Criteria for Equilibrium

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Criteria for Phase Equilibrium

- **Assume at the beginning that we know nothing about the conditions under which two phases can be in equilibrium.**
- **The only things we know from the Second Law are the criteria for equilibrium under certain conditions. That is,**

$$dS_{E,V} \geq 0, \quad dG_{T,P} \leq 0$$

- **That is: the entropy seeks a maximum, Gibbs free energy seeks a minimum**

Criteria for Phase Equilibrium

- **Consider a multiphase multicomponent system.**
  - **Each phase comprises a different subsystem.**
  - **Repartitionings of extensive variables can be accomplished by shuffling portions of the extensive variables between the different phases,**

$$E = \sum_{\alpha=1}^{\upsilon} E^{(\alpha)}$$

- **Repartitioning of the energy would correspond to changing the $E(\alpha)$'s but keeping the total fixed.**

Criteria for Phase Equilibrium

- **We have**

$$S = \sum_{\alpha=1}^{\upsilon} S^{(\alpha)}$$

$$V = \sum_{\alpha=1}^{\upsilon} V^{(\alpha)}$$

$$n_i = \sum_{\alpha=1}^{\upsilon} n_i^{(\alpha)}$$

- **where** $n_i^{(\alpha)}$ **is the number of moles of species** ***i*** **in phase** α**.**

Criteria for Phase Equilibrium

- **Form the definition of δ *E* as the first-order variational displacement of *E*,**

$$\delta E = \sum_{\alpha=1}^{v} \left[T^{(\alpha)} \delta S^{(\alpha)} - p^{(\alpha)} \delta V^{(\alpha)} + \sum_{i}^{r} \mu_i^{(\alpha)} \delta n_i^{(\alpha)} \right]$$

v **different phases,** r **different species**

- **From the Second Law, at the equilibrium, *E* must be it's minimum, therefore, any deviation must** $\left(\delta E\right)_{S,V,n_i} \geq 0$

Criteria for Phase Equilibrium

- **Consider repartition** $S^{(\alpha)}, V^{(\alpha)}, n_i^{(\alpha)}$ **processes, while keeping the total *S*, *V*, n_i fixed.**
- **Which requires**

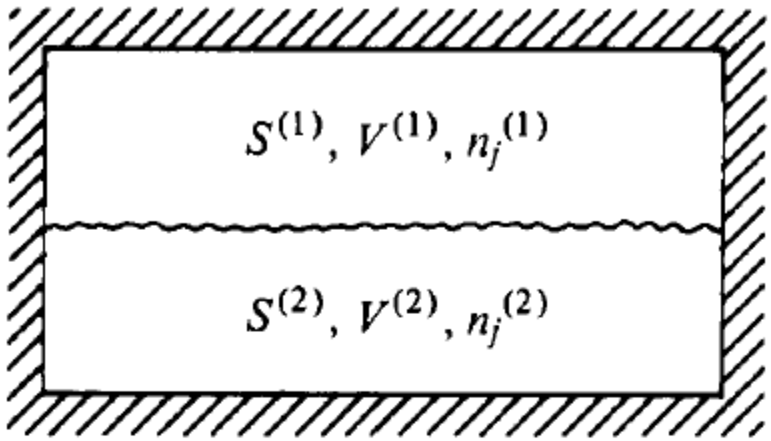
$$\sum_{\alpha=1}^{\upsilon} \delta S^{(\alpha)} = 0$$

$$\sum_{\alpha=1}^{\upsilon} \delta V^{(\alpha)} = 0$$

$$\sum_{\alpha=1}^{\upsilon} \delta n_i^{(\alpha)} = 0 \quad \text{for } i = 1,2,\ldots,r$$

Criteria for Phase Equilibrium

- **Consider a two-phase system**



$$\delta S^{(1)} = -\delta S^{(2)}$$
$$\delta V^{(1)} = -\delta V^{(2)}$$
$$\delta n_j^{(1)} = -\delta n_j^{(2)}$$

A two-phase system

Criteria for Phase Equilibrium

- **The consistency of *S*, *V*, n_i corresponds to**

$$\delta S^{(1)} = -\delta S^{(2)}$$

$$\delta V^{(1)} = -\delta V^{(2)}$$

$$\delta n_1^{(1)} = -\delta n_1^{(2)}$$

$$\delta n_2^{(1)} = -\delta n_2^{(2)}$$

$$\vdots \qquad \vdots$$

$$\delta n_r^{(1)} = -\delta n_r^{(2)}$$

Criteria for Phase Equilibrium

- **Therefore, the first order displacement of *E* at constant *S*, *V*, n_i is,**

$$0 \le \left(\delta E\right)_{S,V,n_i} = \left(T^{(1)} - T^{(2)}\right)\delta S^{(1)} - \left(p^{(1)} - p^{(2)}\right)\delta V^{(1)}$$

$$+\sum_{i=1}^{r}\left(\mu_i^{(1)} - \mu_i^{2}\right)\delta n_i^{(1)}$$

- **Since these variables are independent and their variations are uncoupled, the only solution to the** $\left(\delta E\right)_{S,V,n_i} \ge 0$

Criteria for Phase Equilibrium

which will guarantees $\left(\delta E\right)_{S,V,n_i} = 0$ **is**

$$T^{(1)} = T^{(2)}$$

$$p^{(1)} = p^{(2)}$$

$$\mu_i^{(1)} = \mu_i^{(2)}, \quad i = 1,2,\ldots,r$$

- **For multiphase,**

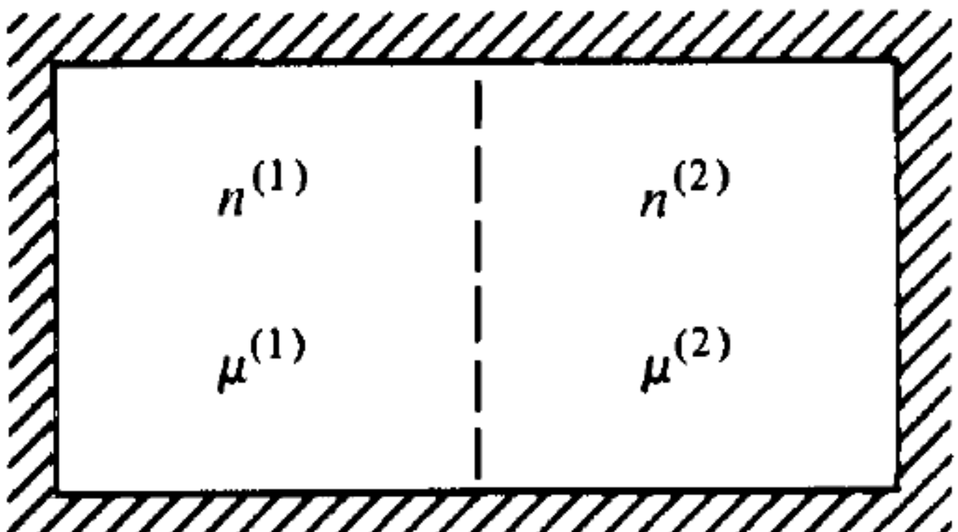
$$T^{(1)} = T^{(2)} = \cdots, = T^{(v)}$$

$$p^{(1)} = p^{(2)} = \cdots, = p^{(v)}$$

$$\mu_i^{(1)} = \mu_i^{(2)} = \cdots, = \mu_i^{(v)}, \quad i = 1,2,\ldots,r$$

Further Discuss

- **Since $\mu^{(1)} = \mu^{(2)}$ guarantees mass equilibrium, it is interesting to study what action a gradient in μ produces.**



Composite system.

Further Discuss

- **Consider the system is prepared initially with $\mu^{(1)} > \mu^{(2)}$, Mass flow will bring it to equilibrium with $\mu^{(1)}_{final} = \mu^{(2)}_{final}$. If no work is done on the total system and there is no heat flow into and out the system, $\Delta S > 0$.**
- **Recall**

$$\delta E = \sum_{\alpha=1}^{v} \left[T^{(\alpha)} \delta S^{(\alpha)} - p^{(\alpha)} \delta V^{(\alpha)} + \sum_{i}^{r} \mu_i^{(\alpha)} \delta n_i^{(\alpha)} \right]$$

Further Discuss

- **Assuming displacements from equilibrium are small**

$$\mu_{final}^{(1)} = \mu_{final}^{(2)}$$

$$\Delta S = -\frac{\mu^{(1)}}{T}\Delta n^{(1)} - \frac{\mu^{(2)}}{T}\Delta n^{(2)} = -\left(\frac{\mu^{(1)}}{T} - \frac{\mu^{(2)}}{T}\right)\Delta n^{(1)}$$

since $\Delta n^{(1)} = -\Delta n^{(2)}$.

- **$\Delta S > 0$, when $\mu^{(1)} > \mu^{(2)}$, implies $\Delta n^{(1)} < 0$, that is matter flows from high μ to low μ.**

Further Discuss

- **The gradients in μ (or more precisely, gradients in μ/T) produce mass flow.**
- $-\nabla(\mu / T)$ **is a generalized force.**
- **In the variant statement of the Second Law, we see a similar form,**
- $-\nabla(1 / T)$ **is a generalized force that causes heat to flow from high T to low T.**

The Phase Rule

- **Suppose v phases are coexisting in equilibrium. The conditions for equilibrium**

$$\mu_i^{(\alpha)}\left(T, p, x_1^{(\alpha)}, \ldots, x_{r-1}^{(\alpha)}\right) = \mu_i^{(\gamma)}\left(T, p, x_1^{(\gamma)}, \ldots, x_{r-1}^{(\gamma)}\right)$$

- **where 1 ≤ α < γ ≤ υ and 1 ≤ l ≤ r**
- **There are *r*(υ-1) independent equations which couple together 2 + υ(*r*-1) different intensive variables (*T*, *p*, and the mole fractions for each phase).**

The Phase Rule

- **Hence, the thermodynamic degrees of freedom (the number of independent intensive thermodynamic variables) is**

$$\begin{aligned} f &= 2 + v(r-1) - r(v-1) \\ &= 2 + r - v \end{aligned}$$

- **This is the Gibbs phase rule.**

Topics in Phase Equilibria

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Binary Solid-liquid Equilibria of *n*-decanol and *n*-dodecanol

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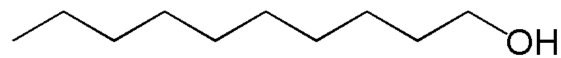
Introduction



n-decanol = Capric alcohol, 1-decanol, decan-1-ol, decyl alochol

n-dodecanol = Lauric alcohol, lauryl alcohol, 1-dodecanol, dodecan-1-ol

Fatty alcohols

- Natural: from fats, oils and waxes of plant or animal origin
- Synthetic: from petrochemicals

$CH_3(CH_2)_nCH_2OH$

n = 4-20

Introduction

Fatty alcohols from natural sources

- Plant or animal origin

decanol	dodecanol
osmanthus absolute (9.20%)	violet leaf (3.60%)
coriander leaf oil (0.89-2.09%)	cochlospermum planchonii oil (0.70%)
ambrette seed oil (0.60%)	cochlospermum tinctorium oil (0.70%)
frankincense oil from Somalia (0.40%)	ambrette seed oil (0.30%)
citronella oil from Zimbabwe (0.33%)	coriander leaf oil (0.09-0.18%)
kachur oil (0.10%)	

Coriander leaf

Ambrette seed

Violet leaf

Introduction

Uses of fatty alcohols

- Surfactants (ca. 70-75%)
- Oil additives
- Cosmetics and pharmaceutical preparations
- Polymer processing
- Preservatives for food

Emulsions and microemulsions

(cosmetics creams and lotions)

Fragrance Materials = fragrance compound + water + alcohol

(creams, deodorants, lotions…)

	Decanol	Dodecanol
Odour type	Fatty	Waxy
Odour strength	Medium	Medium
Odour description at 100%	Fatty waxy floral orange sweet clean watery	Earthy soapy waxy fatty honey coconut
Taste description	Aldehydic waxy green fatty tart perfumistic	Soapy waxy aldehydic earthy fatty

Real binary liquid mixture Gibbs energy

For the calculation of phase equilibria, it is necessary to minimize the total Gibbs Energy:

$$\underline{G} = \sum_{i=1}^{F} n_i \underline{G}_i = \text{minimum}$$

$$\underline{G} = \underline{G}_T(T,x) + \underline{G}_P(P,T,x) + \underline{G}_m(T_C,\beta_0,T,x)$$

Real binary liquid mixture Gibbs energy

$$\underline{G}(T,P,\underline{x}) = \sum_{i=1}^{C} x_i \underline{G}_i(T,P)$$

$$\Downarrow$$

Ideal mixture:

$$\underline{G}^{IM}(T,P,\underline{x}) = \sum_{i=1}^{C} x_i \underline{G}_i(T,P) + RT\sum_{i=1}^{C} x_i \ln x_i$$

$$\Downarrow$$

Excess Gibbs free energy

Real mixture:

$$\underline{G}(T,P,\underline{x}) = \sum_{i=1}^{C} x_i \underline{G}_i(T,P) + RT\sum_{i=1}^{C} x_i \ln x_i + \underline{G}^{ex}$$

Real binary liquid mixture Gibbs energy

$$\underline{G}(T,P,\underline{x}) = \sum_{i=1}^{C} x_i \underline{G}_i(T,P) + RT\sum_{i=1}^{C} x_i \ln x_i + \underline{G}^{ex}$$

Redlich-Kister polynomial expansion:

$$\underline{G}^{ex} = x_1 x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i = x_1 x_2 \left[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \cdots\right]$$

Temperature-dependent parameters:

$$A = V_1 + V_2 T$$

Variables to be optimized

Real binary liquid mixture Gibbs energy

$$\underline{G}(T,P,\underline{x}) = \sum_{i=1}^{C} x_i \underline{G}_i(T,P) + RT\sum_{i=1}^{C} x_i \ln x_i + \underline{G}^{ex}$$

$$\Delta\underline{G}_i(T,P) = \Delta\underline{H}_i - T\Delta\underline{S}_i = \Delta\underline{H}_{i,T_{tr}} - T\Delta\underline{S}_{i,T_{tr}} + \int_{T_{tr}}^{T} Cp_i^* dT - T\int_{T_{tr}}^{T} \frac{Cp_i^*}{T} dT$$

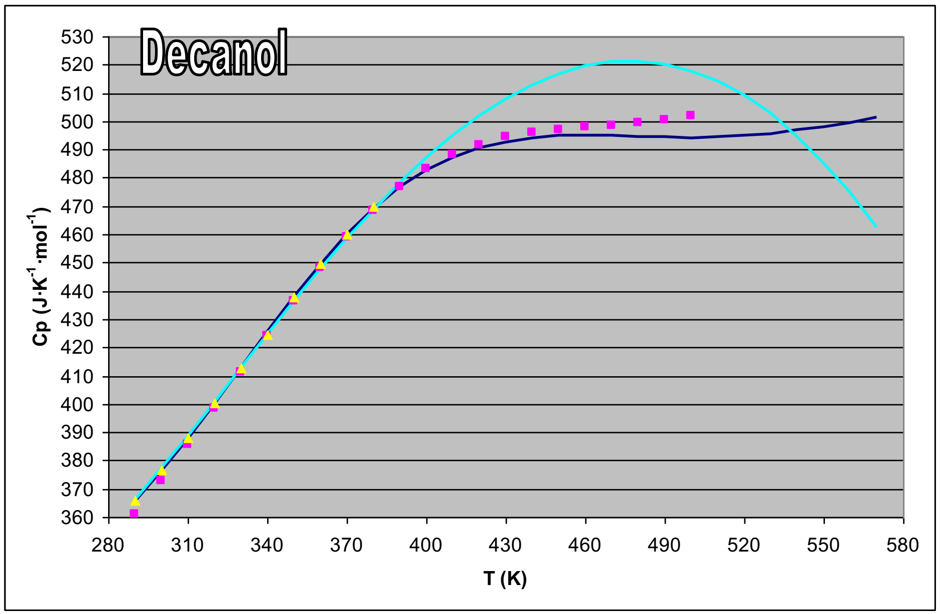
$$\Delta\underline{S}_{i,T_{tr}} = \frac{\Delta\underline{H}_{i,T_{tr}}}{T_{tr}}$$

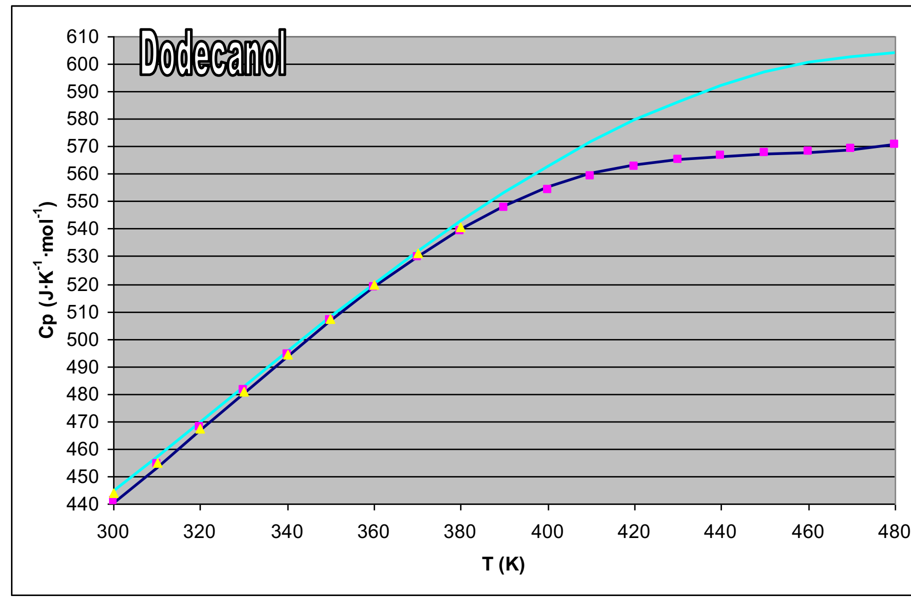
$$Cp_i^* = C_1 + C_2T + C_3T^2 + C_4T^3$$

$$\Delta\underline{G}_i = -C_1T\ln T + \left(-\frac{\Delta H_{i,T_{tr}}}{Tr} + C_1 + C_1\ln T_{tr} + C_2T_{tr} + \frac{C_3}{2}T_{tr}^2 + \frac{C_4}{3}T_{tr}^3\right)T - $$
$$-\frac{C_2}{2}T^2 - \frac{C_3}{6}T^3 - \frac{C_4}{12}T^4 + \left(\Delta H_{i,T_{tr}} - C_1T_{tr} - \frac{C_2}{2}T_{tr}^2 - \frac{C_3}{3}T_{tr}^3 - \frac{C_4}{4}T_{tr}^4\right)$$

Dependence of heat capacities with temperature

$$Cp_i^* = C_1 + C_2 T + C_3 T^2 + C_4 T^3$$





Růžička (2004)
Zábranský (1990)
Cees (2003)
Equation

$$Cp = -3163.5 + 21.0156n + 0.04223nT + 9.89055T + \frac{322705.7}{T} - 0.0093225T^2$$

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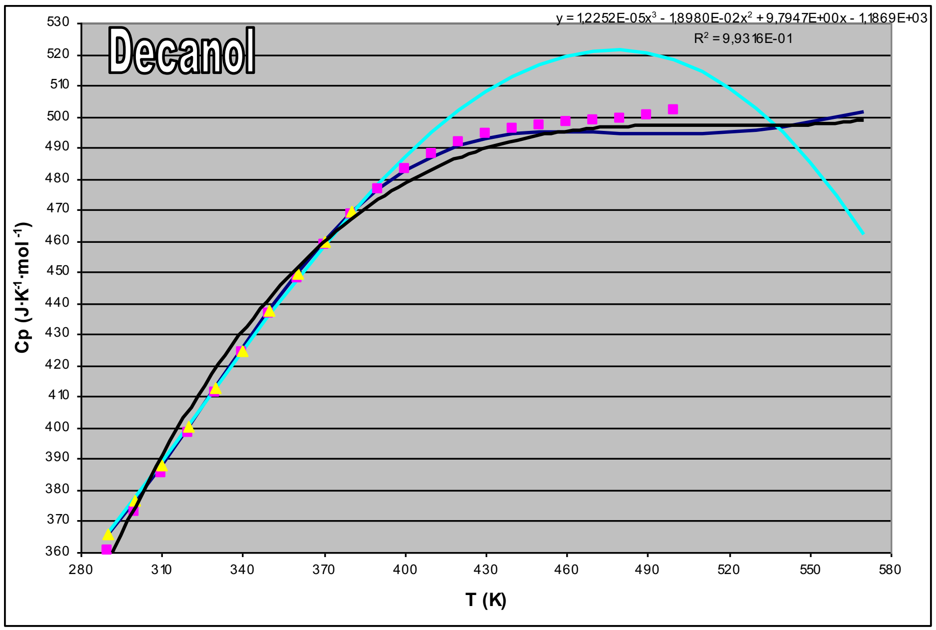
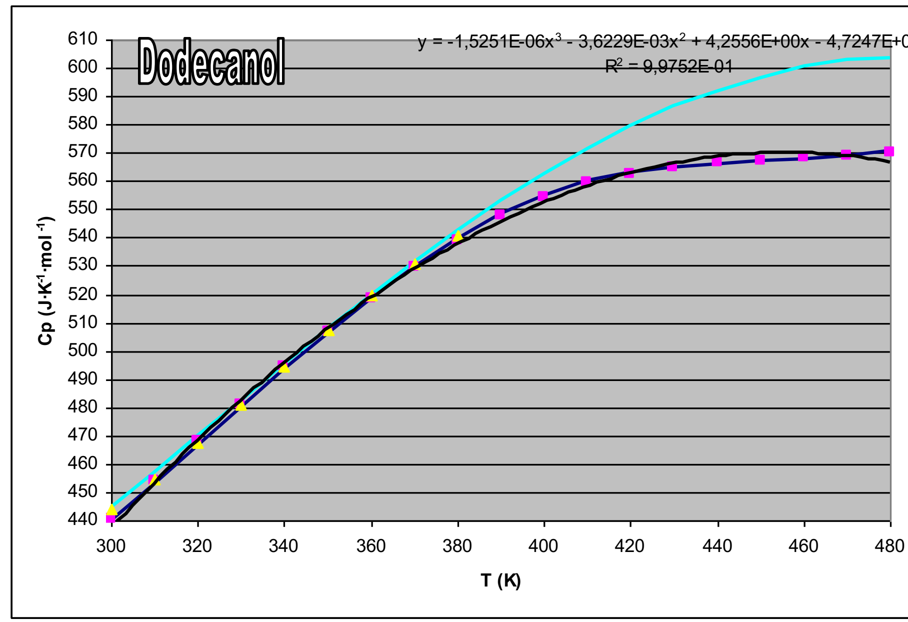
Thermodynamics

Dependence of heat capacities with temperature





$$Cp^*_{DE} = -1.1869\cdot10^3 + 9.7947T - 1.8980\cdot10^{-2}T^2 + 1.2252\cdot10^{-5}T^3$$

$$Cp^*_{DO} = -4.7247\cdot10^2 + 4.2556T - 3.6229\cdot10^{-3}T^2 - 1.5251\cdot10^{-6}T^3$$

Růžička (2004)
Zábranský (1990)
Cees (2003)
Equation
Polynomial (Růžička (2004))

Gibbs energy functions

$$Cp^{*}_{DE} = -1.1869\cdot 10^{3} + 9.7947T - 1.8980\cdot 10^{-2}T^{2} + 1.2252\cdot 10^{-5}T^{3}$$

$$Cp^{*}_{DO} = -4.7247\cdot 10^{2} + 4.2556T - 3.6229\cdot 10^{-3}T^{2} - 1.5251\cdot 10^{-6}T^{3}$$

$$\Delta \underline{G}_{i} = -C_{1}T\ln T + \left(-\frac{\Delta H_{i,T_{tr}}}{Tr} + C_{1} + C_{1}\ln T_{tr} + C_{2}T_{tr} + \frac{C_{3}}{2}T_{tr}^{2} + \frac{C_{4}}{3}T_{tr}^{3}\right)T - \frac{C_{2}}{2}T^{2} - \frac{C_{3}}{6}T^{3} - \frac{C_{4}}{12}T^{4} + \left(\Delta H_{i,T_{tr}} - C_{1}T_{tr} - \frac{C_{2}}{2}T_{tr}^{2} - \frac{C_{3}}{3}T_{tr}^{3} - \frac{C_{4}}{4}T_{tr}^{4}\right)$$

$$T_{m}(DE) = 280.1\ K$$

$$T_{m}(DO) = 300.2\ K$$

$$\Delta \underline{H}_{fus}(DE) = 37.66\ kJ\cdot mol^{-1}$$

$$\Delta \underline{H}_{fus}(DO) = 40.17\ kJ\cdot mol^{-1}$$

$$\underline{G}_{DE} = 1.1869\cdot 10^{3}T\ln T - 5.9210\cdot 10^{3}T - 4.8974T^{2} + 3.1633\cdot 10^{-3}T^{3} - 1.0210\cdot 10^{-6}T^{4} + 1.0606\cdot 10^{5}$$

$$\underline{G}_{DO} = 4.7247\cdot 10^{2}T\ln T - 2.2066\cdot 10^{3}T - 2.1278T^{2} + 6.0382\cdot 10^{-4}T^{3} + 1.2709\cdot 10^{-7}T^{4} + 2.7320\cdot 10^{4}$$

CALPHAD

$$\underline{G}(T,P,\underline{x}) = \sum_{i=1}^{C} x_i \underline{G}_i(T,P) + RT\sum_{i=1}^{C} x_i \ln x_i + \underline{G}^{ex}$$

Gibbs energy functions of pure components

assessment

Experimental data

Binary:
(A, B)

$\underline{G}^{ex}_{bin}$ A-B

Ternary: ≡ 3 independent
(A, B, C) binary systems

Extrapolation $\left(\sum \underline{G}^{ex}_{bin}\right)$ and
assessment: $\underline{G}^{ex}_{ter}$

$\sum \underline{G}^{ex}_{bin} =$ A-B + A-C + B-C

$\underline{G}^{ex}_{ter} =$ A-B-C

Quaternary:
(A, B, C, D)

≡ 6 binary systems
& 4 ternary systems

Extrapolation $\left(\sum \underline{G}^{ex}_{bin} + \sum \underline{G}^{ex}_{ter}\right)$ and
assessment: $\underline{G}^{ex}_{qua}$

$\sum \underline{G}^{ex}_{bin} + \sum \underline{G}^{ex}_{ter} =$
A-B+A-C+A-D+
+B-C+B-D+C-D+
+A-B-C+A-B-D+
+A-C-D+B-C-D

$\underline{G}^{ex}_{qua} =$ A-B-C-D

• • •

CalcPhad

⇩

Output:

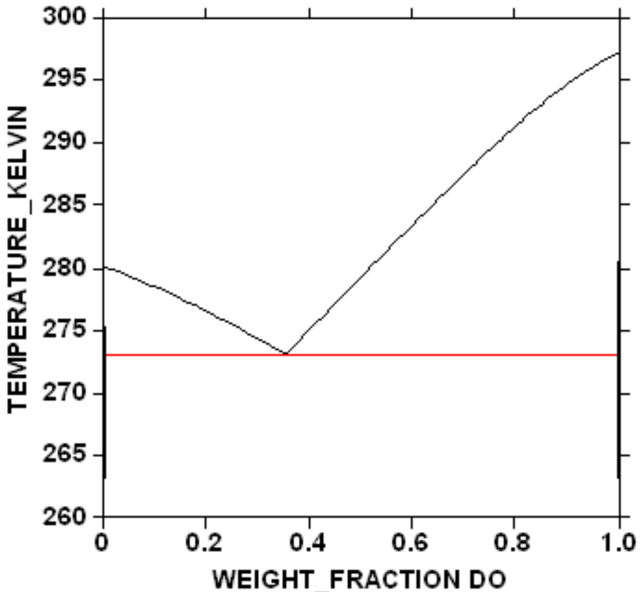
Variable	Value	*RSD*
V11	$3.57729450 \cdot 10^{4}$	$1.38374758 \cdot 10^{1}$
V12	$-1.32979526 \cdot 10^{2}$	2.88416718
V15	$-1.14258537 \cdot 10^{3}$	$7.16573950 \cdot 10^{1}$
V16	$5.70769803 \cdot 10^{1}$	$1.40175298 \cdot 10^{-2}$

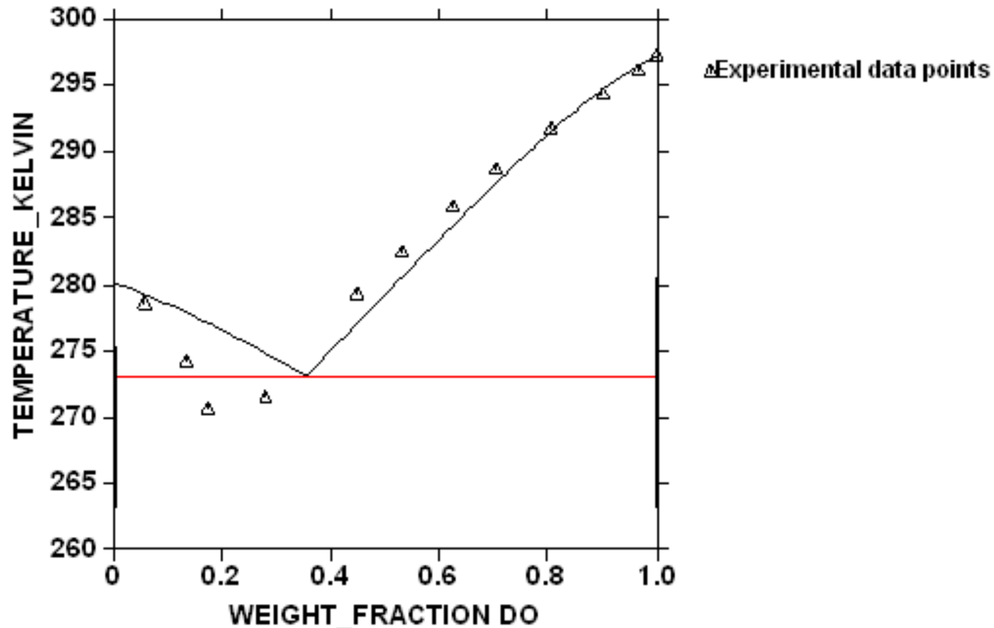
Reduced sum of squares: $1.0359 \cdot 10^{1}$

$$\underline{G}^{ex} = A x_1 x_2 \quad \begin{cases} Liquid\ \ phase: A = V_{11} + V_{12} T \\ Solid\ \ phase: A = V_{15} + V_{16} T \end{cases}$$

⇩

CalPhad





EXP file

Possible causes of discrepancy

1. Fusion enthalpies
2. Heat capacities
3. Experimental data

Possible causes of discrepancy

1. Fusion enthalpies

Other experimental fusion enthalpies: Domańska (2004)

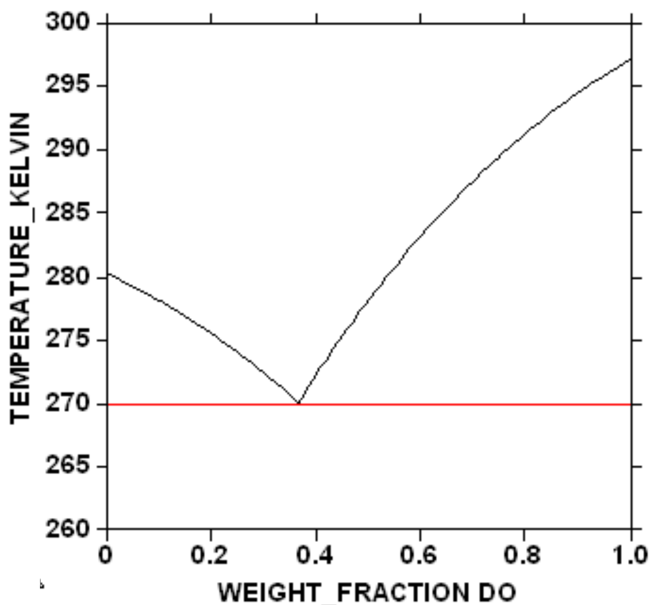
$$\Delta \underline{H}_{fus}(DE) = 28.79\ kJ \cdot mol^{-1}$$
$$\Delta \underline{H}_{fus}(DO) = 37.74\ kJ \cdot mol^{-1}$$

vs

$$\Delta \underline{H}_{fus}(DE) = 37.66\ kJ \cdot mol^{-1}$$
$$\Delta \underline{H}_{fus}(DO) = 40.17\ kJ \cdot mol^{-1}$$

$$\underline{G}_{DE} = 1.1869 \cdot 10^{3}\, T \ln T - 5.8893 \cdot 10^{3}\, T - 4.8974 T^{2} + 3.1633 \cdot 10^{-3} T^{3} - 1.0210 \cdot 10^{-6} T^{4} + 9.7192 \cdot 10^{4}$$

$$\underline{G}_{DO} = 4.7247 \cdot 10^{2}\, T \ln T - 2.1985 \cdot 10^{3}\, T - 2.1278 T^{2} + 6.0382 \cdot 10^{-4} T^{3} + 1.2709 \cdot 10^{-7} T^{4} + 2.4890 \cdot 10^{4}$$



Variable	Value	RSD
V11	$8.03627948 \cdot 10^{3}$	2.83742795
V12	$-3.31208687 \cdot 10^{1}$	2.48241825
V15	$-3.23535636 \cdot 10^{3}$	$2.67013956 \cdot 10^{4}$
V16	$2.65182804 \cdot 10^{2}$	$1.69713840 \cdot 10^{4}$

Reduced sum of squares: 4.8785

Possible causes of discrepancy

1. Fusion enthalpies

Estimated fusion entropies: Chickos (1991)

$$\Delta \underline{S}_{fus} = \sum_i n_i C_i G_i + \sum_j n_j C_j G_j + \sum_k n_k C_K G_k$$

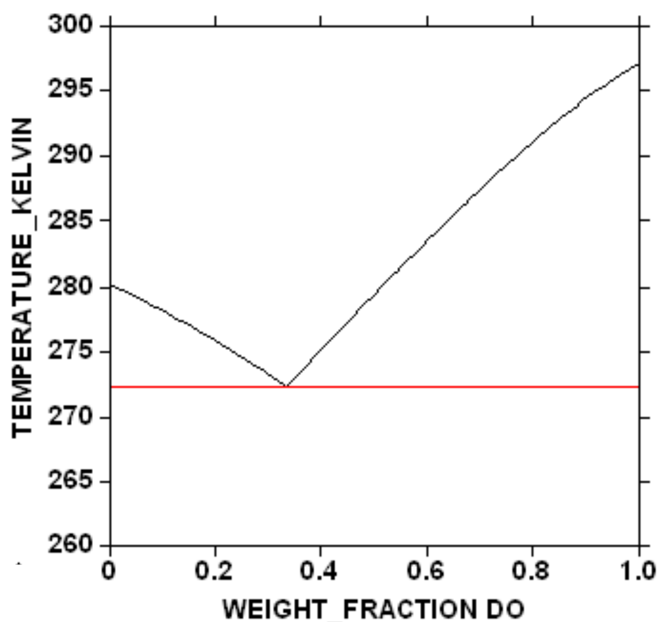
$$\Delta \underline{S}_{fus}(DE) = 24.9\ cal \cdot K^{-1} \cdot mol^{-1}$$

$$\Delta \underline{S}_{fus}(DO) = 29.4 cal \cdot K^{-1} mol^{-1}$$

$$\Delta \underline{S}_{i,T_{tr}} = \frac{\Delta \underline{H}_{i,T_{tr}}}{T_{tr}}$$

$$\Delta \underline{H}_{fus}(DE) = 29.181\ kJ \cdot mol^{-1}$$

$$\Delta \underline{H}_{fus}(DO) = 36.558\ kJ \cdot mol^{-1}$$

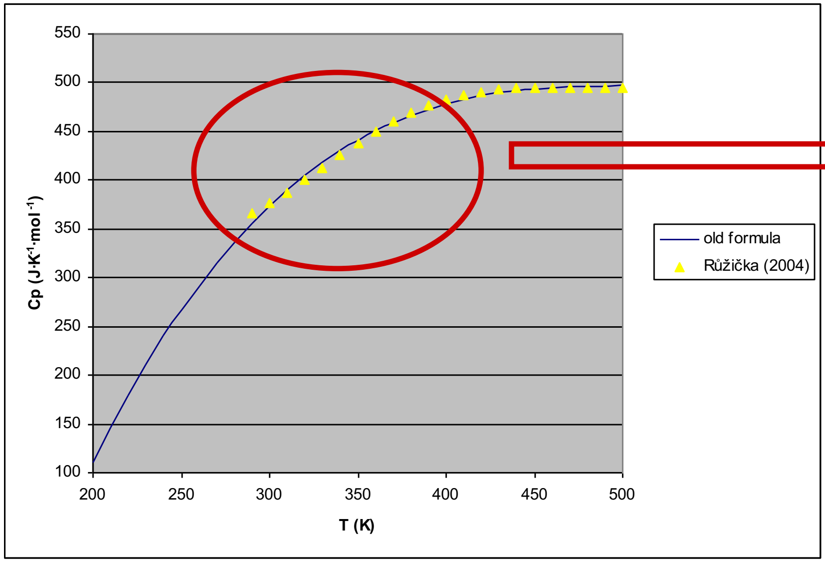


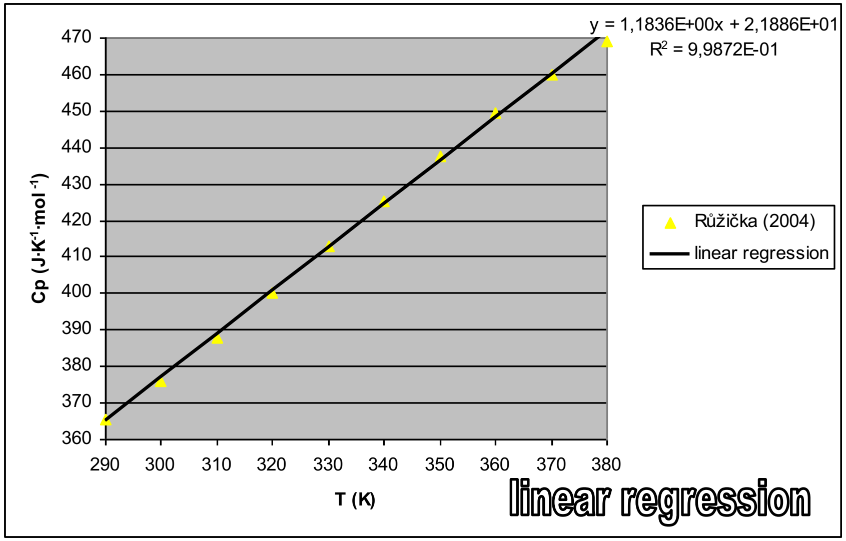
Variable	Value	RSD
V11	$2.78843867 \cdot 10^{4}$	6.63622105
V12	$-1.01597519 \cdot 10^{2}$	6.62042326
V15	$2.73701059 \cdot 10^{1}$	$7.77898557 \cdot 10^{6}$
V16	$5.56925163 \cdot 10^{1}$	$1.33566753 \cdot 10^{4}$

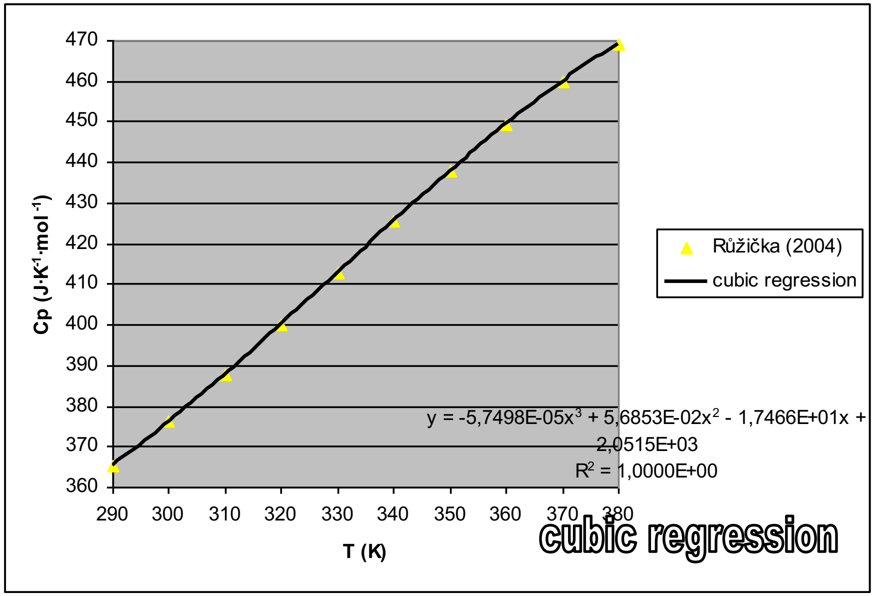
Reduced sum of squares: $3.8364 \cdot 10^{-3}$

Possible causes of discrepancy

2. Heat capacities

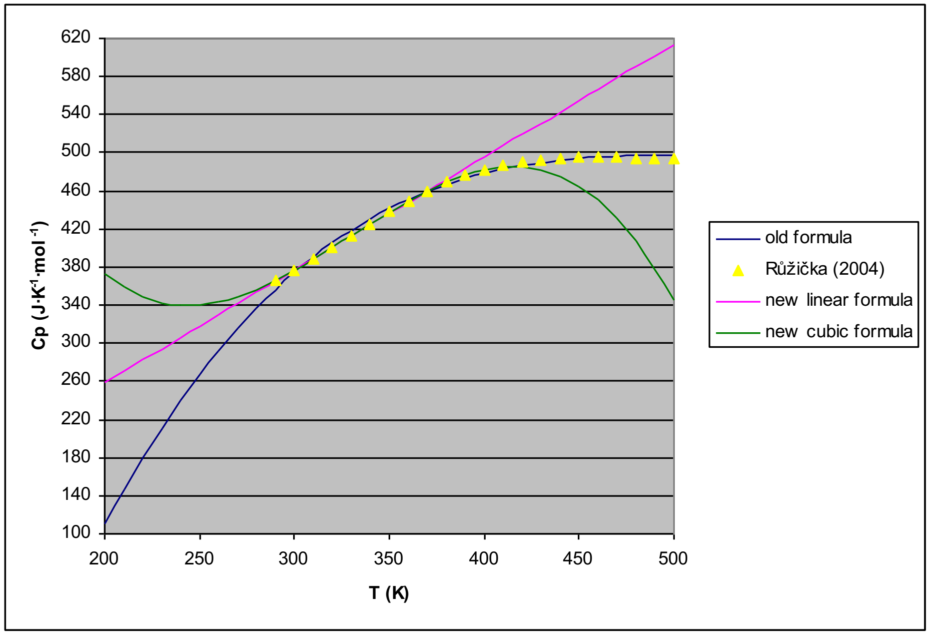






Possible causes of discrepancy

2. Heat capacities



Variable	Value	RSD
V11	$3.45701098 \cdot 10^{4}$	5.35821836
V12	$-1.28415582 \cdot 10^{2}$	5.24342738
V15	$3.39538287 \cdot 10^{-4}$	$1.74739330 \cdot 10^{11}$
V16	$5.35786127 \cdot 10^{1}$	$3.90996426 \cdot 10^{3}$

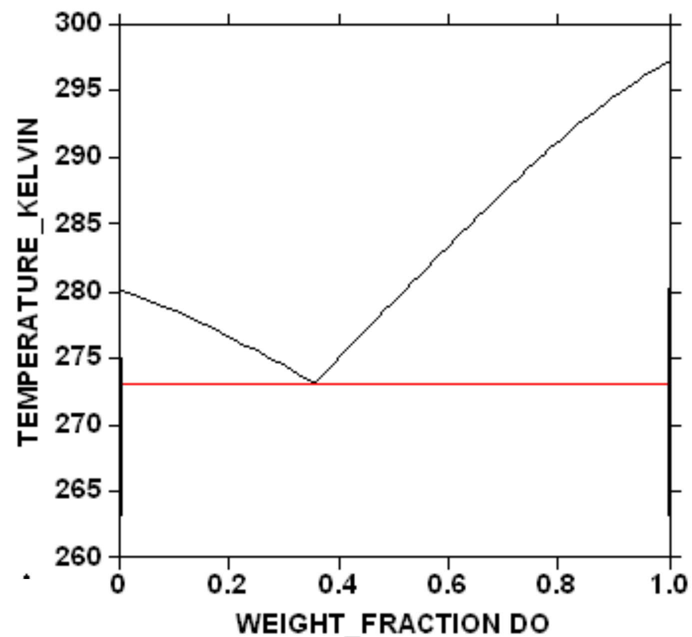
Reduced sum of squares: $8.6490 \cdot 10^{-3}$

$$Cp^{*}_{DE} = 2.1886 \cdot 10^{1} + 1.1836T$$

$$Cp^{*}_{DO} = 4.5191 \cdot 10^{1} + 1.3169T$$

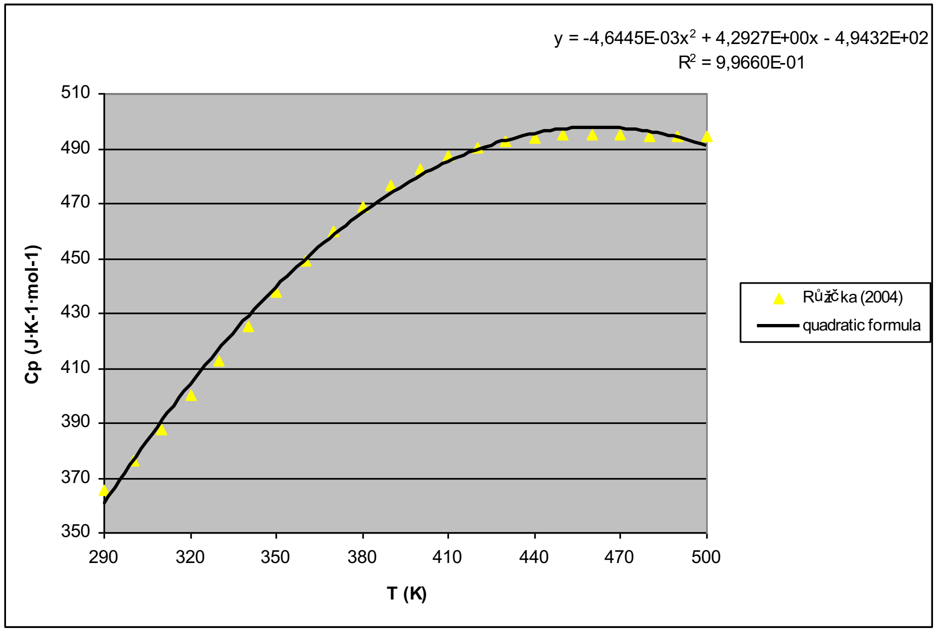
$$\underline{G}_{DE} = -2.1886 \cdot 10^{1} T \ln T + 3.4229 \cdot 10^{2} T - 5.9180 \cdot 10^{-1} T^{2} - 1.4901 \cdot 10^{4}$$

$$\underline{G}_{DO} = -4.5191 \cdot 10^{1} T \ln T + 5.5875 \cdot 10^{2} T - 6.5845 \cdot 10^{-1} T^{2} - 3.1420 \cdot 10^{4}$$



Possible causes of discrepancy

2. Heat capacities



$$Cp^*_{DE} = -4.6445 \cdot 10^{-3} T^2 + 4.2927T - 4.9432 \cdot 10^2$$

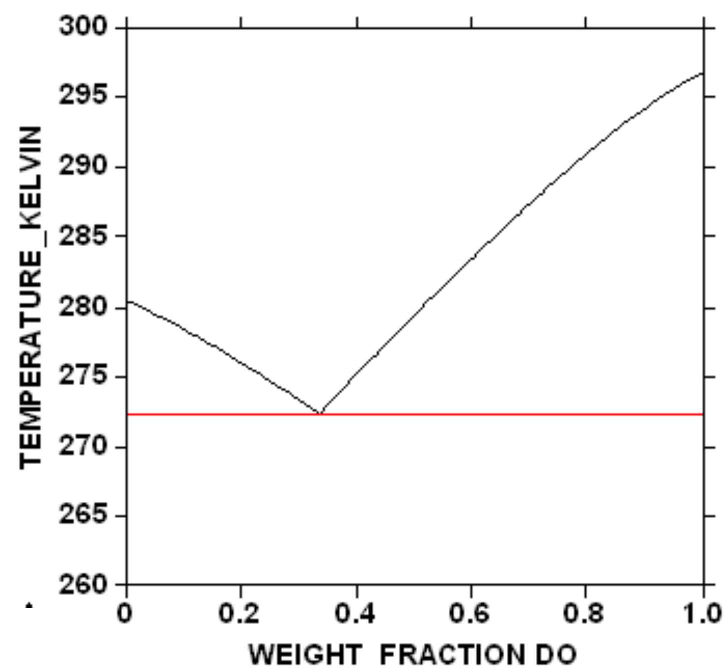
$$Cp^*_{DO} = -5.4073 \cdot 10^{-3} T^2 + 4.9433T - 5.5974 \cdot 10^2$$

$$\underline{G}_{DE} = 494.32T \ln T - 2361.85T - 2.14635T^2 + 7.7408 \cdot 10^{-4} T^3 + 32739.15$$

$$\underline{G}_{DO} = 559.74T \ln T - 2644.25T - 2.4717T^2 + 9.0122 \cdot 10^{-4} T^3 + 33202.86$$

Variable	Value	RSD
V11	$2.80666395 \cdot 10^4$	$2.11481408 \cdot 10^{-2}$
V12	$-1.02775126 \cdot 10^2$	$2.08823286 \cdot 10^{-2}$
V15	$1.82918841 \cdot 10^{-2}$	5.76074009
V16	$6.12723859 \cdot 10^1$	$1.37118907 \cdot 10^{-1}$

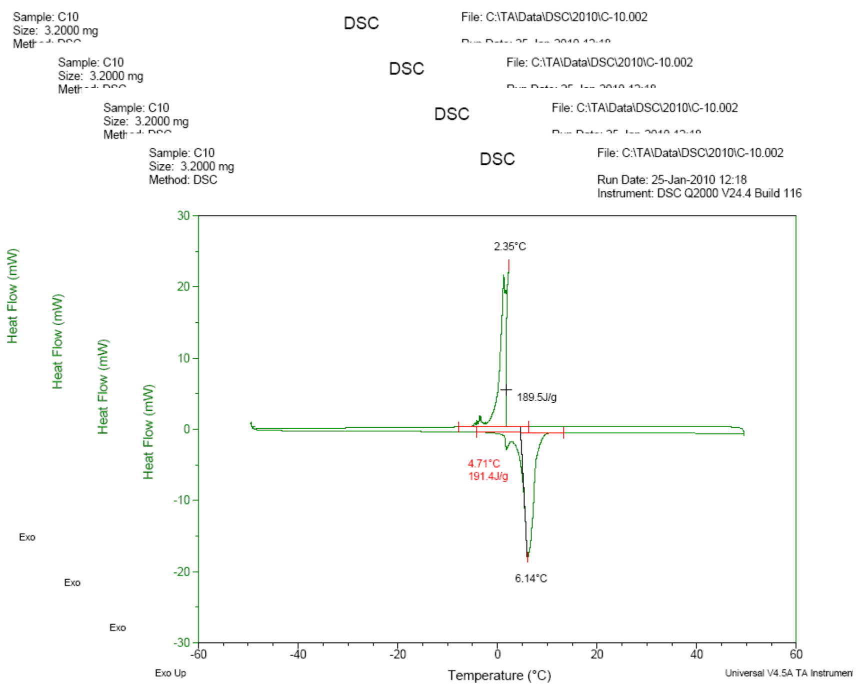
Reduced sum of squares: $4.33899 \cdot 10^{-3}$

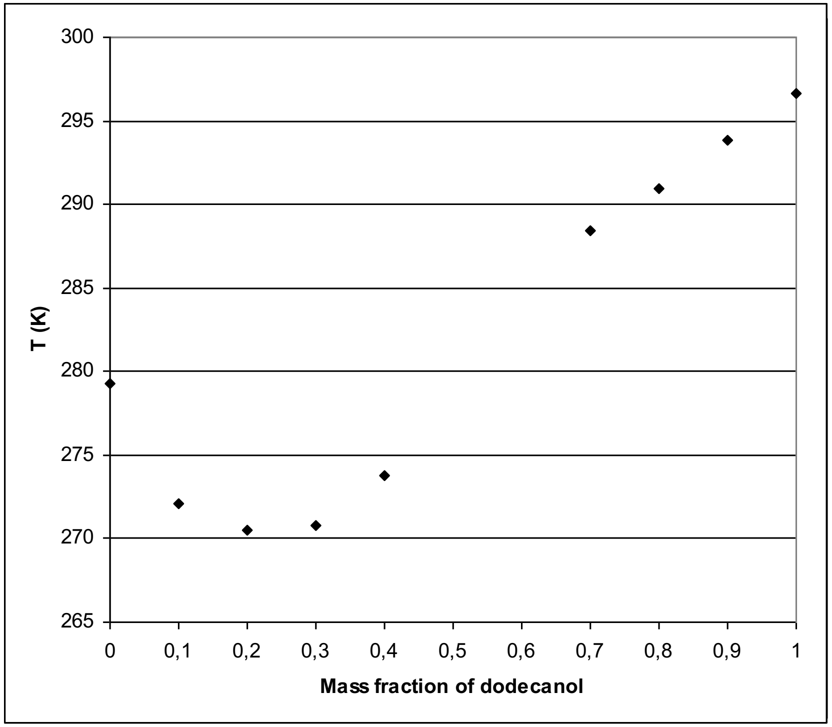


Possible causes of discrepancy

3. Experimental data

Differential Scanning Calorimetry (DSC)

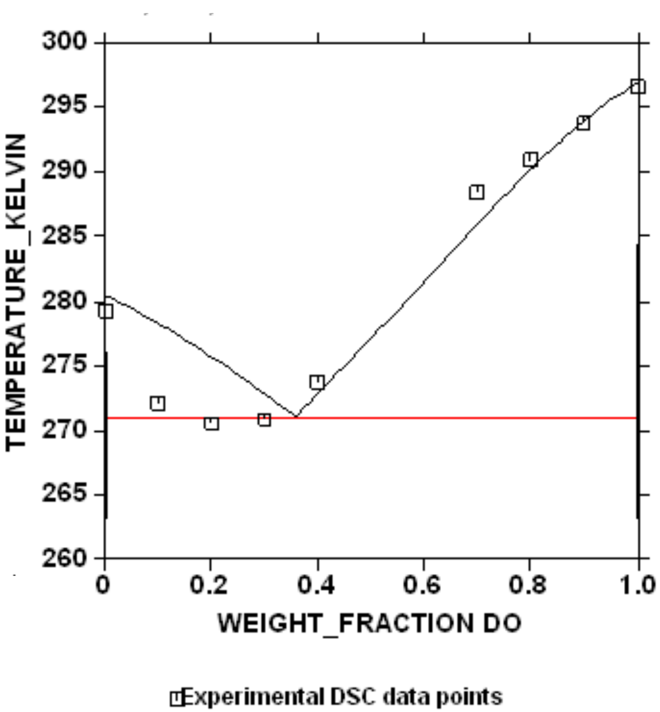




Possible causes of discrepancy

3. Experimental data points

new POP file



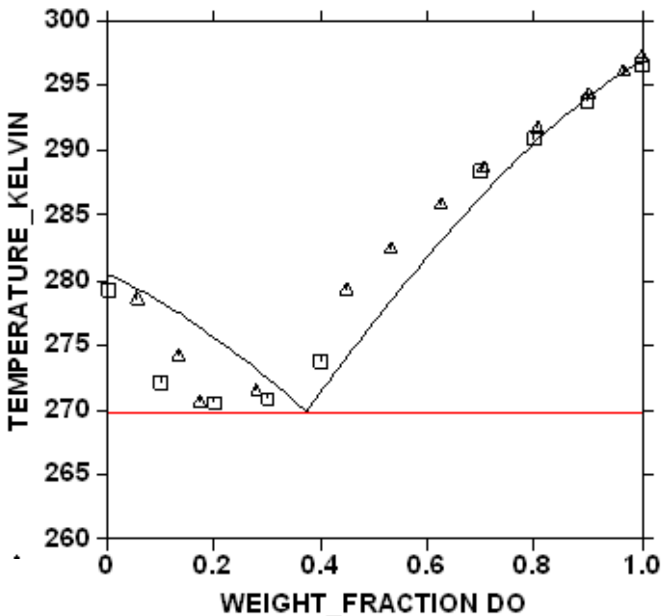
Variable	Value	RSD
V11	$4.30371467 \cdot 10^{4}$	$3.20019842 \cdot 10^{-1}$
V12	$-1.60697579 \cdot 10^{2}$	$3.12444640 \cdot 10^{-1}$
V15	$-1.24197073 \cdot 10^{-2}$	$1.04699276 \cdot 10^{2}$
V16	$4.69106820 \cdot 10^{1}$	$4.73816471 \cdot 10^{-1}$

Reduced sum of squares: $2.3402 \cdot 10^{2}$

Possible causes of discrepancy

3. Experimental data points

Assessment with all the experimental data available → new POP file



△Data points from [18]

□Experimental DSC data points

Variable	Value	RSD
V11	$2.12541399 \cdot 10^{4}$	$9.73327408 \cdot 10^{-1}$
V12	$-8.25529414 \cdot 10^{1}$	$9.51768718 \cdot 10^{-1}$
V15	$1.44869057 \cdot 10^{5}$	$4.25482680 \cdot 10^{1}$
V16	$-4.58345239 \cdot 10^{2}$	$4.51677061 \cdot 10^{1}$

Reduced sum of squares: $6.3462 \cdot 10^{2}$

Subregular Solution Model

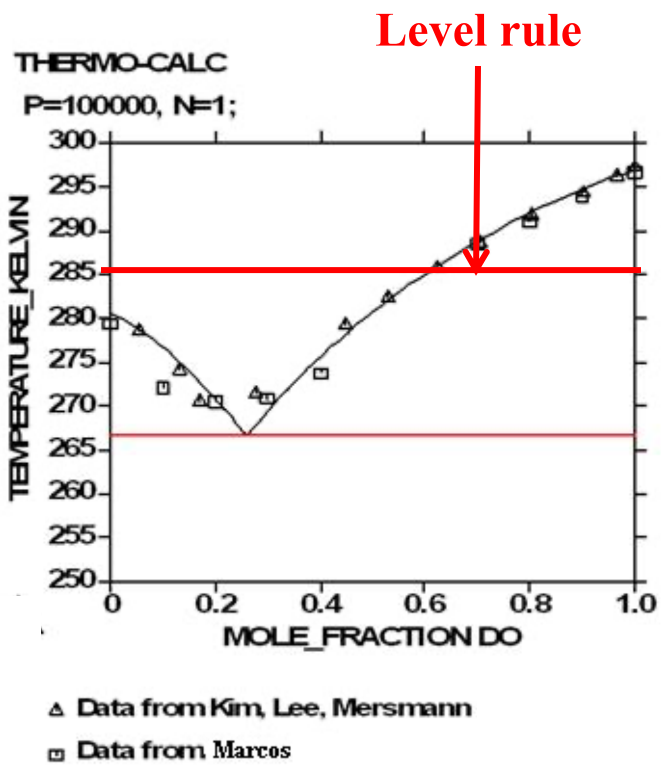
罗婕

4. Subregular Model

$$\lambda_{ij} = A_{ij} + B_{ij}(x_i - x_j)$$

$$^{E}G_m^{\phi} = \sum_{i=1}^{c-1} \sum_{j=i+1}^{c} x_i x_j [A_{ij} + B_{ij}(x_i - x_j)]$$

$$^{E}G_m^{\phi} = x_1 x_2 [A_{1,2} + B_{1,2}(x_1 - x_2)]$$



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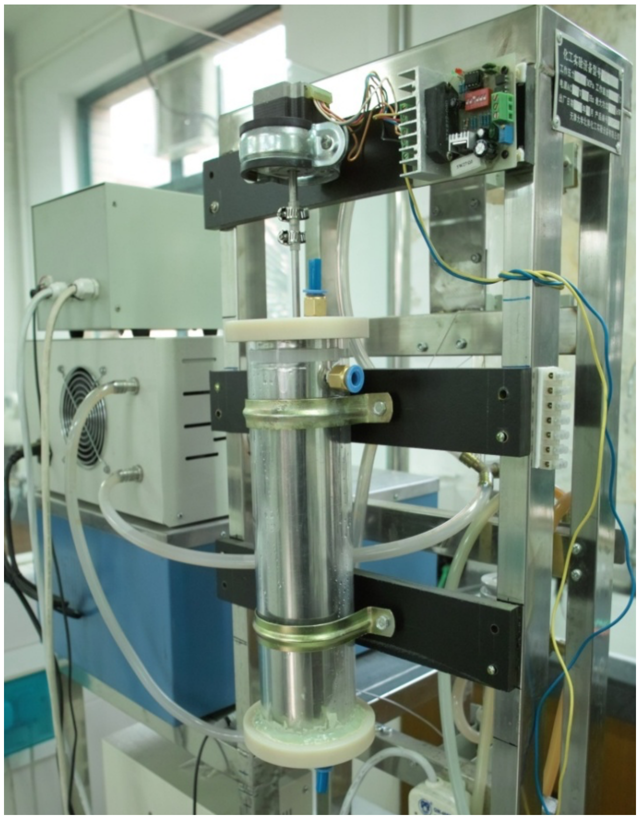
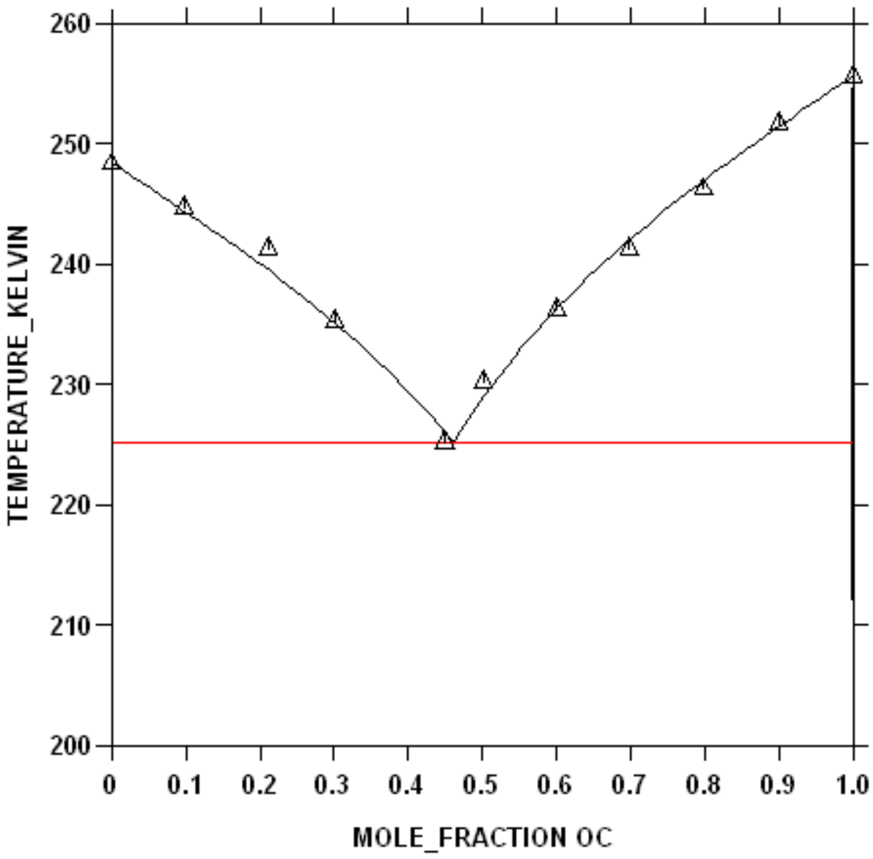
Continue Suspension Crystallization



Continue Suspension Crystallization

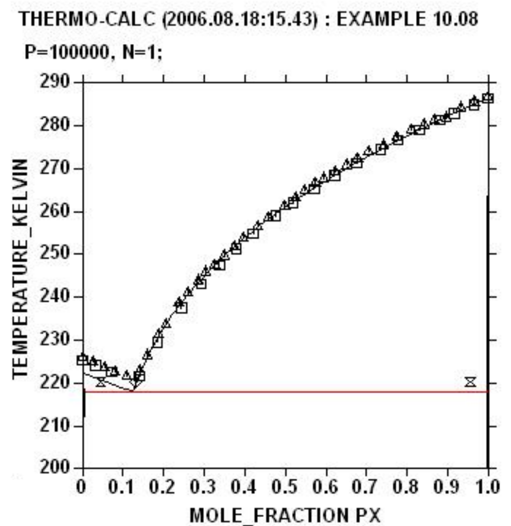
王文静

- OC-MC Binary Solid Liquid Equilibrium using regular solution model

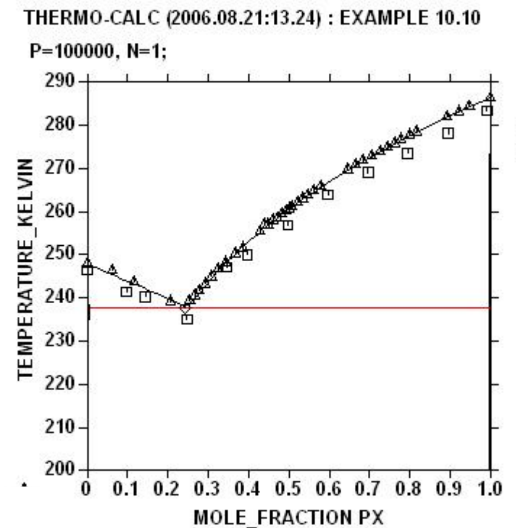


Continue Suspension Crystallization

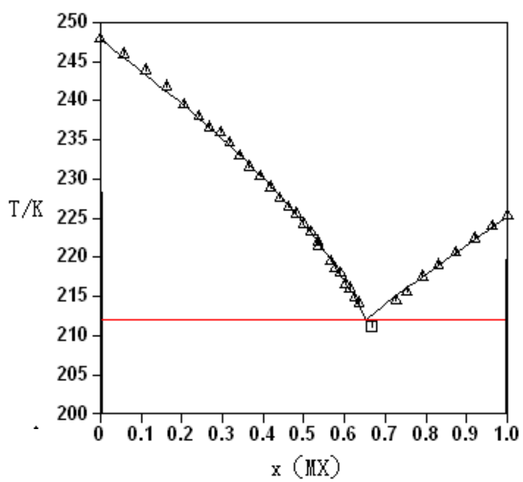
郭艳姿、郭思斯



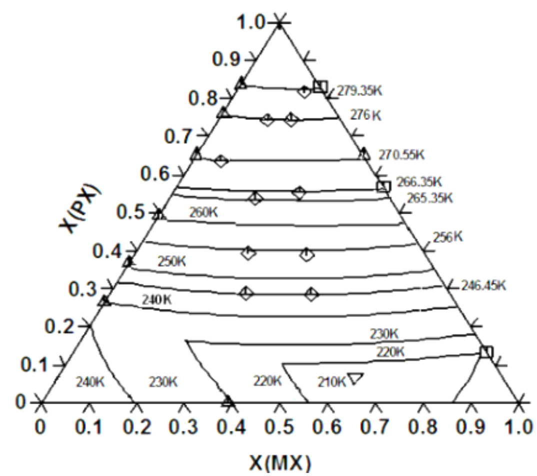
mX-pX



oX-pX



oX-mX



pX-mX-oX Ternary