

Integration of the LeChatelier—Shreder equation for different forms of temperature dependence of ΔC_p

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Integral form of the LeChatelier—Shreder equation derived for different forms of temperature dependence of ΔC_p is presented. The temperature dependence may be given either by a functional relationship or by the table of values. If the functional relationship is chosen, then it is recommended to use a polynomial in difference of temperatures from the melting point instead of a polynomial in absolute temperature. In practical applications the former procedure is better founded.

В работе приведен интегральный вид уравнения ЛеШателье — Шредера для различных типов температурной зависимости ΔC_p : как для функционально заданной, так и для заданной в виде таблицы. В случае функциональной зависимости предложена степенная формула, в которой, однако, используется не абсолютная температура, а разность от температуры плавления. Этот способ более обоснован для практического использования.

Phase equilibrium solidus—liquidus is described by the LeChatelier—Shreder equation the differential form of which is presented by Malinovsky [1]

$$d \ln a = \frac{\Delta H^{l/s}}{RT^2} dT \quad (1)$$

where a is the activity of component in liquid phase, $\Delta H^{l/s}$ is the enthalpy of phase transition solidus—liquidus, R is gas constant, and T is absolute temperature.

Integral form of the LeChatelier—Shreder equation can be obtained by integration of eqn (1) in limits (T, T_i)

$$\ln a = -\frac{1}{R} \int_T^{T_i} \frac{\Delta H^{l/s}}{T^2} dT \quad (2)$$

(At $T = T_i$ the activity of pure component equals one.) By integration of the right side of eqn (2) the following cases can occur:

1. $\Delta H^{l/s} = \text{const} = \Delta H^f$ (it does not depend on temperature). Then the integration (2) yields the simplest form of the LeChatelier—Shreder equation

$$\ln a = \frac{\Delta H^t}{R} (1/T_i - 1/T) \quad (3)$$

2. $\Delta H^{t/s}$ depends on temperature according to Kirchhoff's relation

$$d(\Delta H^{t/s}) = \Delta C_p^{t/s} dT \quad (4)$$

but $\Delta C_p^{t/s}$ is constant. Integrating eqn (4) in limits (T , T_i) gives

$$\Delta H^{t/s} = \Delta H^t - \Delta C_p^{t/s} (T_i - T) \quad (5)$$

and finally by integration of eqn (2) we obtain

$$\ln a = \frac{\Delta H^t}{R} \left(\frac{1}{T_i} - \frac{1}{T} \right) + \frac{\Delta C_p}{R} \left(\frac{T_i}{T} - 1 - \ln \frac{T_i}{T} \right) \quad (6)$$

3. $\Delta C_p^{t/s}$ is an arbitrary function of temperature. Then it holds

$$\ln a = \frac{\Delta H^t}{R} \left(\frac{1}{T_i} - \frac{1}{T} \right) + \frac{1}{R} \int_T^{T_i} \left[\frac{1}{T^2} \int_T^{T_i} \Delta C_p^{t/s} dT \right] dT \quad (7)$$

4. The temperature dependence of $\Delta C_p^{t/s}$ is given as a polynomial in T , e.g.

$$\Delta C_p^{t/s} = a + bT + cT^{-2} \quad (8)$$

Double integration of eqn (7) gives in this case

$$\frac{1}{R} \left\{ a \left(\frac{T_i}{T} - 1 - \ln \frac{T_i}{T} \right) + \frac{b}{2} \left(\frac{T_i^2}{T} - 2T_i + T \right) + \frac{c}{2} \left(\frac{1}{T} - \frac{1}{T_i} \right)^2 \right\} \quad (9)$$

The last temperature dependence of ΔC_p is most frequently used for the description of heat capacities of solid and liquid substances. However, at the melting point, there is a discontinuous change in the heat capacity from C_p^s to C_p^l . Therefore it is more convenient and more advantageous to express ΔC_p not as a polynomial in T (as in the case of eqn (8)) but in the difference $(T_i - T)$.

Thus

$$\Delta C_p^{t/s}/R = \sum_{k=1}^m a_k (T_i - T)^{n_k} \quad (10)$$

where n_k can be any nonnegative integer. For $n_1=0$ a_1 is identical with $\Delta C_p^{t/s}/R$ at T_i .

If we put eqn (10) into eqn (7) we obtain the final form of the LeChatelier—Shreder equation

$$\ln a = \frac{\Delta H^t}{R} \left(\frac{1}{T_i} - \frac{1}{T} \right) + \sum_{k=1}^m a_k K_k \quad (11)$$

The terms $a_k K_k$ denote the contributions to $\ln a$ corresponding to powers n_k in eqn (10). K (it is further written without index k) replaces the double integral corresponding to power n

$$K = \int_T^{T_i} \left[\frac{1}{T^2} \int_T^{T_i} (T_i - T)^n dT \right] dT \quad (12)$$

Solving this integral we obtain the following expression for K

$$K = -T_i^n \ln\left(\frac{T_i}{T}\right) + \frac{T^n}{n+1} \left(\frac{T_i}{T} - 1\right) \cdot \sum_{i=1}^{n+1} b_i \left(\frac{T_i}{T}\right)^{n+1-i} \quad (13)$$

where

$$b_i = c_i + \sum_{j=i+1}^{n+1} c_j \quad (\text{for } i=1, b_1=1)$$

and

$$c_i = (-1)^i \binom{n+1}{i} / (i-1) \quad i=2, 3, \dots, n+1$$

We shall briefly describe the procedure for application of the derived relations:

- We calculate the binomial coefficients $\binom{n+1}{i}$ for given n .
- The result is divided by $(i-1)$.
- Alternation of signs gives the coefficients c_i .
- Summation of the coefficients c_i gives the coefficients b_i .
- For given T and T_i , K corresponding to chosen n is calculated according to eqn (13).
- Similar procedure is applied also for other powers.
- $\ln a$ is calculated according to eqn (11).

For a more convenient use of this procedure the coefficients b_i were calculated for n ranging from 0 to 7 and they are presented in Table 1. They correspond to the fractions the denominator of which is for given n the same (it is written in the second column of the table).

Table 1. Values of coefficients b_i in eqn (13) ($b_i = B_i/J$)

| n | J | B_1 | B_2 | B_3 | B_4 | B_5 | B_6 | B_7 | B_8 |
|-----|-------|-------|--------|-------|--------|--------|-------|--------|--------|
| 0 | 1 | 1 | | | | | | | |
| 1 | 1 | 1 | 1 | | | | | | |
| 2 | 2 | 2 | 5 | — | 1 | | | | |
| 3 | 6 | 6 | 26 | — | 10 | 2 | | | |
| 4 | 24 | 24 | 154 | — | 86 | 34 | — | 6 | |
| 5 | 120 | 120 | 1 044 | — | 756 | 444 | — | 156 | 24 |
| 6 | 720 | 720 | 8 028 | — | 7 092 | 5 508 | — | 2 892 | 888 |
| 7 | 5 040 | 5 040 | 69 264 | — | 71 856 | 69 264 | — | 48 336 | 22 224 |
| | | | | | | | | —6 000 | 720 |

As an example of application of the relation (13) we present the simplest case of temperature dependence of ΔC_p , viz. ΔC_p is constant ($n_1=0$). Then

$$K_1 = -\ln(T_i/T) + (T_i/T - 1)$$

For $n_2 = 1$ the relation (13) leads to the expression

$$K_2 = -T_i \ln(T_i/T) + T_i/2 \cdot (T_i/T - 1) \cdot (T_i/T + 1)$$

Therefore if ΔC_p is a linear function of temperature,

$$\Delta C_p = a_1 + a_2(T_i - T)$$

and then

$$\ln a = \Delta H_f/R(1/T_i - 1/T) + a_1 K_1 + a_2 K_2$$

Sometimes the temperature dependence of ΔC_p is not given by a functional relationship but in the form of table of values. It can happen that we do not wish or cannot approximate these values by a functional relationship. We encountered this in the case of ΔC_p of water [2] where initial steep increase of ΔC_p observed by undercooling changes after exceeding temperature of homogeneous nucleation to decrease of heat capacity. Description of such a dependence of ΔC_p by a continuous functional relationship is rather difficult (the polynomial (10) requires high powers). It seems to be better to solve the integration in eqn (7) not analytically but numerically. For this purpose it is convenient to rearrange eqn (7) in the following way

$$\ln a = \frac{\Delta H_f}{R} \left(\frac{1}{T_i} - \frac{1}{T} \right) + \frac{1}{R} \left\{ \frac{1}{T} \int_T^{T_i} \Delta C_p dT - \int_T^{T_i} \Delta C_p d \ln T \right\} \quad (14)$$

Then we can use one of the methods suitable for calculation of definite integrals (rectangular or trapezoidal or Simpson's rule, etc.). If the data are spaced unequally, we can use a procedure corresponding to the trapezoidal rule

$$K = \left(\sum_{i=0}^n (C_i + C_{i+1}) \cdot (T_i - T_{i+1}) - \sum_{i=0}^n (C_i + C_{i+1}) \cdot \ln(T_i/T_{i+1}) \right) / 2 \quad (15)$$

where K is the value of difference of both integrals in eqn (14) and C_i are the values of ΔC_p at temperatures T_i . Index zero corresponds to melting temperature and the last index (n) to the temperature T (lower integration limit).

Both the methods proposed for calculation of values of integral in the LeChatelier — Shreder equation can be applied to solution of practical problems and they offer special advantages when computers are used.

References

1. Malinovský, M., *Chem. Zvesti* 30, 721 (1976).
2. Horsák, I. and Sláma, I., *Collect. Czech. Chem. Commun.*, in press.

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