

1993

**Adjustment of activity coefficients  
as a function of changes in temperature,  
using the specific interaction theory**

Eric Giffaut, Pierre Vitorge and H el ene Capdevila

CEA DCC/DESD/SCS/SGC/LAT, Fontenay-aux-Roses, France

The aim of this work is to propose and to check approximations to calculate from only a few experimental measurements, ionic strength  $I$  and temperature  $T$ , influences on Gibbs' energy  $G$ , formal redox potential  $E$  and standard equilibrium constant  $K$ . Series expansions vs.  $T$  are first used:  $S$  and  $C_p/2T^\circ$  are typically the first- and second-order terms in  $-G$ . In the same way,  $-\Delta H$  and  $T^2 \Delta C_p/2$  are the first- and second-order terms of  $R \ln K$  expansions vs.  $1/T$ . This type of approximation is discussed for  $E$  of the  $M^{4+}/M^{3+}$ ,  $MO_2^{2+}/MO_2^+$  and  $MO_2(CO_3)_3^{4-}/MO_2(CO_3)_3^{5-}$  couples ( $M \equiv U$  or  $Pu$ ) measured from 5 to 70 °C, for the standard  $\Delta G$  of some solid U compounds, calculated from 17 to 117 °C, and for  $\Delta C_p$ ,  $\Delta G$  and  $\log K$  of the  $CO_{2(aq)}/HCO_3^-$  equilibrium from 0 to 150 °C. Excess functions  $X^{ex}$  are then calculated from activity coefficients  $\gamma$ : enthalpy  $H$  or heat capacity  $C_p$  adjustment as a function of  $I$  changes is needed only when the  $\gamma$  adjustment as a function of  $T$  changes is needed. The variations in the specific interaction theory coefficient  $\epsilon$  with  $T$  are small and roughly linear for the above redox equilibria and for the mean  $\gamma$  of chloride electrolytes: first-order expansion seems enough to deduce  $\epsilon$ , and then the excess functions  $G^{ex}$ ,  $S^{ex}$  and  $H^{ex}$ , in this  $T$  range; but second-order expansion is more consistent for estimation of  $C_p^{ex}$ .