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## The Dilution/Crystallization Kinetics of RDX and HMX

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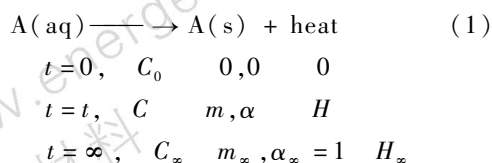
**Abstract:** Three thermokinetic equations describing the crystal growth process and two relationships between the parameters and the constants of the kinetic equations are derived. The thermokinetic data of crystal growth processes of RDX and HMX are treated based on the derived equations and relationships. The results show that the exothermic dilution / crystallization processes of RDX and HMX are the first order reaction and accord with the dislocation theory.

**Key words:** Crystallization kinetics; RDX; HMX; dislocation theory

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In two previous notes<sup>[1,2]</sup>, the crystallization kinetics of RDX and HMX from DMSO and cyclohexanone, and that of HMX from HNO<sub>3</sub> were reported. For exploring the adaptability of the thermokinetic equations to the crystal growth processes of RDX and HMX and obtaining the information about the interdependence between the parameters and the constants of different kinetic equations, three thermokinetic equations describing the crystal growth process are derived. Assuming that in forming the crystal A(s) from A(aq).  $C$  is the solute concentration in the solution at time  $t$  (g/100 g solvent).  $C_{\infty}$  is equilibrium saturation concentration (g/100 g solvent).  $m$  and  $\alpha$  are the mass and fraction of solid deposited during a certain time, respectively.  $H$  is the heat produced during a certain time  $t$ , and when  $t = 0$ ,  $C = C_0$ ,  $m = 0$ ,  $\alpha = 0$  and  $H = 0$ , when  $t = \infty$ ,  $C = C_{\infty}$ ,  $m = m_{\infty}$ ,  $\alpha = \alpha_{\infty} = 1$  and  $H = H_{\infty}$ ,



the relationship between the energy change (i. e. the heat produced) of a reacting system and the extent (i. e.

mass or fraction or concentration) of the reaction (1) may be expressed as

$$\frac{C_0 - C}{C_0 - C_{\infty}} = \frac{0 - m}{0 - m_{\infty}} = \frac{0 - \alpha}{0 - \alpha_{\infty}} = \frac{0 - H}{0 - H_{\infty}} \quad (2)$$

From eq. (2), we obtain

$$\alpha = \frac{H}{H_{\infty}} \quad (3)$$

$$\frac{d\alpha}{dt} = \frac{1}{H_{\infty}} \frac{dH}{dt} \quad (4)$$

$$\frac{dm}{dt} = \left( \frac{m_{\infty}}{H_{\infty}} \right) \frac{dH}{dt} \quad (5)$$

and

$$\frac{C - C_{\infty}}{C_0 - C_{\infty}} = \left( 1 - \frac{H}{H_{\infty}} \right) \quad (6)$$

Inserting eqs. (3) and (4) into the differential kinetic equation (7) of the reaction of the  $n$ th order

$$\frac{d\alpha}{dt} = k (1 - \alpha)^n \quad (7)$$

The thermokinetic equations (8) and (9) are obtained:

$$\frac{dH}{dt} = H_{\infty} k \left( 1 - \frac{H}{H_{\infty}} \right)^n \quad (8)$$

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and

$$\ln \left[ \frac{1}{H_\infty} \left( \frac{dH}{dt} \right)_i \right] = \ln k + n \ln \left[ 1 - \left( \frac{H}{H_\infty} \right)_i \right] \quad (9)$$

$i = 1, 2, \dots, L$

where  $H_\infty$  is the total heat produced (corresponding to the global area under the thermokinetic curve);  $H_i$  is the heat produced in a certain time (corresponding to the partial area under the curve);  $dH_i/dt$  is the rate of heat production at time  $t$ ;  $k$  and  $n$  are the rate constant and reaction order of the crystal growth, respectively.

When  $\ln \left[ \frac{1}{H_\infty} \left( \frac{dH}{dt} \right)_i \right]$  is plotted versus  $\ln \left[ 1 - \left( \frac{H}{H_\infty} \right)_i \right]$  by the least-squares method, this gives the value of  $n$  from the slope and  $k$  from the intercept.

Equation (8) is known as the general form describing the crystal growth process.

According to the Burton-Cabrera-Frank (BCF) dislocation theory<sup>[3]</sup>, for relatively high supersaturations, the rate of crystal growth at time  $t$  ( $dm/dt$ ) may be expressed as

$$\frac{dm}{dt} = km_\infty (C - C_\infty) \quad (10)$$

The combination of eqs. (5), (6) and (10) gives

$$\begin{aligned} \frac{dH}{dt} &= kH_\infty (C_0 - C_\infty) \left( 1 - \frac{H}{H_\infty} \right) \\ &= k_1 \left( 1 - \frac{H}{H_\infty} \right) \end{aligned} \quad (11)$$

where  $k_1 = kH_\infty (C_0 - C_\infty)$  (12)

If  $C_0 \gg C_\infty$ , we have

$$\frac{dH}{dt} = kH_\infty C_0 \left( 1 - \frac{H}{H_\infty} \right) = k_2 \left( 1 - \frac{H}{H_\infty} \right) \quad (13)$$

where  $k_2 = kH_\infty C_0$  (14)

when  $\left( \frac{dH}{dt} \right)_i$  is plotted versus  $1 - \left( \frac{H}{H_\infty} \right)_i$  by the least-squares method, this gives the values of  $k_2$  and  $a$  in the equation (15)

$$\frac{dH}{dt} = k_2 \left( 1 - \frac{H}{H_\infty} \right) + a \quad (15)$$

If equation (10) is written as

$$\frac{dm}{dt} = km_\infty (C - C_\infty) + b \quad (16)$$

The equation (17) is obtained by combining eqs. (5), (6) and (16)

$$\frac{dH}{dt} = \frac{dm}{dt} \left( \frac{H_\infty}{m_\infty} \right) = \frac{H_\infty}{m_\infty} [ km_\infty (C - C_\infty) + b ]$$

$$= \frac{H_\infty}{m_\infty} \left[ km_\infty (C_0 - C_\infty) \left( 1 - \frac{H}{H_\infty} \right) + b \right]$$

$$= H_\infty k (C_0 - C_\infty) \left( 1 - \frac{H}{H_\infty} \right) + \frac{bH_\infty}{m_\infty}$$

$$= H_\infty k C_0 \left( 1 - \frac{H}{H_\infty} \right) + \frac{bH_\infty}{m_\infty} \quad (C_0 \gg C_\infty) \quad (17)$$

Comparing eq. (15) with eq. (17), two relationships [eqs. (18) and (19)] are obtained

$$k = \frac{k_2}{H_\infty C_0} \quad (18)$$

and

$$b = \frac{am_\infty}{H_\infty} \quad (19)$$

Equations (18) and (19) relate  $k$  to  $k_2$  and  $b$  to  $a$ , respectively.

If the values of the constants  $a$  and  $b$  are small in comparison with those of  $k_2$  and  $k$ , the kinetics of the crystal growth processes can be expressed by eqs. (10) and (13).

Equations (10) and (13) are known as the thermokinetic equations of the crystal growth process.

Equation (13) is only an especial example ( $n = 1$ ) of equation (8).

To verify the reliability of eqs. (8), (15) and (16) and obtain information about the kinetic parameters and the constants of RDX and HMX, the original thermokinetic data tabulated in Table 1 are fitted to the eqs. (8), (15) and (16) by the linear least-squares method. Results obtained, including the total heat produced, the reaction order ( $n$ ), the rate constants ( $k_2$  and  $k$ ) during the crystallization of RDX and HMX from DMSO and cyclohexanone at 30 °C and that of HMX from HNO<sub>3</sub> at 34 °C, and the constants ( $a$  and  $b$ ) in eqs. (15) and (16), are shown in Table 2.

Table 1 Thermokinetic data of the crystal growth processes of RDX and HMX

Experimental conditions No. 1					Experimental conditions No. 2				
Temp.	Solute	Solvent	Seed	Diluent	Temp.	Solute	Solvent	Seed	Diluent
30 °C	RDX	DMSO	-	50.1% DMSO-H <sub>2</sub> O	30 °C	RDX	DMSO	RDX	50.1% DMSO-H <sub>2</sub> O
	(0.0084 g)	(0.0250 g)		(0.6896 g)		(0.0084 g)	(0.0250 g)	(0.4000 g)	(0.6896 g)
	<i>t/s</i>	$(dH/dt)_i \cdot 10^4 / J \cdot s^{-1}$		$(H_i)_i \cdot 10^2 / J$		<i>t/s</i>	$(dH/dt)_i \cdot 10^4 / J \cdot s^{-1}$		$(H_i)_i \cdot 10^2 / J$
	210		6.962	3.180		210		10.77	9.623
	240		6.648	5.146		240		9.477	12.18
	270		6.766	7.113		270		8.895	14.73
	300		6.171	9.079		300		8.171	17.07
	330		5.862	10.84		330		7.447	19.25
	360		5.552	12.80		360		6.866	21.21
	390		5.381	14.56		390		6.284	23.01
	420		5.071	16.15		420		5.703	24.64
	450		4.761	17.70		450		5.263	26.44
	480		4.452	19.25		480		4.824	27.87
	510		4.427	20.46		510		4.527	28.91
	540		4.117	21.63		540		4.088	30.12
	570		4.092	23.01		570		3.648	31.17
	600		3.778	23.97		600		3.756	32.22
	630		3.469	25.14		630		3.201	33.10
	660		3.159	26.32		660		2.761	34.10
	690		3.418	27.28		690		2.749	34.94
	720		2.966	28.24		720		2.456	35.73
	750		2.941	29.20		750		2.301	36.25
	780		2.632	30.00		780		2.004	36.90
	810		2.460	30.75		810		1.854	37.36
	840		2.435	31.50		840		1.699	38.03
	∞		0	43.85		∞		0	44.39

Experimental conditions No. 3				Experimental conditions No. 4					
Temp.	Solute	Solvent	Seed	Diluent	Temp.	Solute	Solvent	Seed	Diluent
30 °C	HMX	cyclohexanon	HMX	<i>n</i> -C <sub>7</sub> H <sub>16</sub> /CCl <sub>4</sub> (1:1)	34 °C	HMX	HNO <sub>3</sub>	-	H <sub>2</sub> O
	(0.0022 g)	(0.1000 g)	(0.4771 g)	(0.9555 g)		(0.3648 g)	(2.8685 g)		(0.7910 g)
	<i>t/s</i>		$(dH/dt)_i \cdot 10^5 / J \cdot s^{-1}$	$(H_i)_i \cdot 10^2 / J$		<i>t/min</i>		$(dH/dt)_i / J \cdot \text{min}^{-1}$	$(H_i)_i / J$
	210		111.2	22.72		1.25		21.42	3.473
	240		92.59	26.53		1.50		22.51	8.828
	270		79.71	30.21		1.75		23.05	14.39
	300		71.13	33.30		2.00		20.00	19.20
	330		61.13	35.86		2.25		20.59	25.06
	360		53.97	38.03		2.50		17.07	29.29
	390		42.51	40.04		2.75		15.02	33.05
	420		36.78	41.84		3.00		14.27	37.11
	450		32.47	43.10		5.50		7.322	71.55
	480		23.89	44.35		6.50		5.439	77.7
	510		21.00	45.27		7.50		4.812	83.76
	540		16.74	46.32		8.50		3.515	87.86
	570		12.43	46.65		10.5		2.761	94.98
	600		10.96	47.74		12.5		1.506	99.12
	630		6.653	48.24		14.5		1.172	102.4
	∞		0	50.08		∞		0	106.7

Table 1 (Continued)

Experimental conditions No. 5					Experimental conditions No. 5				
Temp.	Solute	Solvent	Seed	Diluent	Temp.	Solute	Solvent	Seed	Diluent
34 °C	HMX	HNO <sub>3</sub>	HMX	H <sub>2</sub> O	34 °C	HMX	HNO <sub>3</sub>	HMX	H <sub>2</sub> O
	(0.3684 g)	(2.8685 g)	(0.2089 g)	(0.7910 g)		(0.3684 g)	(2.8685 g)	(0.2089 g)	(0.7910 g)
<i>t</i> /min	(dH/dt) <sub>i</sub> /J · min <sup>-1</sup>		(H <sub>i</sub> ) <sub>i</sub> /J	<i>t</i> /min	(dH/dt) <sub>i</sub> /J · min <sup>-1</sup>		(H <sub>i</sub> ) <sub>i</sub> /J		
1.00	44.56		13.43	5.50	4.226		77.07		
1.25	34.18		23.35	7.50	3.096		83.76		
1.50	25.48		30.46	9.50	2.050		87.74		
1.75	21.21		36.57	12.5	0.627		92.76		
2.00	18.70		40.96	∞	0		96.55		
2.75	12.89		53.39						

Table 2 Total heat produced and crystal growth kinetics of RDX and HMX

<i>T</i> /°C	<i>H</i> <sub>∞</sub> /J · g <sup>-1</sup>	$\frac{dH}{dt} = H_{\infty} k \left(1 - \frac{H}{H_{\infty}}\right)^n$			$\frac{dH}{dt} = k_2 \left(1 - \frac{H}{H_{\infty}}\right) + a$			$\frac{dm}{dt} = k m_{\infty} (C - C_{\infty}) + b$	
		<i>k</i> · 10 <sup>3</sup> /s <sup>-1</sup>	<i>n</i>	<i>r</i>	<i>k</i> <sub>2</sub> · 10 <sup>4</sup> /J · s <sup>-1</sup>	<i>a</i> · 10 <sup>5</sup> /J · s <sup>-1</sup>	<i>r</i>	<i>k</i> · 10 <sup>3</sup> /s <sup>-1</sup>	<i>b</i> · 10 <sup>6</sup> /g · s <sup>-1</sup>
30	52.2	1.75	0.906	0.996	7.21	4.59	0.996	1.39	0.879
30	52.8	3.10	1.01	0.999	13.7	-2.86	0.999	2.63	-0.542
30	227	4.23	1.00	0.996	20.1	1.89	0.998	19.5	0.083
34	270	3.63	0.996	0.994	4097	-757	0.990	0.41	-28.0
34	253	7.45	1.33	0.995	7950	-7267	0.964	0.788	-287

From Table 2, the following observations can be made:

(1) The crystal growth processes of RDX and HMX are exothermic. The exothermic process may be expressed by the isothermal differential kinetic equation (8).

(2) The dilution / crystallization reactions of RDX and HMX under the studied conditions are found to be of the first order.

(3) BCF model [eq. (13)] is only an especial example (*n* = 1) of the general form [eq. (8)] of the crystal growth process.

(4) Because *n* ≈ 1 in [eq. (8)], *k*<sub>2</sub> ≫ *a* in [eq. (15)] and *k* ≫ *b* in [eq. (16)], describing the kinetics of the crystal growth processes of RDX and HMX by the eqs. (15) and (16) are tenable. This indicates that the crystal growth processes of RDX and HMX from DMSO and cyclohexanone and that of HMX from HNO<sub>3</sub> accords

with the BCF dislocation theory.

(5) With the addition of seed crystals of RDX and HMX, the value of *k* is larger than that of *k* without seeds. This shows that the total number of nuclei in the seeded solution is greater than that in unseeded solution.

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