Analytical Description Liquidus of the Eutectic Systems

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Abstract
An analytical description of the liquidus in the PbTe –ZnTe system is made. The experimental liquidus temperature on the PbTe side is described by a third degree polynomial, and on the ZnTe side by a fourth degree polynomial:
$T_{(PbTe)}$=1197.00–145.098 N_2 – 426.756 N_2^2,
$T_{(ZnTe)}$= 930.06+1760.86 N_2-2841.39 N_2^2+2765.48 N_2^3-1045.01 N_2^4.
Keywords: Liquidus, Analytical Description, Ternary System.

The analytical description of phase equilibrium lines is a real problem.
1. The phase diagram reflects the nature of phase equilibria, but does not permit without distortion the reproduction of information between users. Graphical representation of phase equilibrium information is rough and insufficiently precise. The geometric form of the phase diagram is only qualitative and demonstrates the nature of phase equilibrium. For calculation purposes, it is necessary to have an analytical equation for the fundamental lines of the phase equilibrium; the liquidus and solidus.
2. The final step of a phase diagram investigation is to make locate the position of the eutectic point co-ordinate. The crystallisation temperature of the eutectic is determined from temperature arrests on cooling curves of alloys that solidify to give the eutectic microstructure. The eutectic composition is determined in an iterative manner, by examining the microstructures of hyper- and hypo-eutectic alloys. In other cases, the eutectic composition can be determined using Tamman's triangle.
Another method of determination of eutectic temperatures consists of using "scientific intuition," extrapolating liquidus lines to their intersection at the eutectic temperature. Such a method of determination of the eutectic composition does not correspond to the scientific requirements of a chemical experiment; therefore the provision of an analytical method is attractive.
3. If an analytical expression of two liquidus lines is known, general solution reveals the binary eutectic co-ordinates. General solution of three liquidus lines reveals the composition and temperature of a ternary eutectic or peritectic. The purpose of this investigation is the substantiation of the analytical description method and the determination of the binary eutectic composition.

In this paper, our previously obtained experimental results are given. Determination of the binary eutectic compositions is achieved by extrapolation of the two liquidus lines to intersection at the eutectic temperature by general solution of the equations: $T_1 = f_1(X_2)$ and $T_2 = f_2(X_2)$. At the eutectic temperature, $f_1(X_2) = f_2(X_2) = T_e$.
An analytical description of the liquidus in the PbTe–ZnTe system investigated earlier [1980Gry] is described in the paper In this system, the eutectic temperature determined by Tamman's triangle is equal to 1160 K and the composition N_{ZnTe} = 0.17 is determined by graphical extrapolation. The experimental liquidus temperature determined by DTA is shown in Table 1.
For approximation and extrapolation of the liquidus, the following polynomial is used:

$$T = a_0 + a_1N_2 + a_2N_2^2 + a_3 N_2^3 + ... \quad (1)$$

The liquidus curve of the PbTe–ZnTe system from the PbTe side is described by a second-degree polynomial. The value of the coefficient is greatly dependant on the selection of the experimental value. For example, if for calculation the following points 1,2,3,4 (Table 1); 1,2,3,4,e (where e-is eutectic co-ordinate) and 1,3,4,e points were used, then the polynomials will have respectively the following values:

$$T_{2\,(PbTe)(1,2,3,4)} = 1197.00\text{-}140.00\,N_2\text{-}400.00\,N_2^2 \quad (2a)$$

$$T_{2\,(PbTe)(1,2,3,4,e)} = 1196.87\text{-}126.449\,N_2\text{-}515.040\,N_2^2 \quad (2b)$$

$$T_{2(PbTe)(1,3,4,e)} = 1196.96\text{-}122.274N_2\text{-}545.463\,N_2^2 \quad (2c)$$

Equations (2a-2c) show, that a set of experimental points from massive, lie on a smooth liquidus line, the polynomial coefficient

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values can change greatly. The polynomial coefficients are very sensitive to liquidus temperature change. Insignificant changes in the co-ordinates of the points lead to tangible changes in values of the polynomial coefficients.

For polynomial (2a), the co-ordinates of eutectic point are not used, and it is thus referred to as an extrapolation, whereas polynomials (2b) and (2c) are referred to as approximations.

It should be noted that on the left and right liquidus branches, two experimental points (component melting temperature and eutectic temperature) with high statistical weights are located. The temperature of these points is determined with high precision compared with the others. But, the approximation polynomial does not strictly intersect this point. The liquidus line from the PbTe side described by equations (2b) and (2c) do not begin at the melting temperature of the pure component (1197 K), but at a lower temperature (1196.96 and 1196.87 K).

In spite of the fact that this temperature deviates only slightly from the measured experimental point, this deviation must be taken into account and the polynomial coefficients must be corrected. Applying a polynomial normalisation procedure to these points, that consists of temperature correction near the eutectic points and matching the a0 coefficient in equation (1) for approximation the left hand liquidus line (with deviation less than ± 0.01 K) in the PbTe–ZnTe system, the following equation may be used:

$$T_{2\,(PbTe)} = 1197.00 - 145.098\,N_2 - 426.756\,N_2^2 \quad (3)$$

The approximation of the liquidus curve of the PbTe–ZnTe system from the ZnTe side using a three to six-degree polynomial leads to the following equations:

$$T_{3\,(ZnTe)} = 996.21 + 1130.61\,N_2 - 870.14\,N_2^2 + 316.93\,N_2^3 \quad (4)$$

$$T_{4\,(ZnTe)} = 928.07 + 1801.99\,N_2 - 2986.40\,N_2^2 + 2950.73\,N_2^3 - 1123.98\,N_2^4 \quad (5)$$

$$T_{5\,(ZnTe)} = 873.81 + 2464.93\,N_2 - 5864.76\,N_2^2 + 8617.89\,N_2^3 - 6275.38\,N_2^4 + 1754.52\,N_2^5 \quad (6)$$

$$T_{6\,(ZnTe)} = 873.02 + 2476.42\,N_2 - 5928.61\,N_2^2 + 8792.48\,N_2^3 - 6525.83\,N_2^4 + 1934.98\,N_2^5 - 51.46\,N_2^6 \quad (7)$$

The liquidus temperatures that are calculated according to these equations are shown in Table 2.

The investigation of the $T_{3\,(ZnTe)}$ approximation polynomial in relation to minima, maxima and inflection points shows, that in the 0.1≤ N2 ≤1 intervals, extremum points are lacking, however at $N_2 = 0.915$ sagging is observed. At this point, the second derivative changes from positive to negative (convex to concave conversion). Also, the third degree polynomial describes the liquidus curve with big deviations from the experimental data.

The fourth and fifth degree approximation polynomials produce a smooth liquidus curve. Based on this criterion, the fourth degree polynomial is selected, as it does not exhibit bending in the 0.1<N<1.0 interval.

As a result, the experimental liquidus temperature from the PbTe side is satisfactorily described by the third degree polynomial, and by a fourth degree polynomial - from ZnTe side. After normalization, the right hand liquidus branch is described by:

$$T_{4\,(ZnTe)} = 930.06 + 1760.86\,N_2 - 2841.39\,N_2^2 + 2765.48\,N_2^3 - 1045.01\,N_2^4 \quad (8)$$

In order to determine the composition of the intersection of the liquidus branches ($T_{2(PbTe)} = T_{4(ZnTe)}$), the temperature that fulfils the following conditions $T_{2(PbTe)} - T_{4(ZnTe)} = 0$ is found. The co-ordinates of the eutectic point, are determined by the crossing of the two curves that are described by extrapolation polynomials (Table 3).

The results presented in Table 3 show that compositions of the eutectic point determined by the experimental method and polynomial extrapolation are in a good agreement. But, polynomial extrapolation gives a higher eutectic temperature. One of the possible causes of this phenomenon is explained by the fact that the interaction is increasing as liquidus line bends downwards.

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[1980Gry] Grytsiv, V.I., Tomashik, V.N., Oleinik, G.S., Tomashik, Z.F., "Investigation of the PbTe-ZnTe System", *Izv. AN SSSR. Neorgan. materialy*, 16 (3), 543-544 (1980)

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Table 1: Experimental Data for Temperature Liquidus of the PbTe–ZnTe System [1980Gry]

N_2	0	0.05	0.10	0.15	0.17	0.20	0.30
Point	1	2	3	4	e	-	-
T, K	1197	1189*	1179	1167	1160	1193	1270
N_2	0.40	0.50	0.60	0.70	0.80	0.90	1.00
T, K	1332	1379	1426	1470	1509**	1543	1571

Note: * extrapolated and ** smoothed experimental values.

Table 2: The Comparison of Experimental Liquidus Temperature with those Calculated Using the Approximation Polynomials with n = 3-6.

$N_{(ZnTe)}$	Polynomial degree n				
	3	4	5	6	Exper.
1.00	1573.6	1570.4	1571.0	1571.0	1571
0.90	1540.0	1544.5	1543.0	1543.0	1543
0.80	1506.1	1508.8	1509.2	1509.2	1509
0.70	1470.0	1468.4	1469.6	1469.6	1470
0.60	1429.8	1425.8	1426.1	1426.1	1426
0.50	1383.6	1381.1	1379.9	1379.9	1379
0.40	1329.5	1331.1	1330.3	1330.3	1332
0.30	1265.6	1270.5	1271.6	1271.6	1270
0.20	1190.1	1190.8	1191.7	1191.7	1193
0.17	1164.8	1161.7	1160.7	1160.7	1160

Table 3: The co-ordinates of the Eutectic Point in the PbTe-ZnTe System, are Determined Using the Extrapolation Polynomial with n = 4-6

	Polynomial degree n (liquidus from ZnTe side)		
	4	5	6
Eutectic composition, N_2	0.167	0.169	0.166
Eutectic temperature, T,K	1162.5	1162.0	1162.8

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