

## ON TEMPERATURE DEPENDENCE OF EXCESS GIBBS ENERGY

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Temperature dependence of  $G^E$  is discussed for three widely used equations linear and non-linear in parameters. It is shown that the Wilson equation predicts always positive excess heat capacity regardless of values of its parameters. Several temperature modifications of the Redlich-Kister, Wilson and NRTL equations are discussed with respect to the sign of the excess Gibbs energy, excess enthalpy and excess heat capacity.

**Key words:** Liquid mixtures; Excess functions; Temperature dependence; Chemical thermodynamics.

Knowledge of suitable functional forms for the temperature dependence of the excess Gibbs energy,  $G^E$ , would be useful for several reasons. First, it would enable the extrapolation of the equilibrium vapor-liquid experimental results beyond ranges of measured values. Second, it would allow simultaneous correlation of vapor-liquid and solid-liquid equilibrium data typically obtained in distant temperature intervals. Third, it would enable predictions of excess enthalpies,  $H^E$ , and excess isobaric heat capacities,  $c_p^E$ , from the phase equilibrium data using thermodynamic relations

$$H^E = -T^2 \frac{\partial G^E / T}{\partial T} \quad \text{and} \quad c_p^E = \frac{\partial}{\partial T} \left( -T^2 \frac{\partial G^E / T}{\partial T} \right) . \quad (1)$$

Many empirical and semi-empirical equations describing composition dependence of  $G^E$  have been proposed (see, e.g., ref.<sup>1</sup>). Temperature dependence of  $G^E$  has been studied much less. The aim of this note is to point out certain difficulties in constructing models for  $G^E$  as a function of temperature. Binary systems will be considered for simplicity.

For the purpose of this work, we sort out the equations for  $Q^E = G^E/(RT)$  as functions of composition into two groups: those with no temperature dependence built-in *a priori*, and those describing both the composition and the temperature dependence. A typical representative of the first group is, *e.g.*, the Redlich–Kister equation<sup>2</sup>. Typical representatives of the second group are equations based on the “local composition” concept such as, *e.g.*, the Wilson<sup>3</sup> and the NRTL (ref.<sup>4</sup>) equations.

### Redlich–Kister Equation

Consider the two-parameter Redlich–Kister equation

$$\frac{G^E}{RT} = x_1 x_2 [a + b(x_1 - x_2)] \quad . \quad (2)$$

Consider further temperature independent  $c_p^E$  for simplicity. Using Eqs (1), we obtain

$$a = a_1 + a_2 / T + a_3 \ln T \quad , \quad (3)$$

$$b = b_1 + b_2 / T + b_3 \ln T \quad . \quad (4)$$

There are six parameters to describe both the composition and the temperature dependence of  $G^E$ . The parameters can be fitted to vapor–liquid and/or solid–liquid phase equilibrium data. However, such fitting is numerically ill-conditioned even if data covering large temperature ranges are used. This can be demonstrated by the fact that the correlation coefficients  $\rho$  are close to unity<sup>5</sup>

$$|\rho(a_i, a_j)| = \left| \frac{\text{Cov}(a_i, a_j)}{\sqrt{\text{Cov}(a_i, a_i)}\sqrt{\text{Cov}(a_j, a_j)}} \right| \approx 1 \quad i \neq j, \quad i, j = 1, 2, 3 \quad , \quad (5)$$

and the same holds for parameters  $b_i$ . Mutual correlation of the parameters deteriorates an extrapolation in temperature beyond the range of the fitted data, and it also leads to uncertain values of derived quantities ( $H^E$  and  $c_p^E$ ). The use of the Redlich–Kister equation with more than two parameters even worsens the situation.

Let us try to avoid the parameter compensation problem by modeling the temperature dependence of  $a$  using a simple one-parameter function and by keeping parameter  $b$  temperature-independent. From the point of view of the excess functions signs, four cases exist:

$$1. \text{sign } G^E \neq \text{sign } H^E = \text{sign } c_p^E.$$

Such systems can be described by, e.g., the following simple temperature functions:  $a = a_1 T$  or  $a = a_1 \ln T$  or  $a = a_1 T^{1/2}$ .

$$2. \text{sign } G^E = \text{sign } H^E \neq \text{sign } c_p^E.$$

This behavior can be described by, e.g.,  $a = a_1/T^n$ ,  $n \geq 1$ . For  $n = 0$  is  $c_p^E = 0$ .)

$$3. \text{sign } G^E = \text{sign } H^E = \text{sign } c_p^E.$$

This is possible to describe by, e.g.,  $a = a_1/T^{1/2}$ .

$$4. \text{sign } G^E = \text{sign } c_p^E \neq \text{sign } H^E.$$

This is possible to describe by, e.g.,  $a = a_1(1 - e^{-T})$ .

No simple temperature function has been found that would describe all four above mentioned cases. A particular form of  $a = a(T)$ , that describes experimental  $G^E$  data significantly better than the other forms, is expected to yield more reliable estimated of the signs of  $H^E$  and  $c_p^E$ . On the other hand, knowledge of the signs of  $H^E$  and  $c_p^E$  gives an additional information on the specific form of  $G^E = f(T)$ .

### Wilson Equation

The Wilson equation for a binary system is given by

$$\frac{G^E}{RT} = -\sum_{i=1}^2 x_i \ln S_i \quad , \quad (6)$$

where

$$S_i = x_i + x_j \Lambda_{ij} \quad \text{and} \quad \Lambda_{ij} = \frac{V_j}{V_i} e^{-a_{ij}/T} .$$

If we analyse this equation assuming

$$\frac{V_j}{V_i} \neq f(T)$$

we find

$$c_p^E = R x_1 x_2 \sum_{i=1}^2 a_{ij}^2 \frac{x_i \Lambda_{ij}}{S_i^2 T^2} > 0 \quad (7)$$

which disables description of systems with negative  $c_p^E$ .

We note that an attempt<sup>6,7</sup> to increase the flexibility of Eq. (6) by setting

$$a_{ij} = a_{ij1} + a_{ij2}T$$

changes only the volume ratio to a (positive) adjustable parameter and, as can be easily proved, it also predicts positive  $c_p^E$ .

The signs of  $G^E$  and  $H^E$  depend on the values of  $a_{12}$ ,  $a_{21}$ , as shown in Fig. 1. For the pairs of values on the left from the dashed curve, the excess quantities are negative, for the pairs on the right from the curve, the quantities are positive. In the vicinity of the dashed curve, both  $H^E$  and  $G^E$  are S-shaped.

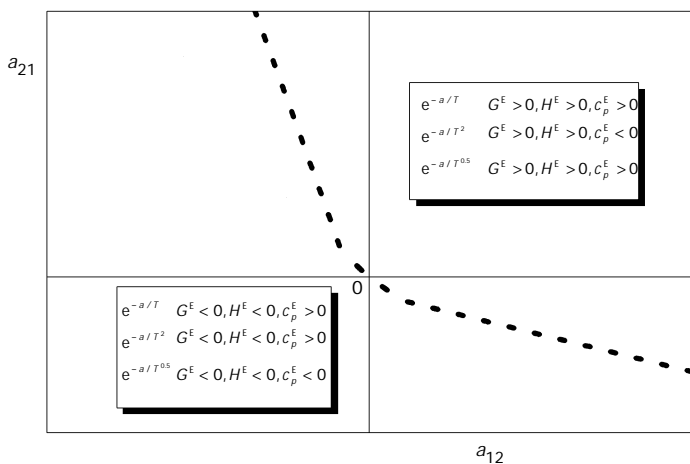


FIG. 1

The Wilson equation – signs of excess functions for different pairs of parameters

### Modified Forms of the Wilson Equation

We have tested two simple modifications of the Wilson equation changing  $1/T$  in the exponents of  $\Lambda_{ij}$  into  $1/T^2$  and  $1/T^{1/2}$ . The results for the two modifications are shown in Fig. 1 and summarized in Table I. For the parameters on the left from the dashed curve,  $G^E$ ,  $H^E$ ,  $c_p^E$  are negative for  $1/T^{1/2}$ . For  $1/T^2$ ,  $G^E$  and  $H^E$  are negative but  $c_p^E$  is positive. For the parameters on the right from the curve, the quantities change the signs. At the boundary, the signs of the thermodynamic functions change and are usually S-shaped. However, it is possible to find a pair of parameters for which  $H^E$  is negative while the other excess functions are positive.

No pair of parameters was found to give the following combinations of excess functions.

$$\begin{array}{ccc} G^E & H^E & c_p^E \\ + & - & - \\ - & + & + \\ - & + & - \end{array}$$

### NRTL Equation

The NRTL equation for a binary systems is

$$\frac{G^E}{RT} = - \sum_{i=1}^2 x_i \frac{\sum_{j=1}^2 x_j \tau_{ji} G_{ji}}{\sum_{j=1}^2 x_j G_{ji}}, \quad (8)$$

where

$$G_{ij} = \exp(-a\tau_{ij}).$$

Three temperature functions were examined: the original  $\tau_{ij} = k_{ij}/T$  and again the two modifications  $\tau_{ij} = k_{ij}/T^2$  and  $\tau_{ij} = k_{ij}/T^{1/2}$ .

The results for the original as well as for the modified NRTL equations are summarized in Table II.

As the bracketed signs were found only for nearly ideal systems, not much has been gained by modification of the temperature function. S-Shaped and even multi-inflexed curves ( $c_p^E$  for  $1/T^2$  modification) are quite common for this equation.

No pair of parameters was found to give the following combinations of the excess functions.

$$\begin{array}{ccc} G^E & H^E & c_p^E \\ + & - & - \\ - & + & + \end{array}$$

TABLE I  
Signs of excess functions for the Wilson equation and its temperature modifications

Function	Location in $a_{12} \times a_{21}$ area	$G^E$	$H^E$	$c_p^E$
$1/T$	left	-	-	+
	right	+	+	+
	near the curve	S	S	+
$1/T^2$	left	-	-	+
	right	+	+	-
	near the curve	+	-	+
$1/\sqrt{T}$	left	-	-	-
	right	+	+	+
	near the curve	+	-	+

TABLE II  
Signs of excess functions for the NRTL equation and its temperature modifications

Function	$G^E$	$H^E$	$c_p^E$	$G^E$	$H^E$	$c_p^E$
	$a > 0$			$a < 0$		
$1/T$	+	+	+	+	+	-
	-	-	+	-	-	+
	(+)	-	(+)	(-	- or +	(-)
$1/T^2$	+	+	-	+	+	-
	-	-	+	-	-	+
	(+)	+	(+)	(-	- or +	(-)
$1/\sqrt{T}$	+	+	+	+	+	-
	-	-	+	-	-	-
	(+)	-	(+)	(-	+	(-)

## CONCLUSIONS

Simple models of  $G^E$ -temperature dependence are not able to cover all possibilities concerning signs of its derivatives. The chosen temperature dependence of the fitting equation for  $G^E$ , linear in parameters, determines the signs of  $H^E$  and  $c_p^E$ . The use of more competing functions is impossible due to their high correlation.

Also equations based on the "local composition" concept and its simple temperature modifications are not able to describe all possibilities in signs of the excess functions. Although these conclusions were derived for binary systems, they can be extended for mixtures of an arbitrary number of components.

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