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Thermochimica Acta 297 (1997) 161–168

thermochimica acta

Measurement of the eutectic composition and temperature of energetic materials
Part 3. The TX-phase diagram of ternary system

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Received 1 December 1995

Abstract

A diagram for the dependence of the composition on temperature (TX-phase diagram) for the ternary system has been constructed by calculating from the data of three binary systems on the basis of certain assumptions. Two sets of equations for the liquidus line of the eutectic compositions and temperatures. The TX-phase diagrams, i.e. the temperature dependence on composition, of four ternary systems of the energetic materials, including AK/EDD/NQ, AK/EDD/NTO, Tetryl/PETN/RDX and TNB/Tetryl/PETN, were constructed. It is shown that the errors for the calculation of the eutectic composition and temperature are within ±2.0 mol% and ±2°C respectively. © 1997 Elsevier Science B.V.

Keywords: Ternary system; Energetic material; Eutectic

1. Introduction

Many methods for constructing the phase diagram of a ternary system have been described in the literature [1–8]. However, the calculation of the phase diagram of the ternary system from the thermodynamic data of pure components is more difficult for some energetic materials due to the lack of data, and also the onset of thermal decomposition near their melting point. Equations for calculating ternary phase diagrams of energetic materials from binary phase diagrams have not been published [9–12] either.

In this work, an attempt has been made, so that a diagram for the dependence of the composition on temperature (TX-phase diagram) for the ternary system should be constructed by calculating from the data of three binary systems for some energetic materials. The data of the binary systems are taken from Part 1 of this work [13].

2. Derivation of the equations of the liquidus line of the ternary systems

2.1. List of symbols

- X_i the mole fraction of component i ($i = 1$, 2 and 3), mol%;
- T_i^0 the melting point of pure component i ($i = 1$, 2 and 3), K;
- T_{ij} the liquidus temperature of component i in the binary system consisting of component i and j ($i, j = 1$, 2 and 3, $i \neq j$), K;

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0040-6031/97/$17.00
PII S0040-6031(97)00081-6

ΔH_{ij} the apparent heat of fusion of component i in the binary systems consisting of component i and j ($i, j = 1$, 2 and 3, $i \neq j$), J mol^{-1};
ΔH_i the apparent heat of fusion of component i in the ternary system ($i = 1$, 2 and 3), J mol^{-1};
T_i the liquidus temperature of component i after the liquefaction of another two components in the ternary system ($i = 1$, 2 and 3), K;
R the gas constant = 8.314 J mol^{-1} K^{-1}.

2.2. *The equations of the liquidus line*

2.2.1. *Method 1*

For a binary system of components i and j, we have

$$\ln X_i = \frac{\Delta H_{ij}}{R}\left(\frac{1}{T_i^0} - \frac{1}{T_{ij}}\right) \tag{1}$$

or

$$\ln(1 - X_i) = \frac{\Delta H_{ji}}{R}\left(\frac{1}{T_j^0} - \frac{1}{T_{ji}}\right). \tag{2}$$

Expanding the left side of Eq. (2) into a series and with $X_i \ll 1$, we have

$$X_i \approx A(T_j^0 - T_{ji}), \tag{3}$$

where

$$A = \Delta H_{ji}/R(T_j^0)^2.$$

When evaluating the liquidus temperature of component 1 for the ternary system, other two liquid components are considered as one component, so that the ternary system at this time is considered as binary system, and when $X_3 < X_2$, the apparent heat of fusion of component 1 in the presence of component 2, ΔH_{12}, is assumed to be that in the presence of mixture liquid of components 2 and 3. By differentiating Eq. (1) with respect to T, we obtain:

$$\frac{\mathrm{d}}{\mathrm{d}T}\ln X_1 = \frac{\Delta H_{12}}{RT_1^2} = \frac{B}{T_1^2}, \tag{4}$$

where

$$B = \frac{\Delta H_{12}}{R}.$$

When $X_3 \ll 1$, from Eq. (3) we obtain:

$$X_3 \approx A(T_1^0 - T_1), \tag{5}$$

where

$$A = \frac{\Delta H_{13}}{R(T_1^0)^2}.$$

Substituting Eq. (5) into Eq. (4), we have

$$\frac{1}{Y - A(T_1^0 - T_1)}\frac{\mathrm{d}}{\mathrm{d}T}[Y - A(T_1^0 - T_1)] = \frac{B}{T_1^2}, \tag{6}$$

where

$$Y = 1 - X_2.$$

From Eq. (6), the following equation of the liquidus temperature of the component 1 for the ternary system are obtained, respectively, at $X_3 < X_2$,

$$T_1 = \frac{\Delta H_{12}}{R}[\ln\frac{1 - X_3}{X_1} + \frac{\Delta H_{12}\Delta H_{13}}{RT_1^0(\Delta H_{13} - RT_1^0 X_3)}] \tag{7}$$

and at $X_3 > X_2$,

$$T_1 = \frac{\Delta H_{13}}{R}[\ln\frac{1 - X_2}{X_1} + \frac{\Delta H_{13}\Delta H_{12}}{RT_1^0(\Delta H_{12} - RT_1^0 X_2)}]. \tag{8}$$

Accordingly, two equations relating T_2 and T_3 for components 2 and 3 can also be obtained respectively.

Now, the liquidus temperature of each component of the ternary system can be calculated from the apparent heat of fusion, ΔH_{ij}, of the corresponding binary systems and melting point.

The isothermal liquidus lines of three components in the TX-phase diagram of the ternary system can be constructed by a set of six equations of the type of Eqs. (7) and (8), as shown in Fig. 1. The curves ae, be and ce in Fig. 1 can be constructed from the points at which isothermal liquidus lines of each pair of components intersect. The coordinates and the temperature at the intersecting point e of these three curves are the eutectic compositions and temperature of the ternary system respectively.

The construction of the TX-phase diagram and the calculation of the eutectic compositions and temperature for the ternary system were carried out on a computer.

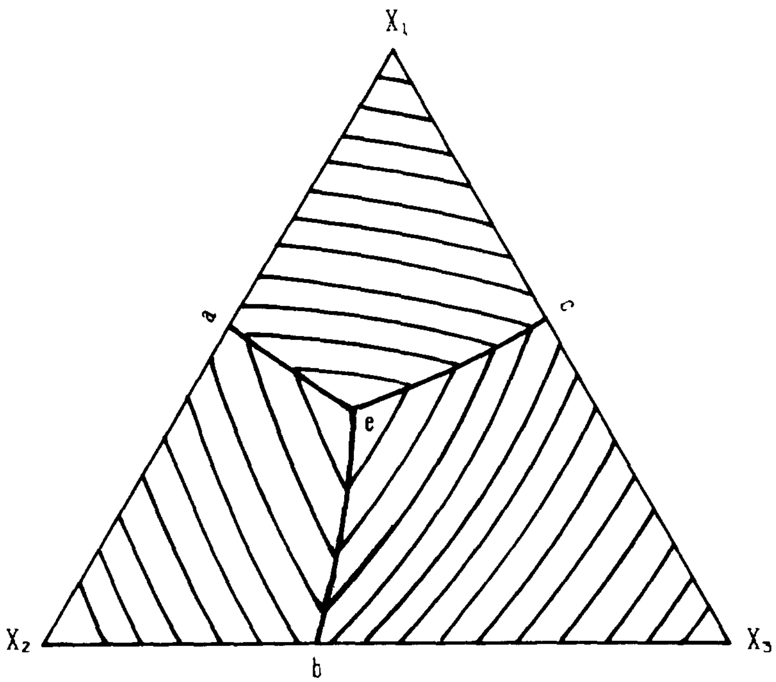

Fig. 1. Schematic diagram of TX method of the ternary system.

2.2.2. Method 2

If the mean apparent heat of fusion of the component *i* obtained from both binary systems, i.e. systems of *i* and *j* and *i* and *k*, on the basis of Eq. (1) may be considered as its apparent heat of fusion in the ternary system of the components *i*, *j* and *k* and as in Method 1. If the liquidus temperature of the component *i* can be calculated in the case of another two components considered as one, then we obtain:

$$\Delta H_i = \frac{X_j}{X_j + X_k}\Delta H_{ij} + \frac{X_k}{X_j + X_k}\Delta H_{ik}. \qquad (9)$$

Substituting Eq. (9) into Eq. (1), we get three equations for the liquidus temperatures:

$$T_i = \frac{T_i^0(X_j\Delta H_{ij} + X_k\Delta H_{ik})}{X_j\Delta H_{ij} + X_k\Delta H_{ik} - RT_i^0(X_j + X_k)\ln X_i}, \qquad (10)$$

where $i, j, k = 1$, 2 and 3, $i \neq j \neq k$.

Thus, the TX-phase diagram of the ternary system can be constructed by a set of Eq. (10), in a similar way to Method 1.

3. Experimental

3.1. Apparatus

A hot stage microscope model Boetius was used to construct the TX-phase diagrams of the binary systems.

3.2. Materials

All samples in this work were obtained from a commercial source. They are 2,4,6-trinitrophenylmethylnitramine (Tetryl), mp. 129.6°C; pentaerythrite tetranitrate (PETN), mp. 141.2°C; cyclotrimethylenetrinitramine (RDX), mp. 204.0°C; 2,4,6-trinitrobenzene (TNB), mp. 121.2°C; ammonium nitrate with 15 wt% potassium nitrate (AK), mp. 159.6°C; ethylenediamine dinitrate (EDD), mp. 188.6°C; nitroguanidine (NQ), mp. 270.5°C (decompn.); 3-nitro-1,2,4-triazol-5-one (NTO), mp. 266.2°C (decompn.).

Table 1
The apparent heat of fusion (ΔH_{ij}) obtained from the TX-phase diagrams of the binary systems and the melting points (T_i^0) of the pure components

Binary system X_1/X_2	T_1^0 °C	T_2^0 °C		ΔH_{12} kJ mol^{-1}	ΔH_{21} kJ mol^{-1}
Tetryl/PETN	129.6	141.1		26.14	59.28
PETN/RDX	141.1	204.1		59.10	50.86
Tetryl/RDX	129.6	204.1		20.54	38.46
TNB/Tetryl	121.2	129.6		17.61	25.02
TNB/PETN	121.2	141.1		17.00	46.76
AK/EDD	159.6	188.6	(EDD_I)	7.93	20.52
		173.2	(EDD_{II})		26.42
EDD/NQ[a]	188.6	270.5		19.47	19.18
AK/NQ[a]	159.6	270.5		10.87	25.07
EDD/NTO	188.6	266.2		19.80	31.70
AK/NTO	159.6	266.2		9.94	44.34

[a]The results for this system are taken from the literature [9].

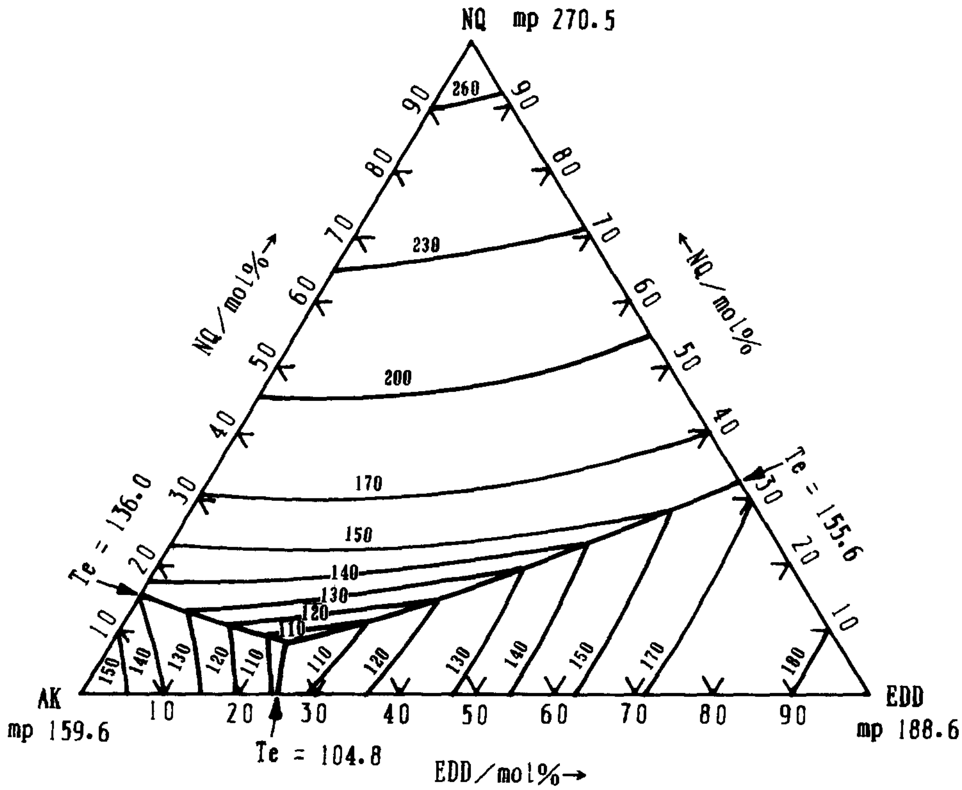

Fig. 2. TX-phase diagram of AK/EDD/NQ.

4. Results and discussion

4.1. The data obtained from the TX-phase diagrams of the binary systems

The apparent heat of fusion ΔH_{ij} of the components, i, in the binary system of i and j and their melting points T_i^0 were obtained from Part 1 of this work[13], shown in Table 1.

4.2. The TX-phase diagrams of the ternary systems from Methods 1 and 2

Using the data in Table 1, the TX-phase diagrams of the AK/EDD/NQ, AK/EDD/NTO, Tetryl/PETN/RDX and TNB/Tetryl/PETN were constructed using Eqs. (7),(8) and (10), respectively. Since the phase diagrams of these ternary systems constructed by the two sets of equations are similar, the phase diagrams constructed by Method 1 are shown in Figs. 2–5. The eutectic compositions and temperatures of these systems were calculated and are listed in Table 2.

In order to compare the data from the TX-method with those in Part 2 of this work [14], this is listed in Table 2. It can be seen from Table 2 that the results of TX Method 1 are in agreement with those of TX Method 2, and these results are also in agreement with those obtained from the HX-method and HPLC or UV analyses or the literature data within ±2.0 mol% for the eutectic compositions and within ±2°C for the eutectic temperatures. Obviously, the TX method in this work is fairly satisfactory for the calculation of the eutectic composition and temperature of the ternary systems.

Since NTO is decomposed in the system of HDD/NTO, its ΔH in the presence of HDD cannot be obtained (see the Part 2 of this work [14]) and thus the ternary phase diagram of AK/HDD/NTO cannot be constructed by the TX-method. Therefore, it is

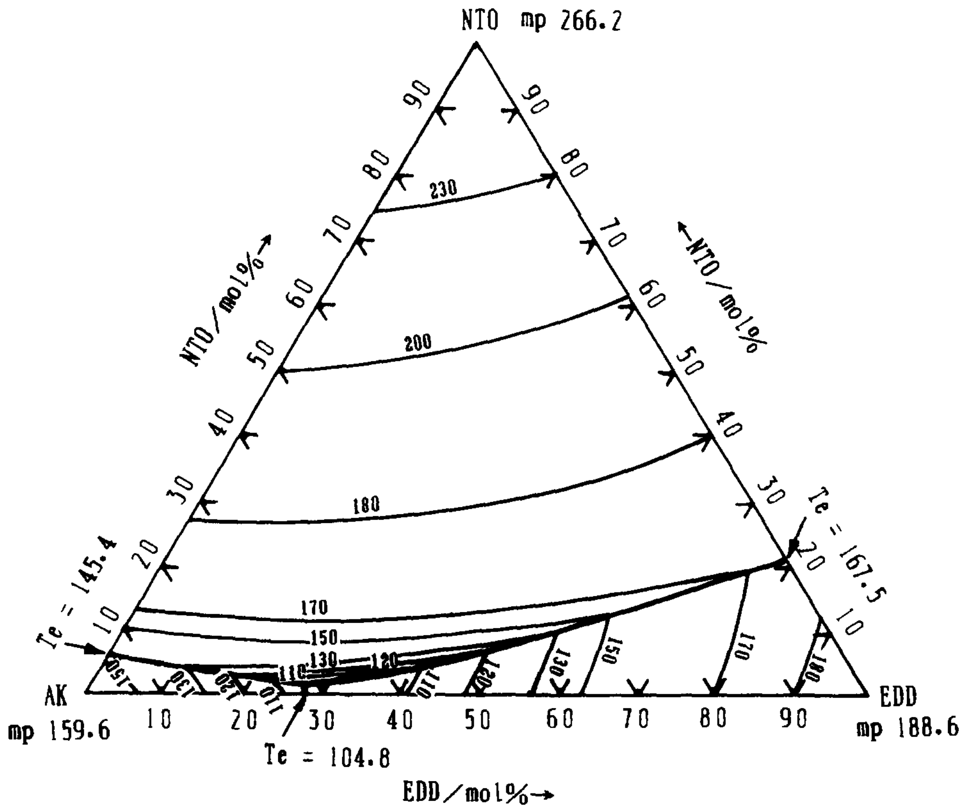

Fig. 3. TX-phase diagram of AK/EDD/NTO.

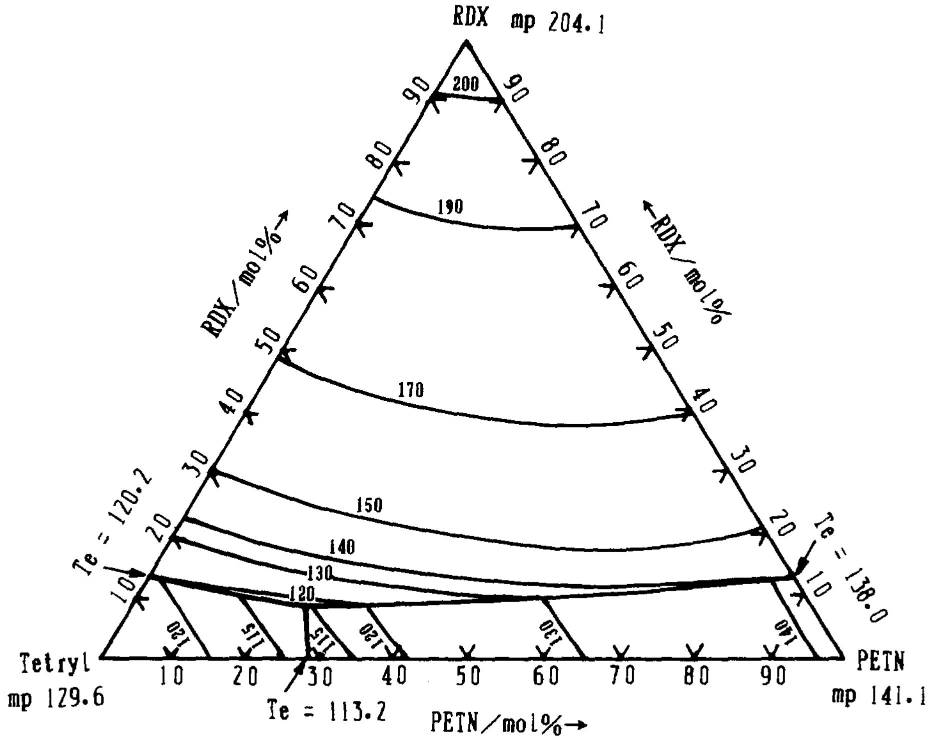

Fig. 4. TX-phase diagram of Tetryl/PETN/RDX.

Table 2
The eutectic compositions X_i (mol%) and temperature T_e (°C) for four ternary systems by the TX-method

System $X_1/X_2/X_3$		Tetryl/PETN/RDX	TNB/Tetryl/PETN	AK/EDD/NQ[a]	AK/EDD/NTO
TX-Method 1	X_1	67.63	55.41	68.28	69.65
	X_2	24.07	35.94	23.72	26.85
	X_3	8.30	8.65	8.00	3.50
	T_e	109.4	81.3	97.9	103.3
TX-Method 2	X_1	67.02	55.39	67.75	70.29
	X_2	24.48	36.46	23.40	26.76
	X_3	8.50	8.15	8.85	2.95
	T_e	109.8	81.9	97.9	103.1
HX-Method	X_1	65.99	56.68	66.94	69.97
	X_2	24.11	34.90	24.78	26.09
	X_3	9.90	8.42	8.28	3.94
DSC Method	T_e	108.3	80.1	98.8	103.5
HPLC or IV analyses[b]	X_1	66.96	57.14	–	–
	X_2	23.29	35.36	–	–
	X_3	9.75	7.50	–	2.97

[a]The eutectic composition and temperature for this system was given in the literature [9] as 67.24/25.30/7.44 mol% and 98.9°C, respectively.
[b]The components X_3 in the system of AK/EDD/NTO was only carried out by UV analysis.

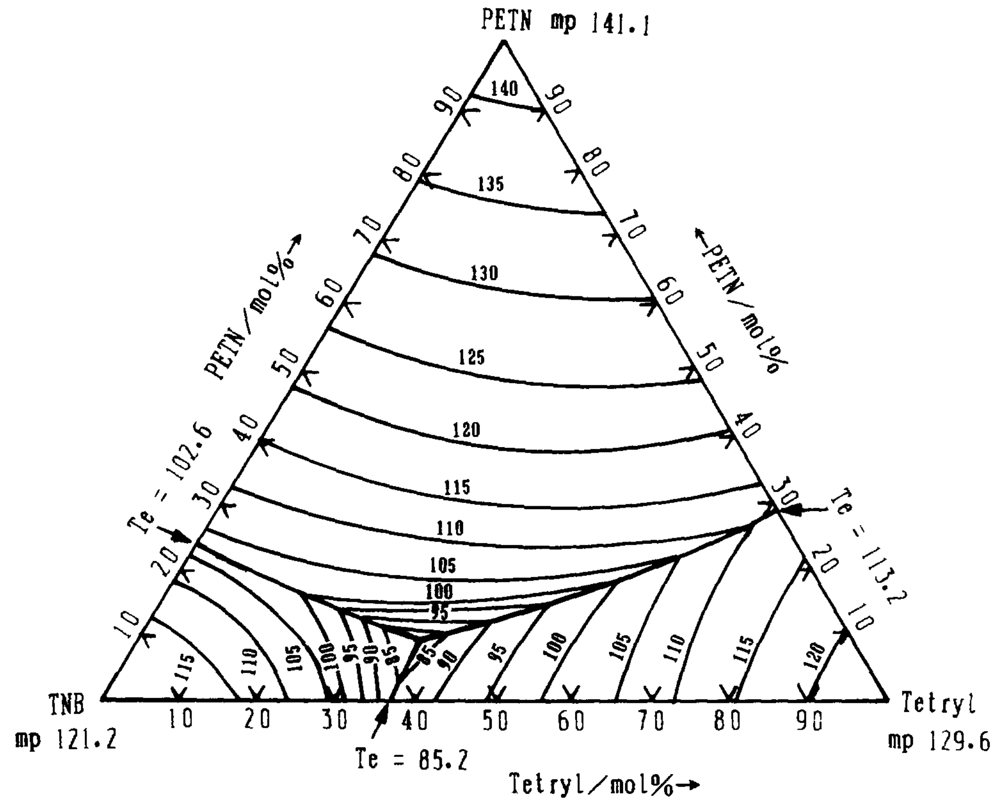

Fig. 5. TX-phase diagram of TNB/Tetryl/PETN.

shown that the TX-method used on the construction of the phase diagram of the energetic materials which decompose on the melting is limitational. However, the HX-method has no difficulty in constructing their HX-phase diagram.

5. Conclusions

1. A diagram for the dependence of the composition on temperature for the ternary systems was constructed by calculating from the data of three binary systems on the basis of certain assumptions. Two sets of equations for the liquidus line of the ternary system were derived and were used to calculate the eutectic compositions and temperatures.
2. These equations can be used to construct the simple ternary phase diagrams of energetic materials. The errors for the calculation of the eutectic composition and temperature are within ±2.0 mol% and ±2°C respectively.

Acknowledgements

The authors express their gratitude to Xi-Mei Guo and Hong-Lin Lu for their assistance to Yun-Qing Gan, Tong Zhao and Zhi-Quan Liu for providing analytic data of HPLC and UV.

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