Thermodynamic Re-assessment of the Mn-C System

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Content

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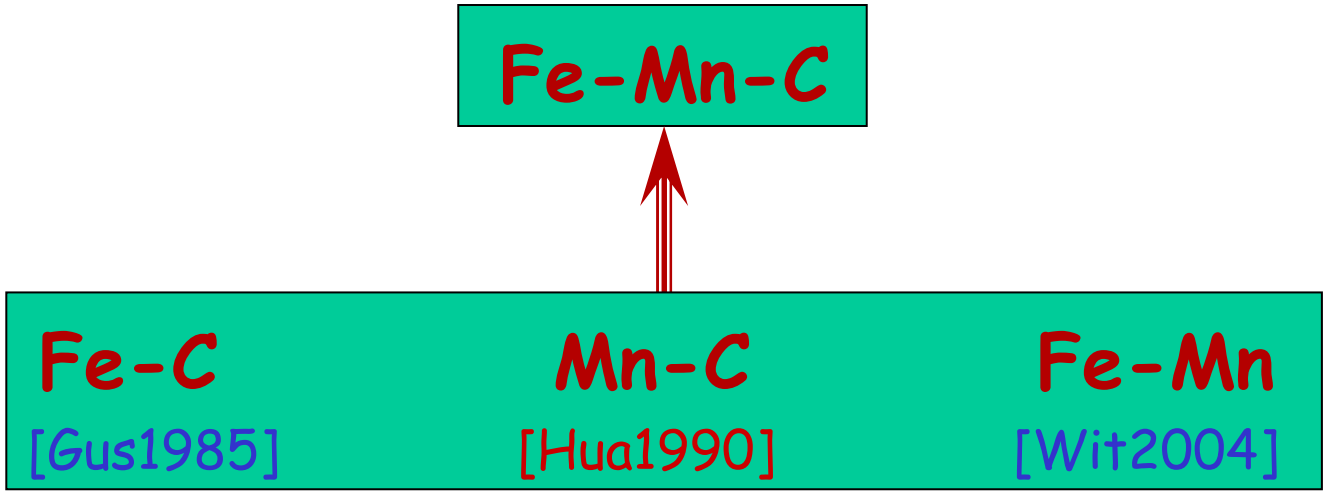
1. Aim of investigations

To provide a thermodynamic description of the Fe-Mn-C system which is as accurate and reliable as possible, especially at low temperatures.



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2. Previous assessment

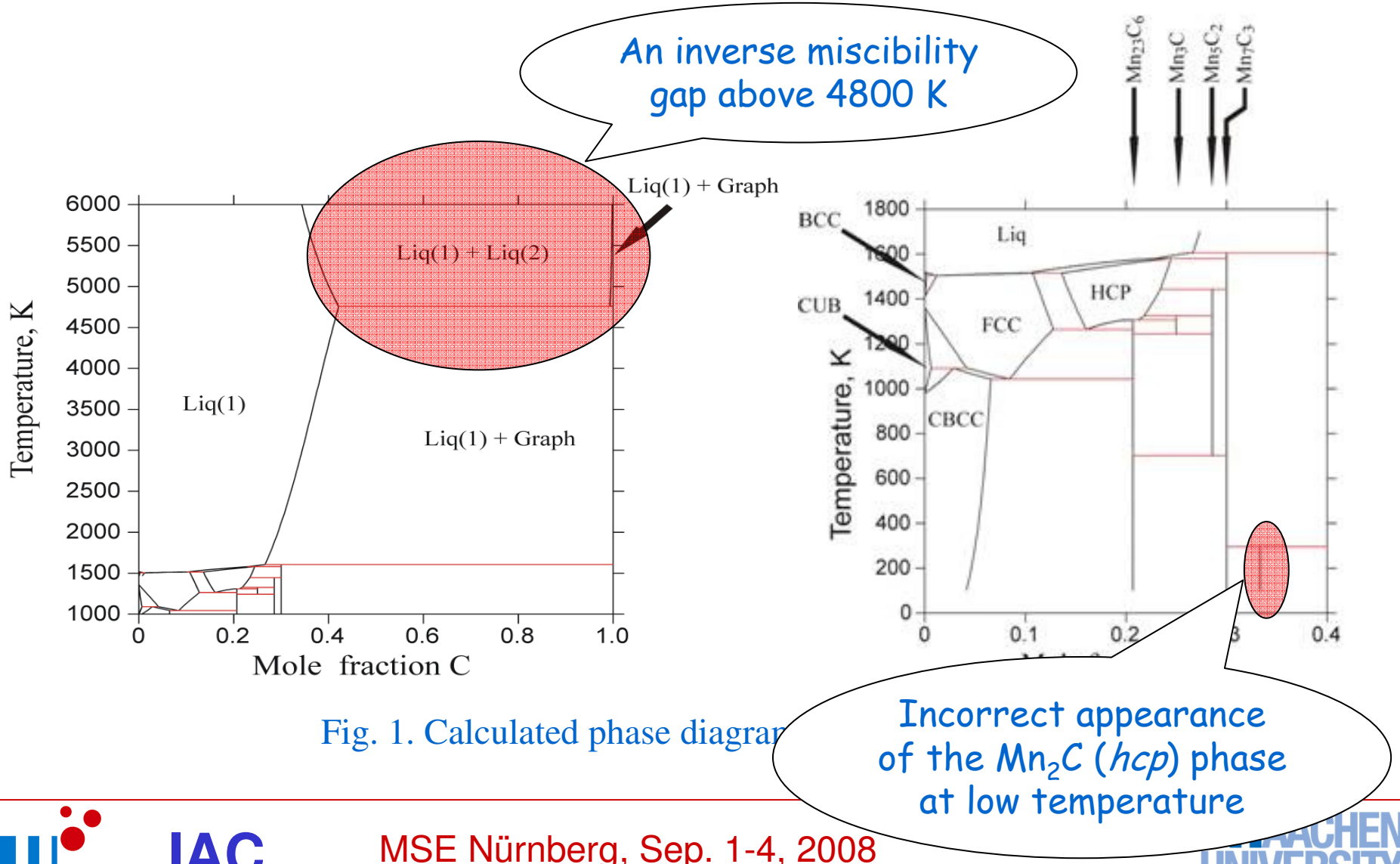

Fig. 1. Calculated phase diagram

3. Thermodynamic modeling

a. Solid Solution Phases

The carbon solution in manganese is described by interstitial solution models with one sublattice occupied by manganese atoms and the other one occupied by the both carbon and vacancies.

CBCC	$(Mn)_1(C,Va)_1$
CUB	$(Mn)_1(C,Va)_1$
FCC	$(Mn)_1(C,Va)_1$
HCP	$(Mn)_1(C,Va)_{0.5}$
BCC	$(Mn)_1(C,Va)_3$

b. Stoichiometric Phases

$Mn_{23}C_6$, Mn_3C, Mn_5C_2 and Mn_7C_3

$$\Delta^\circ G(Mn_nC_m, T) = a + b\,T + \Delta c_p(Mn_nC_m, T)$$

$$\Delta c_p(Mn_nC_m, T) = 0$$ (The Neumann-Kopp rule)

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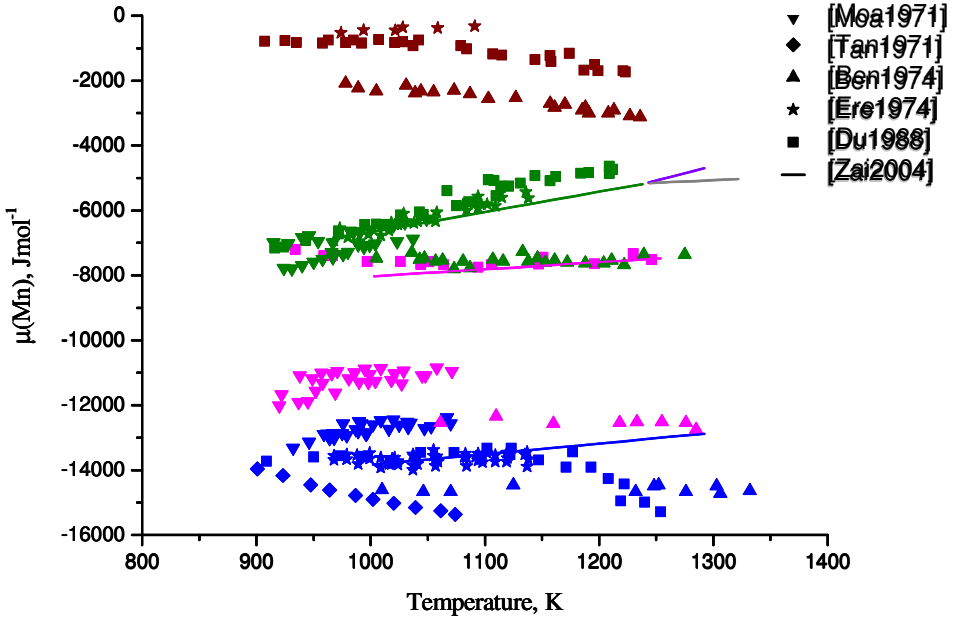

$Mn_{23}C_6/Mn$

$Mn_{23}C_6/Mn_3C$

Mn_5C_2/Mn_3C

$Mn_{23}C_6/Mn_5C_2$

Mn_5C_2/Mn_7C_3

Mn_7C_3/Graphite

Fig. 2. Experimental data on the chemical potential of Mn in various phase equilibria

b. Stoichiometric Phases

Metastable end-members Mn_2C (hcp) and MnC (fcc)

$$\Delta^\circ G(Mn_nC_m, T) = a + b\,T + \Delta c_p(Mn_nC_m, T)$$

$\Delta c_p(Mn_nC_m, T) = 0$ (The Neumann-Kopp rule)

4. Results

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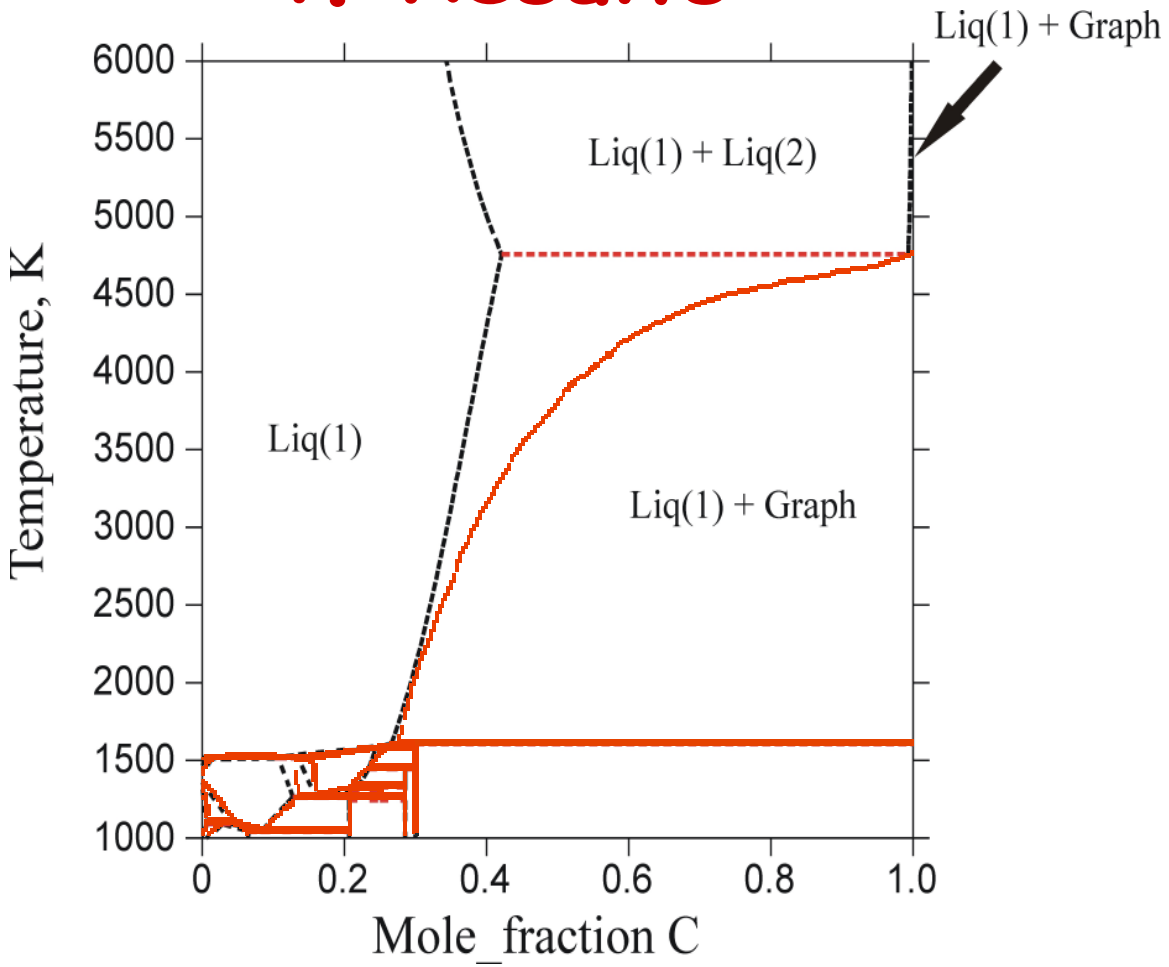

Calculated phase diagram of the Mn-C system

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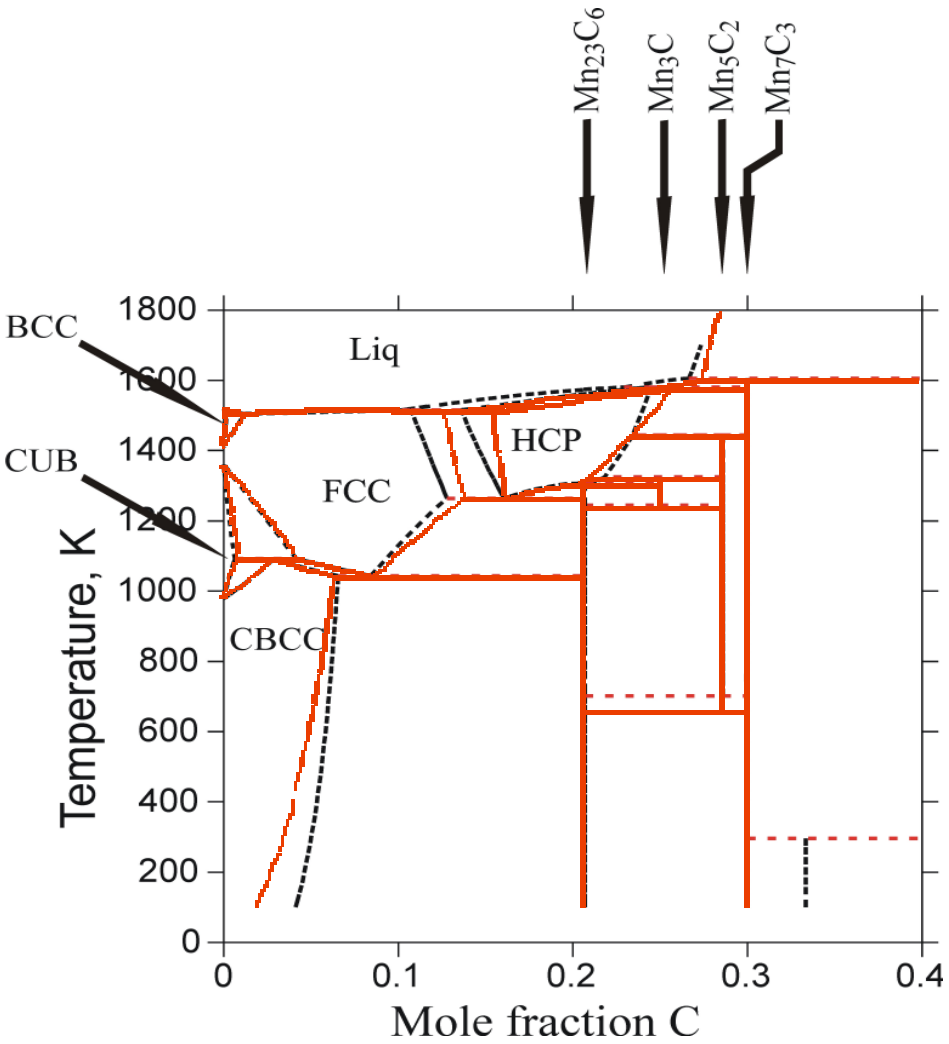
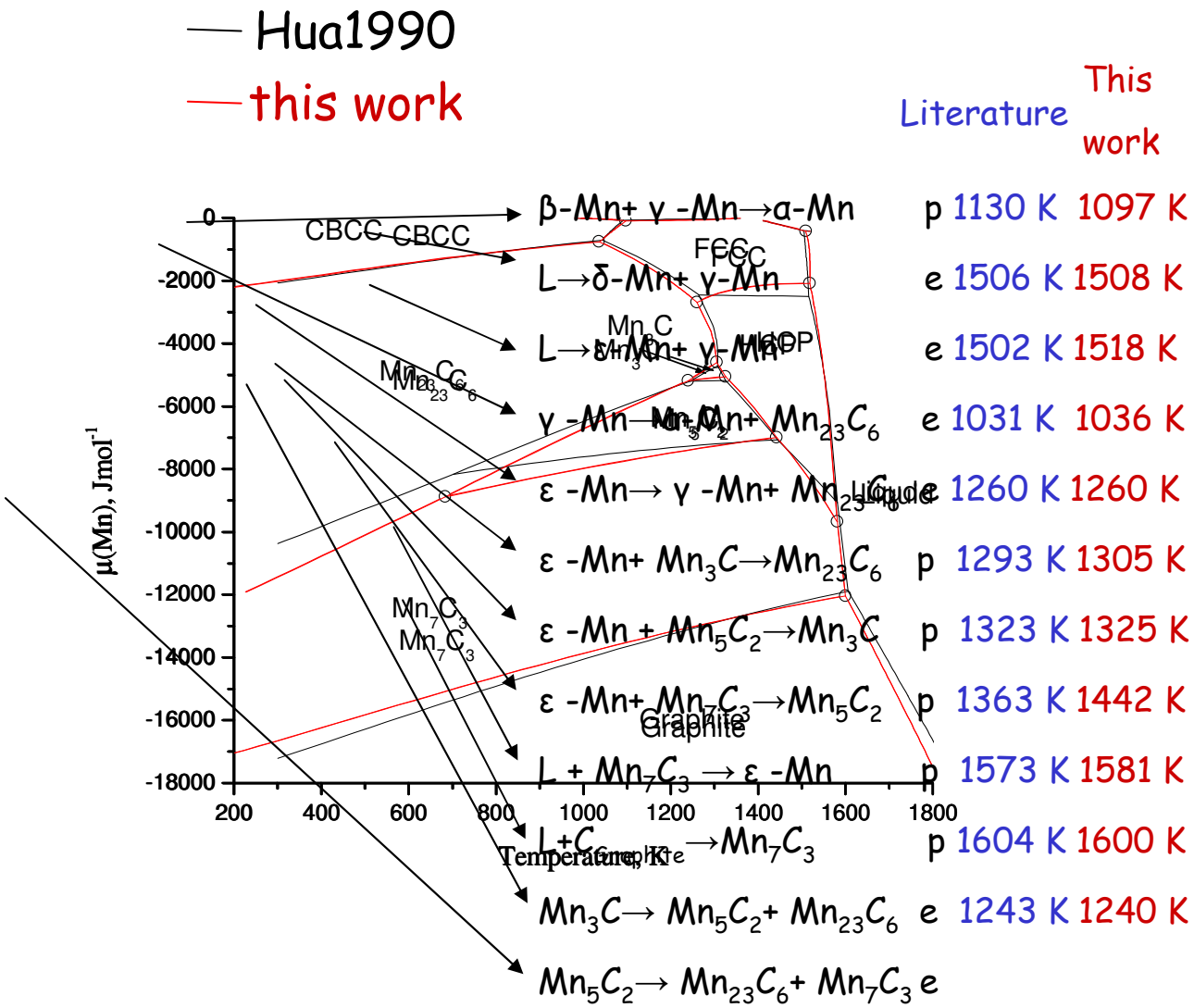


Calculated phase diagram of the Mn-C system



	Literature	This work
β-Mn+ γ -Mn→α-Mn	p 1130 K	1097 K
L→δ-Mn+ γ-Mn	e 1506 K	1508 K
L→ε-Mn+ γ-Mn	e 1502 K	1518 K
γ -Mn→ Mn5C2+ $Mn_{23}C_6$	e 1031 K	1036 K
ε -Mn→ γ -Mn+ $Mn_{23}C_6$	e 1260 K	1260 K
ε -Mn+ Mn_3C→$Mn_{23}C_6$	p 1293 K	1305 K
ε -Mn + Mn_5C_2→Mn_3C	p 1323 K	1325 K
ε -Mn+ Mn_7C_3→Mn_5C_2	p 1363 K	1442 K
L + Mn_7C_3 → ε -Mn	p 1573 K	1581 K
L+C→Mn_7C_3	p 1604 K	1600 K
Mn_3C→ Mn_5C_2+ $Mn_{23}C_6$	e 1243 K	1240 K
Mn_5C_2→ $Mn_{23}C_6$+ Mn_7C_3	e	

Calculated chemical potential of Mn in various phase equilibria

Enthalpies of formation of binary manganese carbides

	$\Delta_f H°_{298}$ (J/mol of atoms)			
	Selected experiment values	Ab initio (T=0K)	Previous assessment	Present work
MnC		27971	251	0
Mn_2C		-3858	-11128	-6000
Mn_7C_3	-10677[1] -9100[2]	-6944	-11176	-10669
Mn_5C_2	-10567[1] -8900[2]	-6476	-10978	-10565
Mn_3C	-9918[1]	-6993	-10094	-9911
$Mn_{23}C_6$	-10716[1] -8465[3]	-8381	-10622	-10706

[1] The effusion method-A. I. Zaitsev et al., Dokl. Phys. Chem, 395 (2004) 94
[2] High-temperature reaction calorimetry-S. V. Meschel et al., J. Alloys. Compd., 257 (1997) 227
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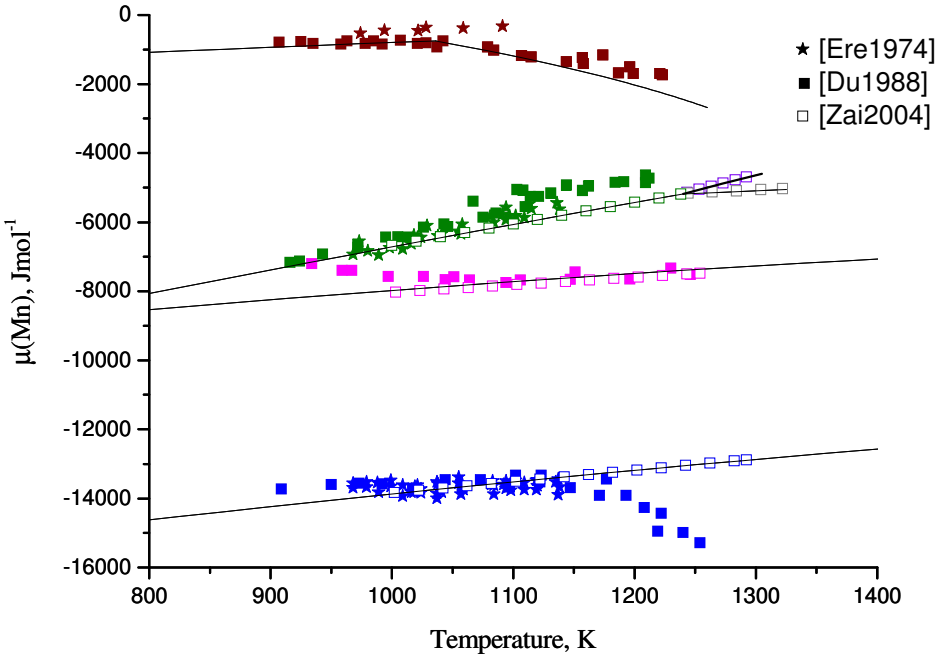
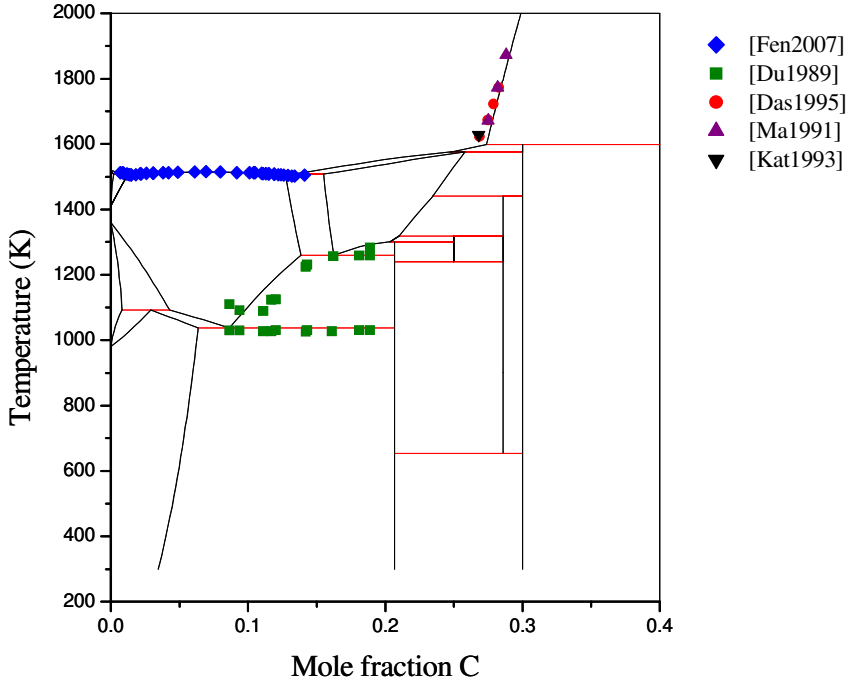


Calculated chemical potential of Mn in various phase equilibria compared with experimental data



Calculated phase diagram of the Mn-C system compared with experimental data

V.N. Eremenko et al., *Tugo plavkie Karbidy* (Russ.), G.V. Samsonov, ed., "Naukova Dumka", Kiev, Ukr. SSR, 1970, 204
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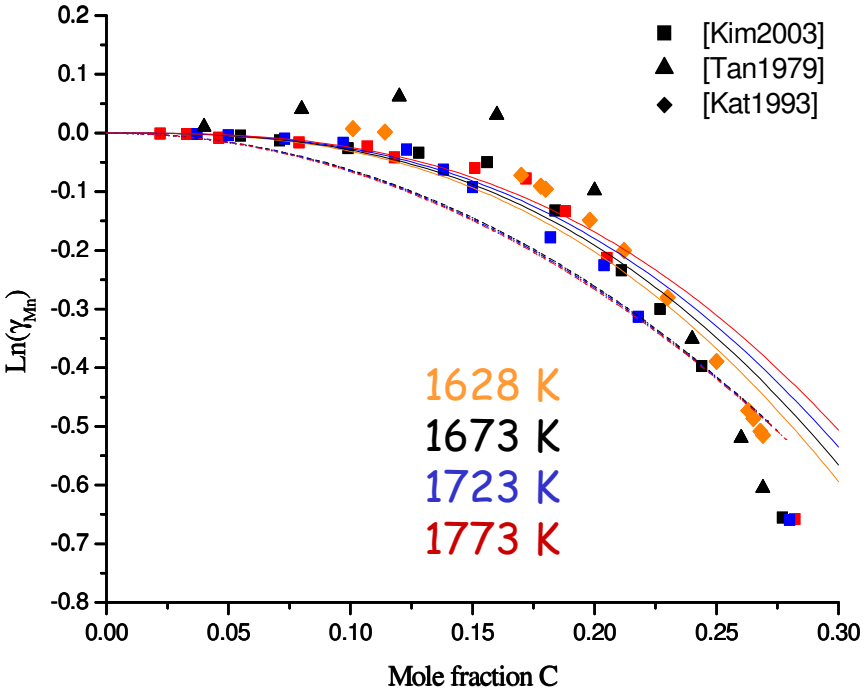

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Activity coefficients of manganese in Mn-C melts

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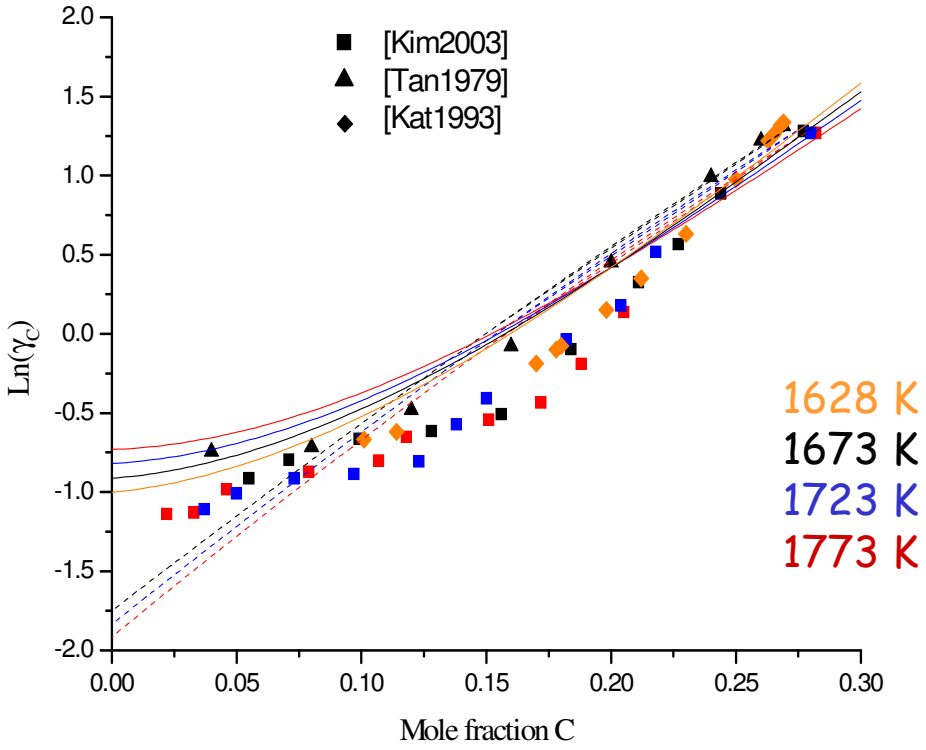

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Activity coefficients of carbon in Mn-C melts

5. Conclusion

The thermodynamic description of Mn-C system has been updated in following ways:

- The Gibbs functions of the stable manganese carbides have been evaluated using recently published data of Zaitsev et al.
- The Gibbs function of the metastable Mn_2C has been evaluated using enthalpy of formation obtained by ab initio calculation.
- New experimental data on the position of the liquidus line and the activity of manganese and carbon in the Mn-C melts have been used for optimization of liquid phase.

The reevaluation of the phase equilibria and thermodynamic functions gives new thermodynamic description without the weaknesses of the previous one.

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