A simple, general and robust function for equilibria in aqueous electrolyte solutions to high ionic strength and temperature†

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A novel function is proposed to calculate the conditional equilibrium constants of reactions in aqueous solution; two parameters characterise a non-electrolyte-specific response to increasing ionic strength (< 5 M) and temperature (< 250 °C).

How chemical equilibria in solution respond to changing experimental conditions is of considerable theoretical and practical importance. A good function is needed to model natural and industrial systems and to analyse the vast array of experimental data on which such models depend. Since electrolyte solutions depart strongly from ideality, this has proved elusive[1] and, consequently, many different functions have been employed.[2]

Among the most common approaches nowadays are the Pitzer,[3] the Brønsted–Guggenheim–Scatchard Specific Ion Interaction (SIT),[1] the Helgeson–Kirkham–Flowers (HKF)[4] and the Density[5] models. However, none is the obvious method of choice and, of the many tens of thousands of reactions of interest, only a small fraction have been characterised using these functions.[6]

The main problem with the Pitzer, SIT and HKF models lies in the numerical fitting of parameters that they use to describe individual chemical systems. Although very good agreement with experimental data can be achieved, many 'interaction coefficients' are typically involved. Predictions are then put in doubt because (a) the fitted parameters do not capture the essence (*i.e. only* the predominant factors) of the underlying *general* physicochemical behaviour and (b) unique characterisation becomes difficult, and extrapolations thwarted, by mathematical correlation (covariance).

In contrast, the parameters of the Density model are much fewer, are entirely fundamental and can be measured independently. The Density model thus provides an excellent means for assessing and predicting data under ideal conditions, *i.e.* at infinite dilution. It has been used extensively for these purposes at the U.S. Oak Ridge National Laboratories (ORNL),[8] whose results comprise by far the largest single body of reliable equilibrium constants in aqueous electrolyte solutions, especially at higher temperatures.[7]

Unfortunately, the Density model as described by Andersen *et al.*[5] does not deal directly with the effects of ionic strength. Extraneous and varied means are invoked to extrapolate measurements to infinite dilution, a notoriously difficult task even at ambient temperatures with plenty of data. A failure to record properly in databases the particular smoothing function used, and the parameters so obtained, exacerbates the problem. Sometimes more than ten fitting parameters are employed.

To extend the Density model to finite concentrations, I propose here, a novel function that calculates the conditional equilibrium constants of reactions in aqueous solution. The function is based on just two additional semi-empirical parameters that characterise the effects of increasing ionic strength and temperature in a non-electrolyte-specific manner. The need for, and magnitude of, specific interaction coefficients is thus much reduced.

The scientific description of the effect of ionic strength on equilibria in electrolyte solutions has recently been reviewed.[2] Soon after Debye and Hückel demonstrated the dominance in dilute solutions of coulombic interactions between ions, Hückel suggested that the expression for the mean ionic activity coefficient, $\gamma_{\pm}$, could be extended to higher concentrations by introducing a linear term, ascribed to 'ion-solvent interactions'. Guggenheim then proposed a formula for mixtures in which this linear term is expanded into a summation involving the so-called 'ion interaction coefficients'. This formula underpins the SIT model in current use today.

There is considerable experimental evidence showing that activity coefficients (and, hence, conditional equilibrium constants) vary in a way that accords with this linear behaviour. However, no theoretical explanation has prevailed, allowing the proliferation of correction functions described above.

An equation that works satisfactorily[8] at constant temperature (*t*) has the form

$$\log_{10} K' = \log_{10} K^0 + \left(\frac{-\Delta Z^2 A \sqrt{I}}{1 + 1.5\sqrt{I}} \right) + BI \qquad (1)$$

where K' is the conditional equilibrium constant at finite ionic strength, K^0 is the equilibrium constant (at infinite dilution), and A and ΔZ^2 are the usual Debye–Hückel factors. Both B and the factor in the denominator, shown here as 1.5 to accord with the SIT model,[1] must be nearly constant to maintain thermodynamic consistency but their exact values are somewhat arbitrary on account of the covariance between them.

The key observation of the present work is simply that the value of B itself changes linearly with temperature. To represent this behaviour in accord with the Density model (for which all parameters refer to a reference temperature) this variation is conveniently expressed as $B = G_C + G_M (t - 25)$, where the symbols G_C and G_M refer to the intercept and slope respectively of the Guggenheim factor B at 25 °C.

The linearity of the expression for B is important in the maintenance of thermodynamic consistency when the function is applied to reactions in general. Also important is the low correlation between the five parameters of the extended Density model (log K^0, ΔH^0, ΔC_p^0, G_C and G_M).

The new function has been applied in the characterisation of reaction data in the JESS Thermodynamic database.[6] Although much is still to be done, it is clear that in this way the vast majority of compiled equilibrium constants can be rationalised to well within their experimental error. Very few exceptions have been encountered and these exhibit no discernable pattern, leaving experimental error as their most likely explanation.

A very demanding test was provided by the ORNL data, comprising more than 700 equilibrium constants of unsurpassed precision and accuracy for over 30 reactions. All these chemical systems were fitted satisfactorily. The median deviations between observed and calculated data were typically better than 0.05 log K units and the worst rarely greater than 0.1 units.
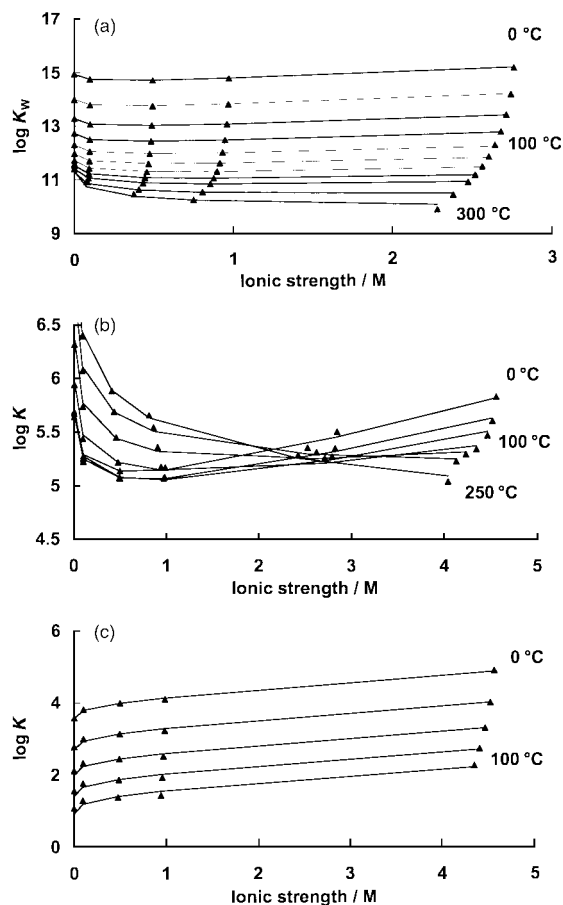

Fig. 1 Illustrative plots of observed and predicted values for conditional equilibrium constants as a function of ionic strength and temperature with three different types of chemical reaction: (a) the hydrolysis of water,[10] (b) the first protonation of succinate[11] and (c) the solubility of gibbsite.[12]

dependent) SIT parameters are many (one for each ion–counter ion, ion–neutral and neutral–neutral interaction[1]) and represent *specific* interactions, just two values, G_C and G_M, are used in this work to characterise the *non-specific* response of the reaction to changing conditions. It seems much better to attribute specific properties only to the *differences* in equilibrium constants observed in different background electrolytes at the same ionic strength and temperature: this isolates behaviour that is common to all electrolytes, such as caused by the general reduction in water activity with increasing concentration, and it keeps the magnitude of the specific factors to a minimum. The effects of individual electrolytes can then simply be described as a direct association between species (see *e.g.* ref. 9), which generally yields even better fits of the data.

The observed data are nonetheless modelled well, albeit not exactly, by the non-specific function on its own. This has all the flexibility needed to follow the main trends exhibited by equilibria to high concentrations (≈ 5 M) and high temperature (≈ 250 °C). It also possesses the three chief attributes necessary to rationalise diverse experimental data and to predict values beyond the range of parameterisation, namely it (a) appears applicable to all types of reaction, (b) involves only a few parameters and (c) offers a reasonable physicochemical basis for avoiding optimisation of values when this is not warranted by the data available.

These differences are small compared to the changes in the measured equilibrium constants which over the intervals $0 \leqslant I \leqslant 5.0$ M and $0 \leqslant t \leqslant 250$ °C typically vary by as much as 3 log K units. It may even be possible to improve on these predictions for data at higher temperatures by taking account of density change in the electrolyte medium, but this remains to be done.

Three examples, representing quite different types of behaviour, are shown in Fig. 1. Plots for 38 chemical systems have been deposited as ESI.†

Despite the formal mathematical similarity between the function being proposed here and that of the SIT method, the two approaches differ diametrically. Whereas the (temperature-

Notes and references

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