} = \Delta G_{P,\varepsilon_r,0}^{\ddagger} - \Delta S_{P,X,\varepsilon_r}^{\ddagger} (T - T_0) + \frac{\alpha}{\gamma+1} (X^{\gamma+1} - X_0^{\gamma+1}) \quad (\text{S11})$$

The regression parameters are  $\Delta G_{P,\varepsilon_r,0}^{\ddagger}$ ,  $\Delta S_{P,X,\varepsilon_r}^{\ddagger}$ ,  $\alpha$ , and  $\gamma$ .

### *Isobaric/Isothermal Expression*

The expression for  $\partial\Delta G_{P,X}^{\ddagger}$  from Equation (2) is:

$$\partial\Delta G_{P,X}^{\ddagger} = \left(\frac{\partial\Delta G^{\ddagger}}{\partial X}\right)_{P,T,\varepsilon_r} dX + \left(\frac{\partial\Delta G^{\ddagger}}{\partial\varepsilon_r}\right)_{P,T,X} d\varepsilon_r \quad (\text{S12})$$

Using the solvent models presented earlier, Equation (S12) can be integrated to yield:

$$\Delta G_{P,T}^{\ddagger} = \Delta G_{P,T,0}^{\ddagger} - \frac{3AQ(\varepsilon_r - \varepsilon_{r,0})}{(2\varepsilon_r + 1)(2\varepsilon_{r,0} + 1)} + \frac{\alpha}{\gamma + 1} (X^{\gamma+1} - X_0^{\gamma+1}) \quad (\text{S13})$$

The regression parameters are  $\Delta G_{P,T,0}^{\ddagger}$ ,  $Q$ ,  $\alpha$ , and  $\gamma$ .

### *Regression Analyses for Composite Data Sets*

Consider the following general function, f:

$$y_i = f[\{a_j\}, x_i] \quad (\text{S14})$$

in which y is the dependent variable, x is the independent variable, “i” represents a data point, and  $\{a_j\}$  represents the set of fitting parameters in the equation. Now suppose similar data sets are generated at different conditions such that the same number of data points is taken for each data set, and the independent variables have the same values. If the parameters are treated as constant for each data set, then the set of equations for each data point can be summed to yield the following composite expression:

$$\frac{1}{K} \sum_k y_{i,k} = \frac{1}{K} \sum_k f_k[\{a_j\}, x_i] \quad (\text{S15})$$

in which K is the number of data sets, and  $f_k$  is the function specific to data set “k”. The advantage of this expression is only a single regression analysis is required, for which the fitted parameters represent the statistical averages over all the data sets. We note that Equation (S15) is not applicable if  $a_j$  is not the same for the different experimental conditions represented by the summation index k.

In this work reaction rate data was acquired at several mole fractions under isobaric/isomole fraction conditions using the same temperatures for each data set. An analysis was done using the following composite expression with temperature as the independent variable:

$$\frac{1}{K} \sum_k \Delta G_{P,X,i,k}^{\ddagger} = \frac{1}{K} \sum_k \Delta G_{P,X,0,k}^{\ddagger} - \Delta S_{P,X,\varepsilon_r}^{\ddagger} (T_i - T_0) - \frac{3AQ}{K} \sum_k \frac{\varepsilon_{r,i,k} - \varepsilon_{r,0,k}}{(2\varepsilon_{r,i,k} + 1)(2\varepsilon_{r,0,k} + 1)} \quad (\text{S16})$$

in which the summation is over the data sets for data point “i”.