Models for the Excess Gibbs Energy

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Models for the Excess Gibbs Energy

- **G^E/RT is a function of T, P, and composition,**

$$\bar{G}_i^E = RT \ln \gamma_i$$

- **Therefore,**

$$\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i$$

- **But for liquids at low to moderate pressures it is a very weak function of P. Therefore the pressure dependence of activity coefficients is usually neglected.**

Models for the Excess Gibbs Energy

- **Thus,**

$$\frac{G^E}{RT} = g\left(x_1, x_2, \ldots, x_N\right)$$

- **For binary systems, the function most often represented by a power series in x_1**

$$\frac{G^E}{x_1 x_2 RT} = a + b x_1 + c x_1^2 + \cdots$$

Models for the Excess Gibbs Energy

- **Since $x_2 = 1 - x_1$, therefore,**

$$\frac{G^E}{x_1 x_2 RT} = A + B\left(x_1 - x_2\right) + C\left(x_1 - x_2\right)^2 + \cdots$$

- **This is know as the Redlich/Kister expansion which is the most commonly used polynomial in regular and subregular solution models**

Regular Solution

- **Recall** $\bar{G}_i^{id} = G_i + RT \ln x_i$

$$\overline{\Delta G_i^{id}} = RT \ln x_i = \cancel{\overline{\Delta H_i^{id}}} + T\overline{\Delta S_i^{id}}$$

- **Let** $\overline{\Delta G_i^{RS}} = \overline{G_i^{RS}} - \overline{G_i^{id}}$
- **Regular solution is an non ideal solution with small deviation from ideal solution**
- **Regular solution is defined as a solution possesses an enthalpy of mixing but no entropy of mixing.**

Regular Solution

- **That is**

$$\overline{\Delta G^{RS}} = \overline{\Delta H^{RS}} - \overline{T\Delta S^{RS}}$$

$$= \overline{\Delta H^{RS}} - \overline{T\Delta S^{id}}$$

- **Since**

$$\overline{\Delta G_i^{id}} = \cancel{\overline{\Delta H_i^{id}}} - \overline{T\Delta S_i^{id}}$$

- **Therefore,**

$$\overline{G_i^{RS}} - \overline{G_i^{id}} = \overline{H_i^{RS}} - \cancel{\overline{H_i^{id}}} = \overline{\Delta H_i^{RS}}$$

Enthalpy of Regular Solution

- **The word regular implies that the molecules mix in a completely random manner, which means that there is no segregation or preference.**
- **Consider two neighbors in a solution. The probability that one of the neighbors is A or B is simply**

$$P_A = \frac{N_A}{N_A + N_B} = x_A$$

$$P_B = \frac{N_B}{N_A + N_B} = x_B$$

Enthalpy of Regular Solution

- Therefore the probability that a given ``bond'' is A—B type is

$$P_{(AB)} = P_{AB} + P_{BA} = \frac{2N_A N_B}{\left(N_A + N_B\right)^2} = 2x_A x_B$$

- If each atom has z nearest neighbors, the number of bonds, total, is

$$B^{total} = \frac{z}{2}\left(N_A + N_B\right), \quad \frac{B^{total}}{} = \frac{z}{2}$$

Enthalpy of Regular Solution

- **The bond density of A-B type is:**

$$\underline{B_{(AB)}} = P_{(AB)}\underline{B^{total}} = zx_A x_B$$

- **If the energy per bond is w$_{(AB)}$ then the enthalpy density (due to the A-B bonds) is:**

$$\underline{H^{RS}_{(AB)}} = zw_{(AB)}x_A x_B$$

- **Similarly**

$$\underline{H^{RS}_{(AA)}} = \tfrac{z}{2}w_{(AA)}x_A x_A, \qquad P_{(AA)} = x_A^2$$

$$\underline{H^{RS}_{(BB)}} = \tfrac{z}{2}w_{(BB)}x_B x_B$$

Enthalpy of Regular Solution

- **Therefore,**

$$\underline{\Delta H_{mixing}} = \underline{H^{sol}} - \underline{H^{pure}}$$

- **Since**

$$x_A = 1 - x_B \text{ and } x_B = 1 - x_A$$

- **Therefore,**

$$\underline{\Delta H_{(AB)}^{RS}} = \frac{z}{2} x_A x_B \left(2w_{(AB)} - w_{AA} - w_{BB}\right)$$

$$\equiv \frac{z}{2} x_A x_B w^{RS}$$

Regular Solution

- **According to the definition of Regular solution, entropy of mixing equals to ideal solution**
- **Therefore,**

$$\underline{\Delta G_{(AB)}^{RS}} = \underline{\Delta H_{(AB)}^{RS}} - T\,\underline{\Delta S_{(AB)}^{id}}$$

$$= \frac{z}{2} x_A x_B w^{RS} - T\left[(-R)(\ln x_A + \ln x_B)\right]$$

$$\underline{G^{E,RS}} = \frac{z}{2} x_A x_B w^{RS} \equiv \omega x_A x_B$$

Regular Solution

Gibbs-Duhem →

$$\overline{H}_B^{E,RS} = \underline{H_{(AB)}^{RS}} + x_A \left(\frac{\partial \underline{\underline{H_{(AB)}^{RS}}}}{\partial x_B} \right)$$

$$= \omega x_A x_B + x_A \left(\frac{\partial \left(\omega x_A x_B \right)}{\partial x_B} \right)$$

$$= \omega x_A x_B + x_A \omega \left(x_A - x_B \right)$$

$$= \omega x_A^2$$

$$\underline{H_{(AB)}^{RS}} = x_A \overline{H}_A^{RS} + x_B \overline{H}_B^{RS}$$

$$\boxed{\frac{\partial \underline{H_{(AB)}^{RS}}}{\partial x_B} = -\overline{H}_A^{RS} + \overline{H}_B^{RS}}$$

$$x_A \left(\frac{\partial \underline{H_{(AB)}^{RS}}}{\partial x_B} \right) = -x_A \overline{H}_A^{RS} + x_A \overline{H}_B^{RS}$$

$$x_A \left(\frac{\partial \underline{H_{(AB)}^{RS}}}{\partial x_B} \right) = -x_A \overline{H}_A^{RS} + \left(1 - x_B\right) \overline{H}_B^{RS} = \overline{H}_B^{RS} - x_A \overline{H}_A^{RS} - x_B \overline{H}_B^{RS}$$

$$\underline{H_{(AB)}^{RS}} + x_A \left(\frac{\partial \underline{H_{(AB)}^{RS}}}{\partial x_B} \right) = \vec{H}_B^{RS}$$

Regular Solution

- **Since** $\overline{G}_i^{\boxed{E,RS}} = \overline{G}_i^{\boxed{E}} = RT \ln \gamma_i$

- **Therefore,**

$$\frac{\overline{G}_A^{E,RS}}{RT} = \ln \gamma_A = \frac{\omega}{RT} x_B^2$$

$$\frac{\overline{G}_B^{E,RS}}{RT} = \ln \gamma_B = \frac{\omega}{RT} x_A^2$$

Otto Redlich AND A. T. Kister Expansion

- **Recall**

$$\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i$$

- **For binary system,**

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

$$\frac{d\left(\frac{G^E}{RT}\right)}{dx_1} = \ln\left(\frac{\gamma_1}{\gamma_2}\right)$$

Otto Redlich AND A. T. Kister Expansion

- **Therefore,**

Used in $H^{E,RS}$ →

$$\ln \gamma_1 = \left(\frac{G^E}{RT}\right) + \left(1 - x_1\right)\frac{d\left(\frac{G^E}{RT}\right)}{dx_1}$$

$$\ln \gamma_2 = \left(\frac{G^E}{RT}\right) - x_1 \frac{d\left(\frac{G^E}{RT}\right)}{dx_1}$$

- **Let** $Q = \frac{G^E}{RT}$

Otto Redlich AND A. T. Kister Expansion

- Since Q *= 0 for x = 0 and* x_1 *= 1, each term must contain the* factor $x_1(1 - x_1)$.
- Introduce the expansion,

$$\frac{G^E}{RT} = Q = x_1(1 - x_1)\left(B + C(2x_1 - 1) + D(2x_1 - 1)^2 + \cdots\right)$$

- The coefficients may be determined by

$$\frac{Q}{x_1(1 - x_1)} = \frac{\ln\gamma_1}{1 - x_1} + \frac{\ln\gamma_2}{x_1}$$

- This is know as the Redlich/Kister expansion

Otto Redlich AND A. T. Kister Expansion

- **Or**

$$\ln\left(\frac{\gamma_1}{\gamma_2}\right)=\frac{dQ}{dx_1}=B\left(1-2x_1\right)+C\left(6x_1\left(1-x_1\right)-1\right)+\cdots$$

- **Case 1, ideal solution**

$$\ln\left(\frac{\gamma_1}{\gamma_2}\right)=0$$

- **Case 2, B ≠ 0, C,D,…=0, a form of regular**
- **Case 3, B ≠ 0, C ≠ 0, D,E,…=0, subregular**
- **…**

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 δE 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**

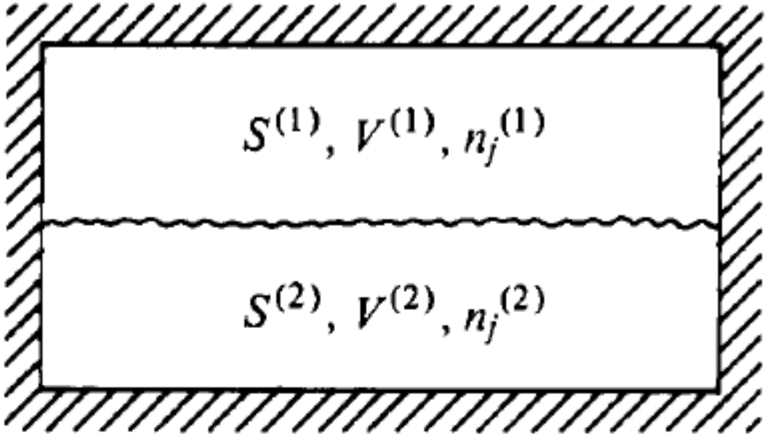
$$\sum_{\alpha=1}^{\upsilon} \delta S^{(\alpha)} = 0$$

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

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

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**

$$\begin{aligned}
\delta S^{(1)} &= -\delta S^{(2)} \\
\delta V^{(1)} &= -\delta V^{(2)} \\
\delta n_1^{(1)} &= -\delta n_1^{(2)} \\
\delta n_2^{(1)} &= -\delta n_2^{(2)} \\
\vdots \quad & \quad \vdots \\
\delta n_r^{(1)} &= -\delta n_r^{(2)}
\end{aligned}$$

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,**

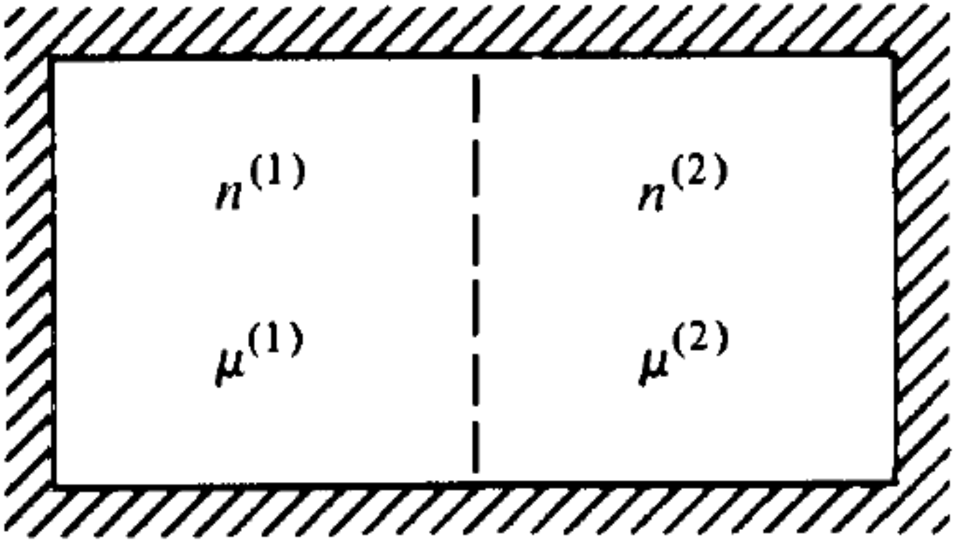
$$T^{(1)} = T^{(2)} = \cdots, = T^{(v)}$$

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

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

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

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

Further Discuss

- **Assuming displacements from equilibrium are small**

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

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

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

- **$\Delta S > 0$, 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.
- $-\nabla\left(\mu / T\right)$ is a generalized force.
- In the variant statement of the Second Law, we see a similar form,
- $-\nabla\left(1 / T\right)$ 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 ≤ I ≤ 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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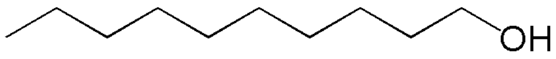
Introduction



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

$CH_3(CH_2)_nCH_2OH$

$n = 4\text{-}20$

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

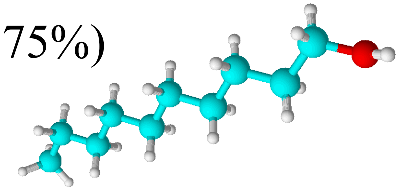
Ambrette seed

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

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

Ideal mixture:

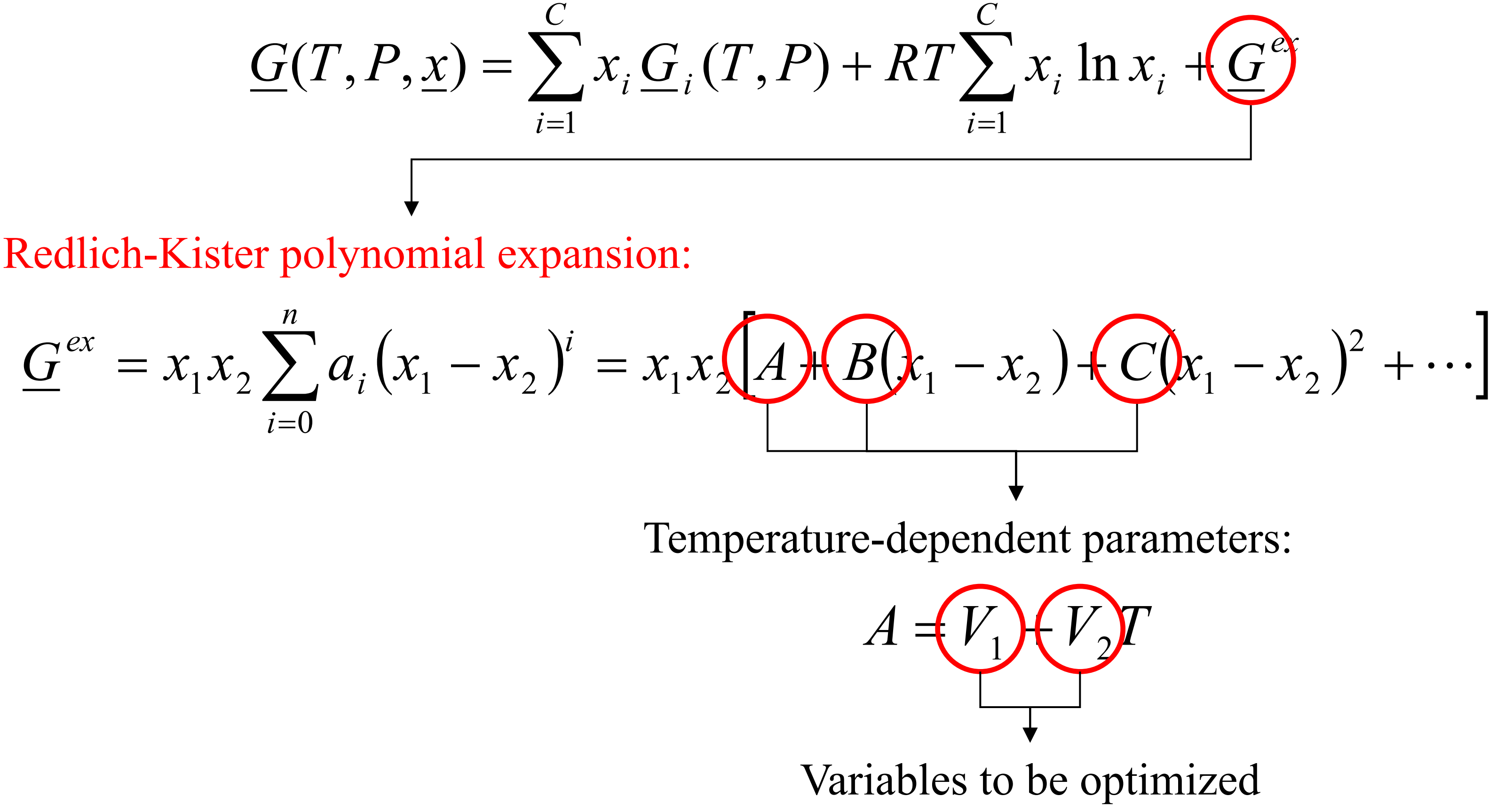
$$\underline{G}^{IM}(T,P,\underline{x}) = \sum_{i=1}^{C} x_i \underline{G}_i(T,P) + RT\sum_{i=1}^{C} x_i \ln x_i$$

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

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

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

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

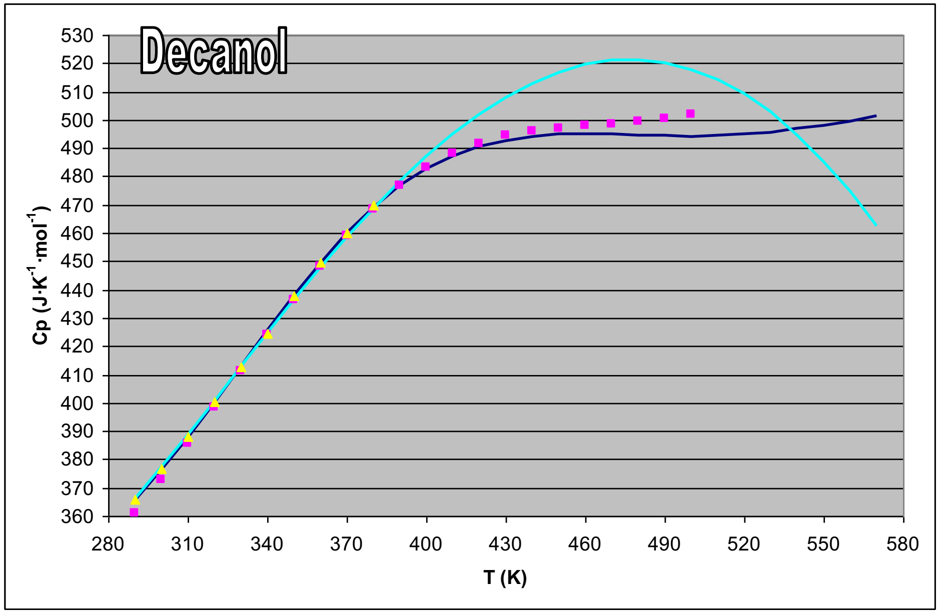
$$Cp_i^* = C_1 + C_2 T + C_3 T^2 + C_4 T^3$$

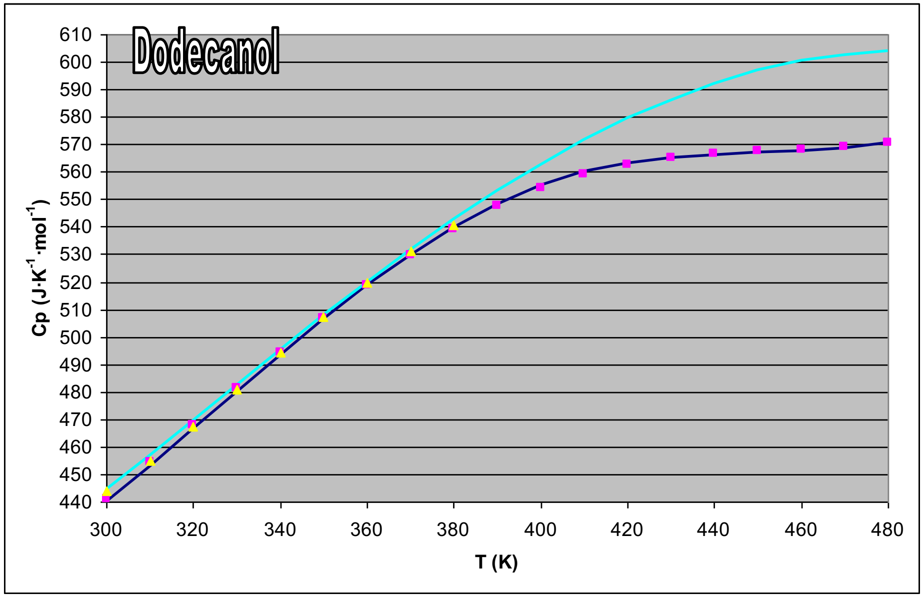
$$\Delta\underline{G}_i = -C_1 T \ln T + \left(-\frac{\Delta H_{i,T_{tr}}}{Tr} + C_1 + C_1 \ln T_{tr} + C_2 T_{tr} + \frac{C_3}{2} T_{tr}^2 + \frac{C_4}{3} T_{tr}^3\right) T -$$

$$-\frac{C_2}{2} T^2 - \frac{C_3}{6} T^3 - \frac{C_4}{12} T^4 + \left(\Delta H_{i,T_{tr}} - C_1 T_{tr} - \frac{C_2}{2} T_{tr}^2 - \frac{C_3}{3} T_{tr}^3 - \frac{C_4}{4} T_{tr}^4\right)$$

Dependence of heat capacities with temperature

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

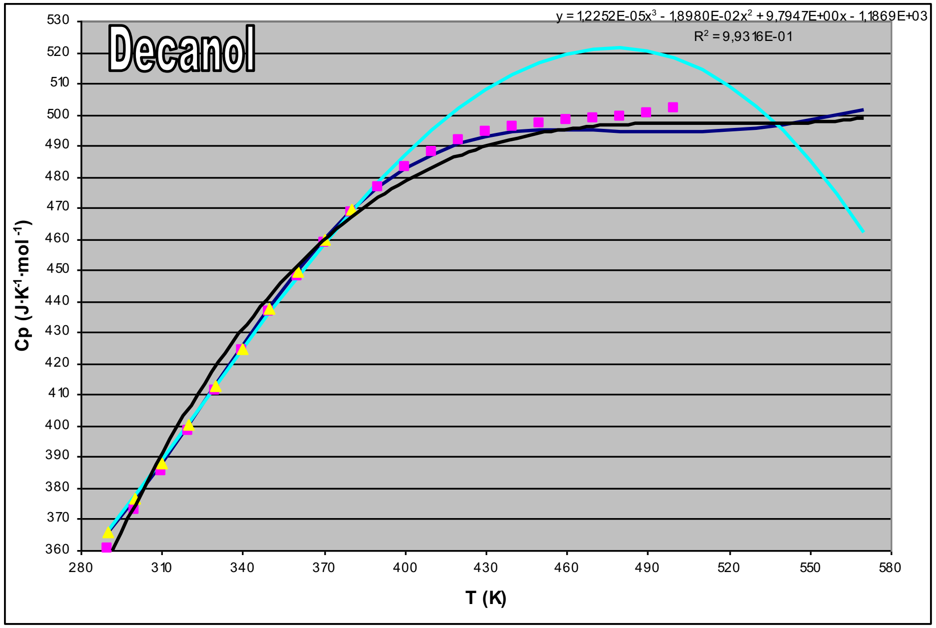


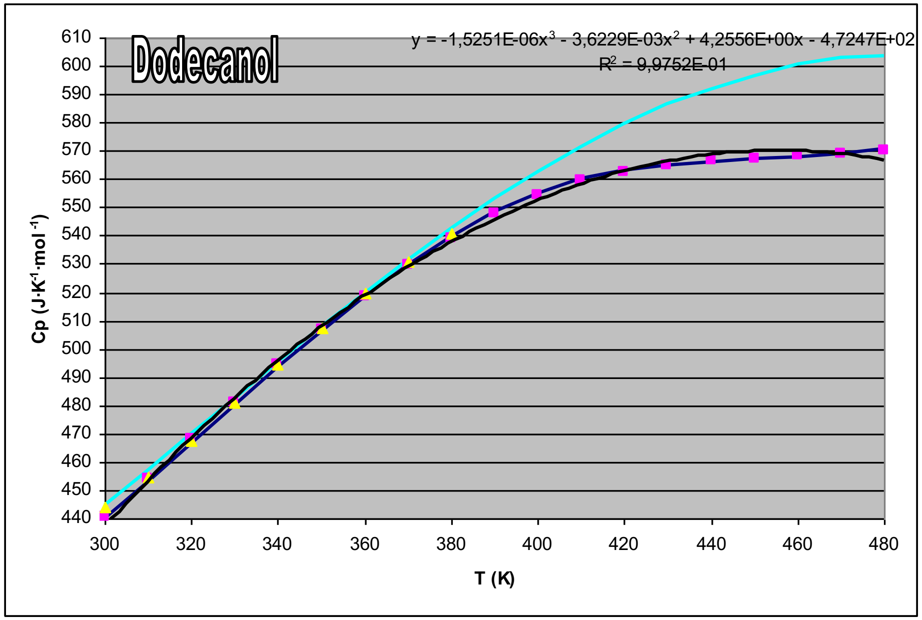


- Růžička (2004)
- ■ Zábranský (1990)
- ▲ Cees (2003)
- Equation

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

Dependence of heat capacities with temperature





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

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

— Růžička (2004)
■ Zábranský (1990)
▲ Cees (2003)
— Equation
— Polynomial (Růžička (2004))

Gibbs energy functions

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

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

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

$$\Big\downarrow$$

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

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

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

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

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

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

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

Gibbs energy functions of pure components

Experimental data

assessment

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**

• • •

⇩

Output:

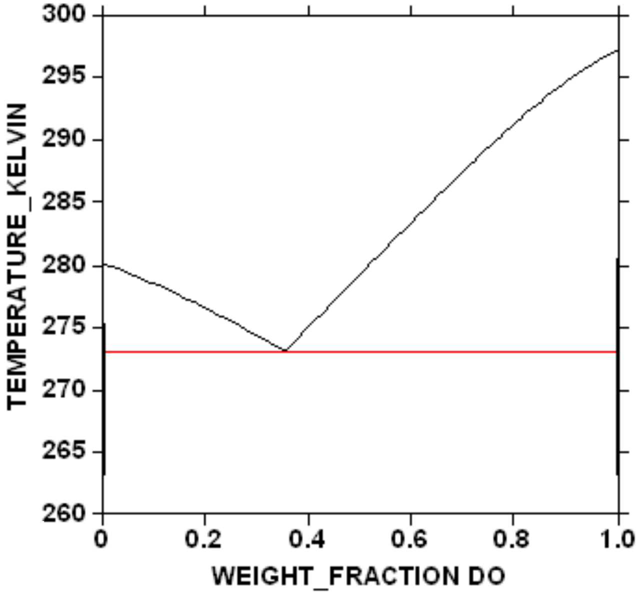
Variable	Value	*RSD*
V11	$3.57729450\cdot10^{4}$	$1.38374758\cdot10^{1}$
V12	$-1.32979526\cdot10^{2}$	2.88416718
V15	$-1.14258537\cdot10^{3}$	$7.16573950\cdot10^{1}$
V16	$5.70769803\cdot10^{1}$	$1.40175298\cdot10^{-2}$

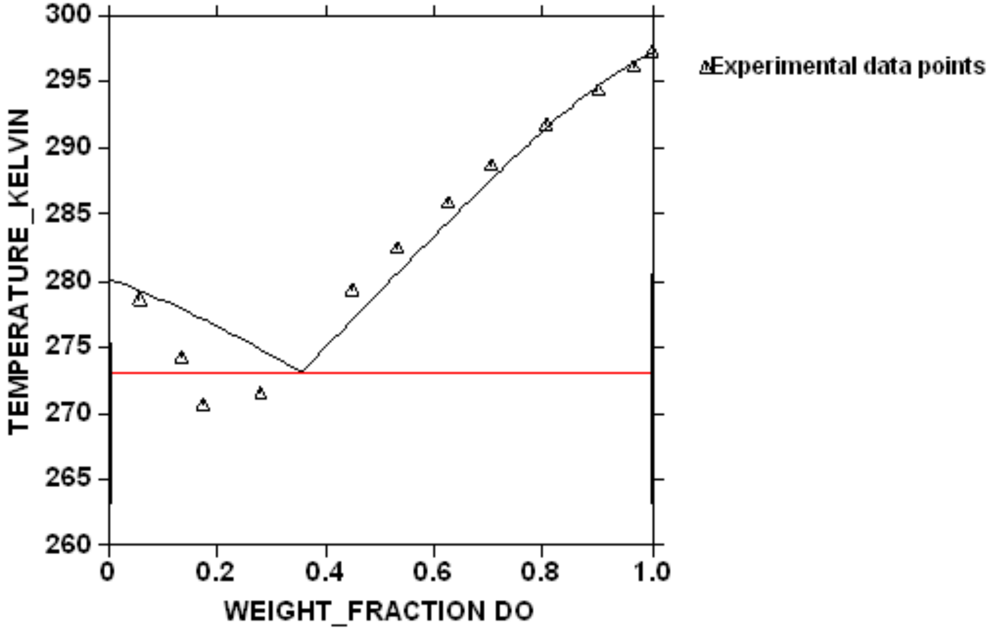
Reduced sum of squares: $1.0359\cdot10^{1}$

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

⇩

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)

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

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

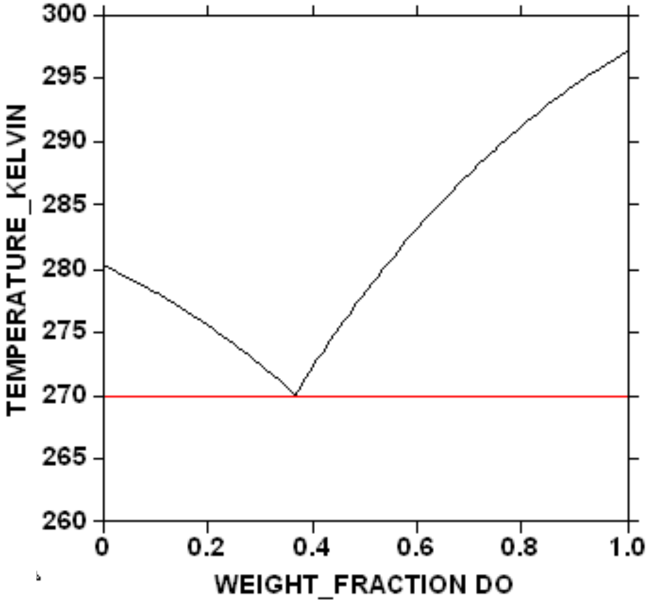
vs

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

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

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

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



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)

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

↓

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

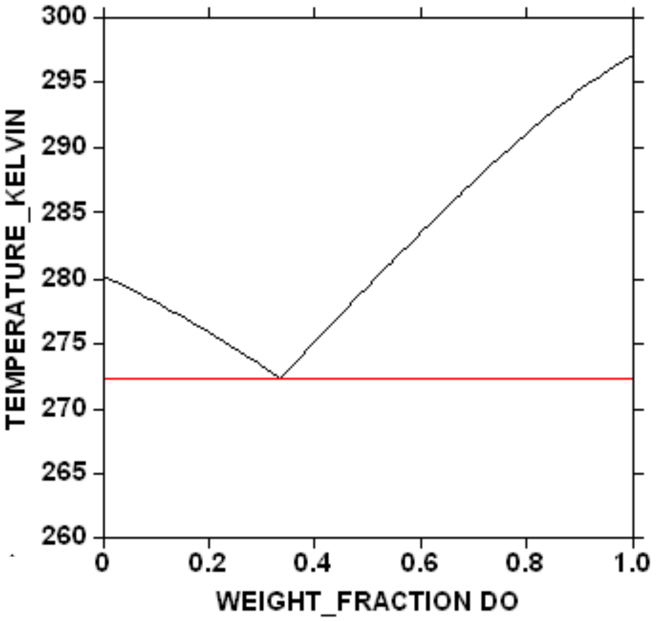
$$\Delta \underline{S}_{fus}(DO) = 29.4 cal \cdot K^{-1} mol^{-1}$$

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

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

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

⇩

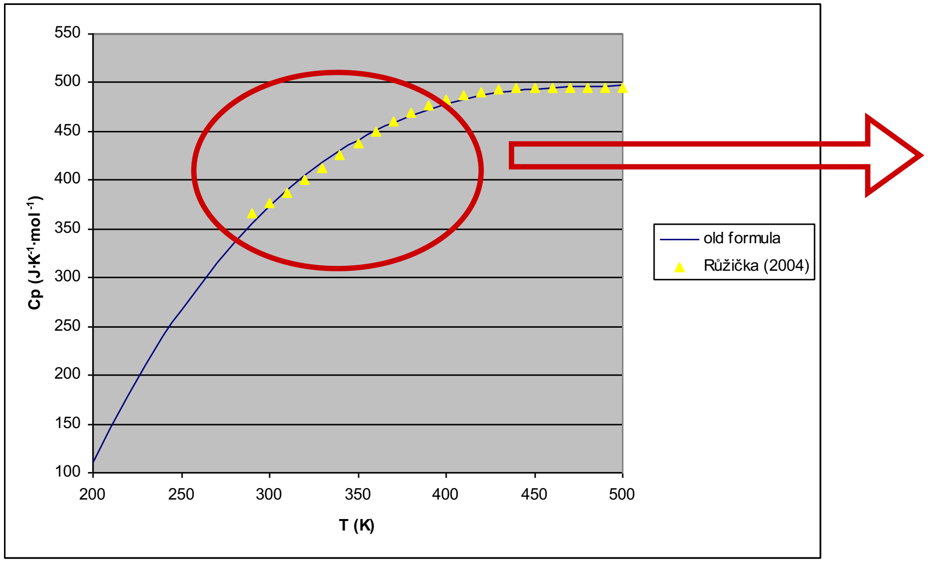


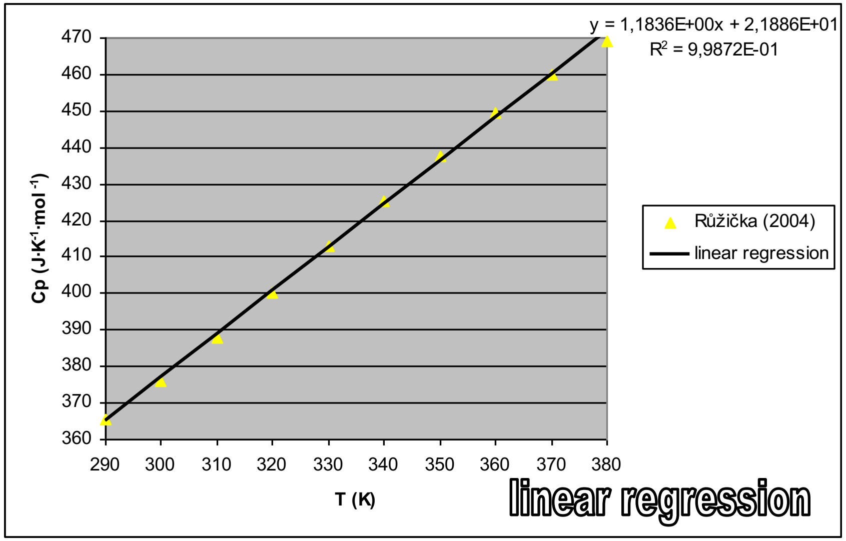
Variable	Value	RSD
V11	$2.78843867\cdot 10^{4}$	6.63622105
V12	$-1.01597519\cdot 10^{2}$	6.62042326
V15	$2.73701059\cdot 10^{1}$	$7.77898557\cdot 10^{6}$
V16	$5.56925163\cdot 10^{1}$	$1.33566753\cdot 10^{4}$

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

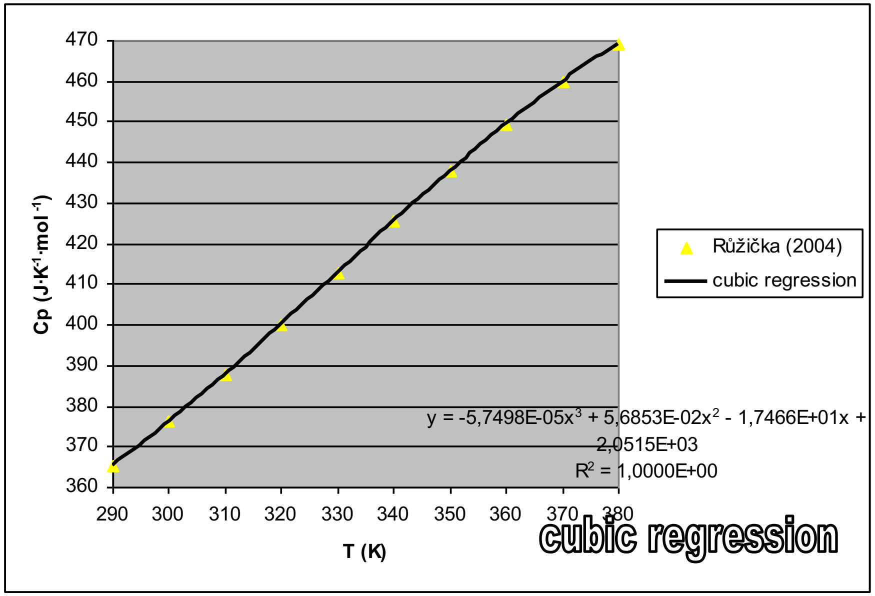
Possible causes of discrepancy

2. Heat capacities





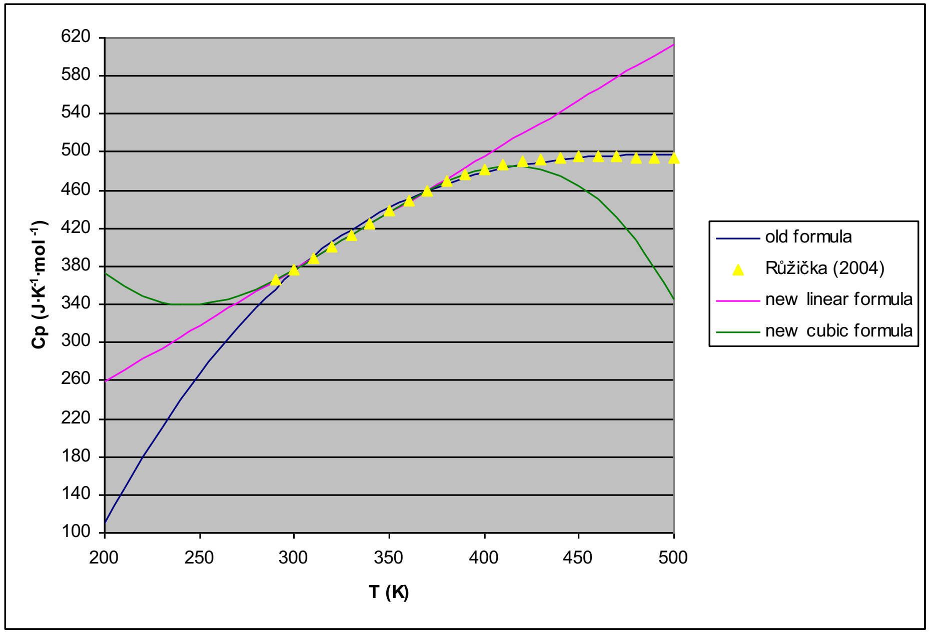
linear regression



cubic regression

Possible causes of discrepancy

2. Heat capacities



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

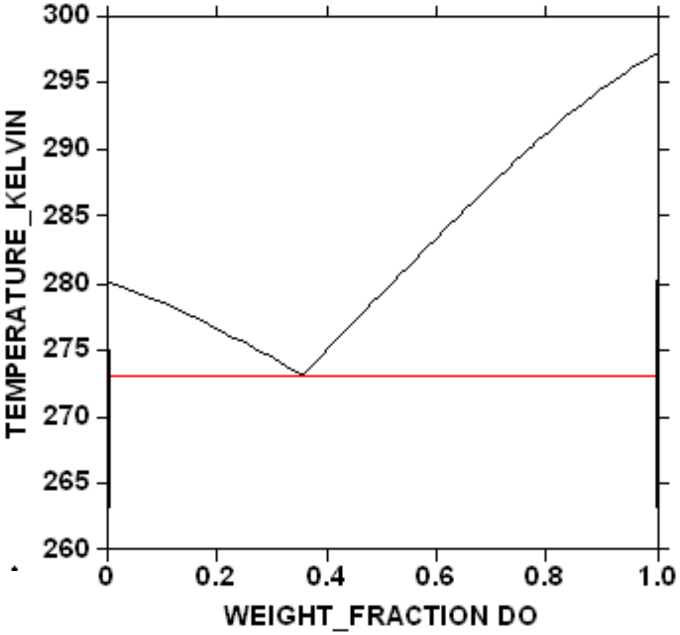
$$Cp^*_{DO} = 4.5191 \cdot 10^1 + 1.3169T$$

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

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

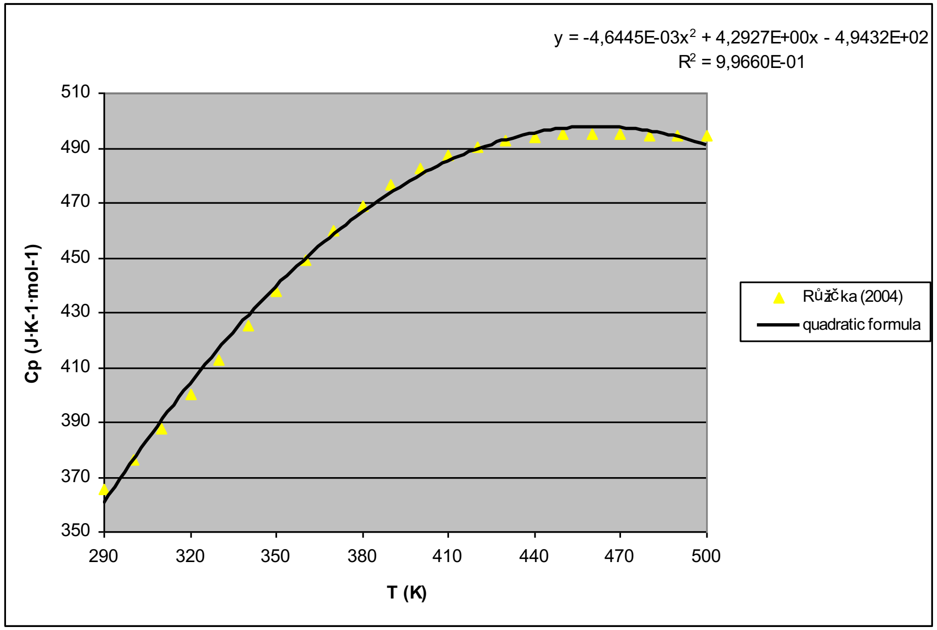
Variable	Value	RSD
V11	$3.45701098 \cdot 10^4$	5.35821836
V12	$-1.28415582 \cdot 10^2$	5.24342738
V15	$3.39538287 \cdot 10^{-4}$	$1.74739330 \cdot 10^{11}$
V16	$5.35786127 \cdot 10^1$	$3.90996426 \cdot 10^3$

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



Possible causes of discrepancy

2. Heat capacities



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	$6.12723859 \cdot 10^{1}$	$1.37118907 \cdot 10^{-1}$

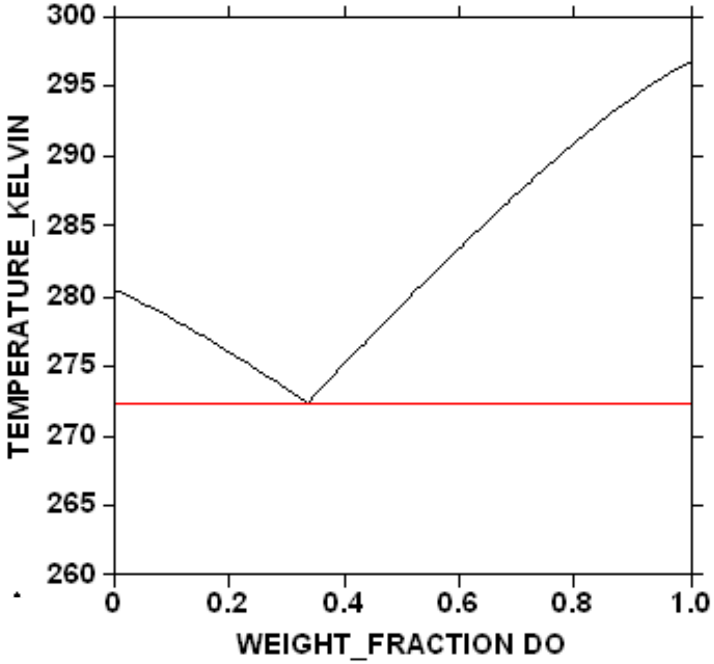
Reduced sum of squares: $4.33899 \cdot 10^{-3}$

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

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

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

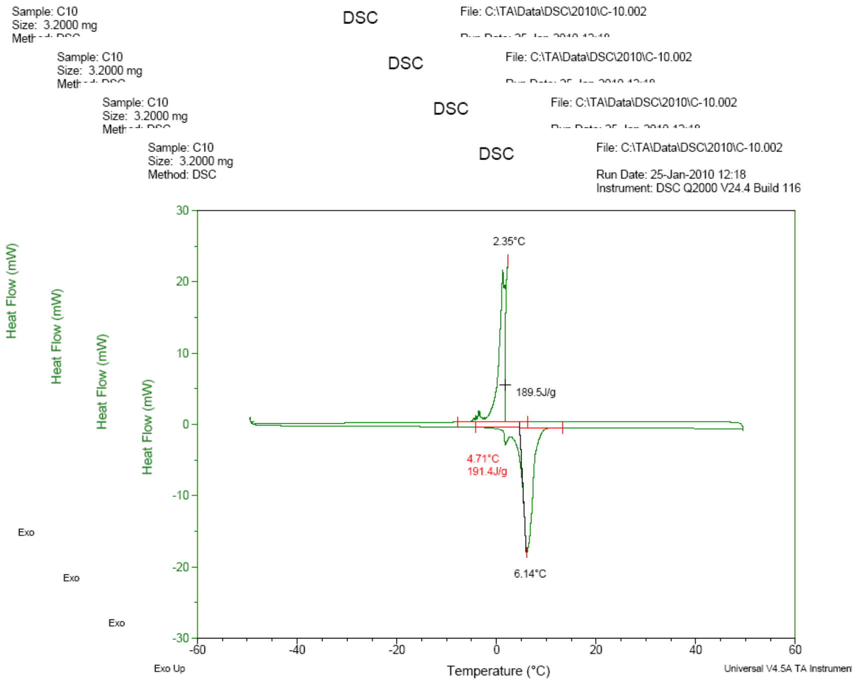
$$\underline{G}_{DO} = 559.74T \ln T - 2644.25T - 2.4717T^2 + 9.0122 \cdot 10^{-4} T^3 + 33202.86$$

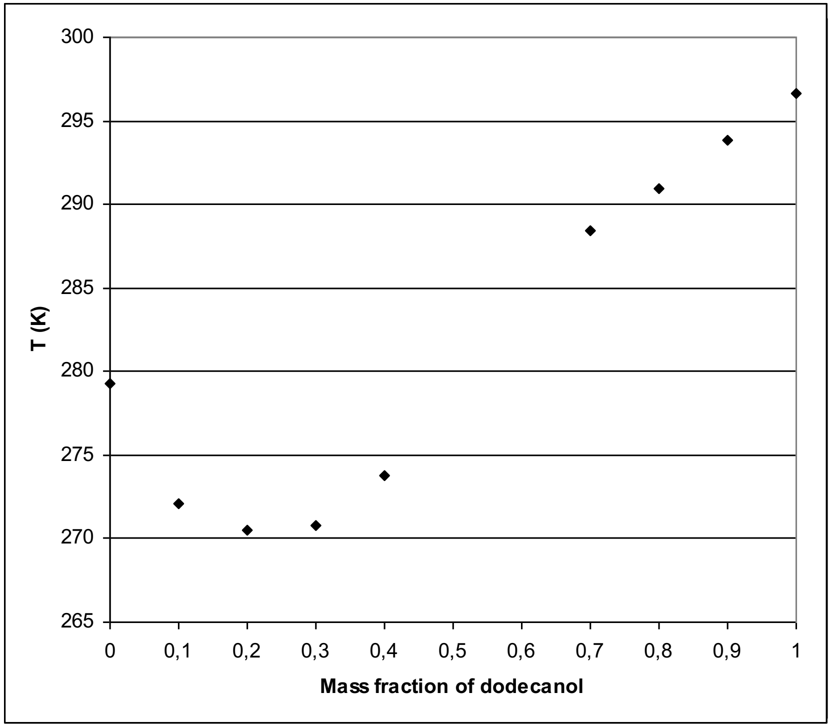


Possible causes of discrepancy

3. Experimental data

Differential Scanning Calorimetry (DSC)

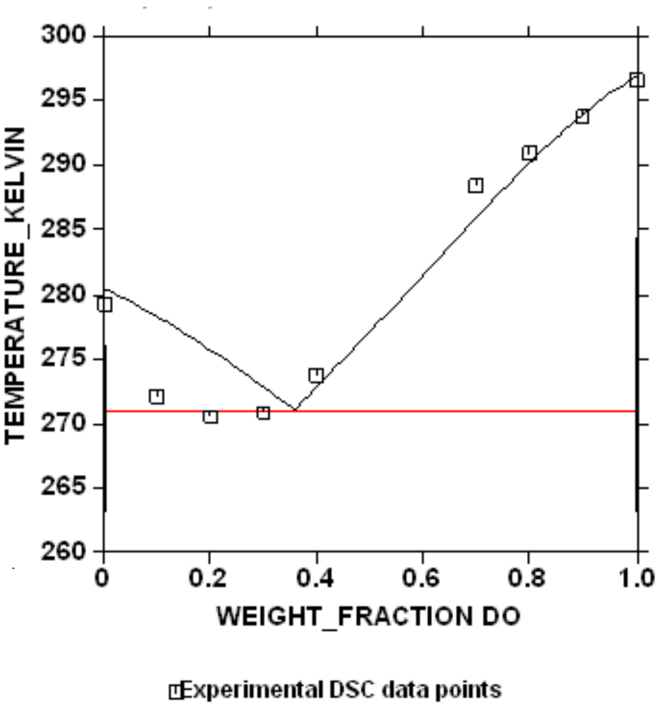




Possible causes of discrepancy

3. Experimental data points

new POP file



Variable	Value	RSD
V11	$4.30371467\cdot10^{4}$	$3.20019842\cdot10^{-1}$
V12	$-1.60697579\cdot10^{2}$	$3.12444640\cdot10^{-1}$
V15	$-1.24197073\cdot10^{-2}$	$1.04699276\cdot10^{2}$
V16	$4.69106820\cdot10^{1}$	$4.73816471\cdot10^{-1}$

Reduced sum of squares: $2.3402\cdot10^{2}$

Possible causes of discrepancy

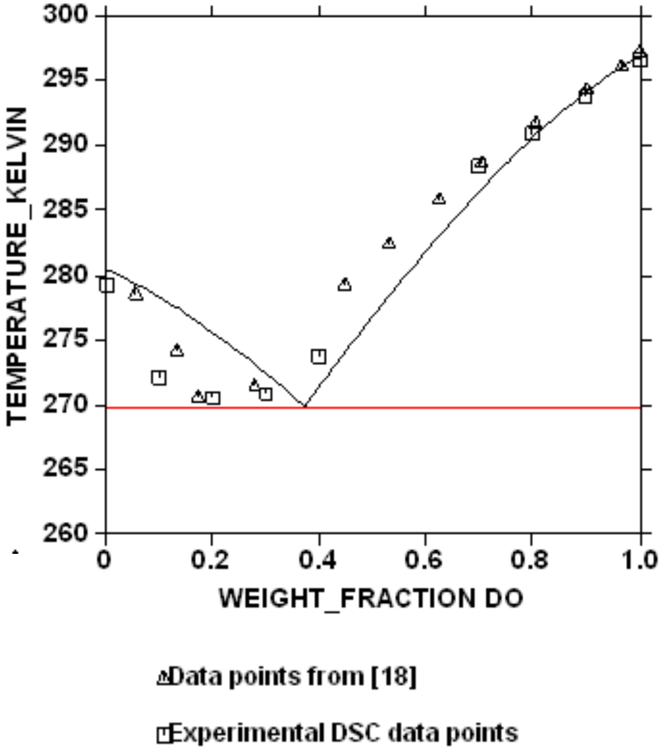
3. Experimental data points

Assessment with all the experimental data available

→

new POP file

↓



Variable	Value	RSD
V11	$2.12541399\cdot10^{4}$	$9.73327408\cdot10^{-1}$
V12	$-8.25529414\cdot10^{1}$	$9.51768718\cdot10^{-1}$
V15	$1.44869057\cdot10^{5}$	$4.25482680\cdot10^{1}$
V16	$-4.58345239\cdot10^{2}$	$4.51677061\cdot10^{1}$

Reduced sum of squares: $6.3462\cdot10^{2}$

Subregular Solution Model

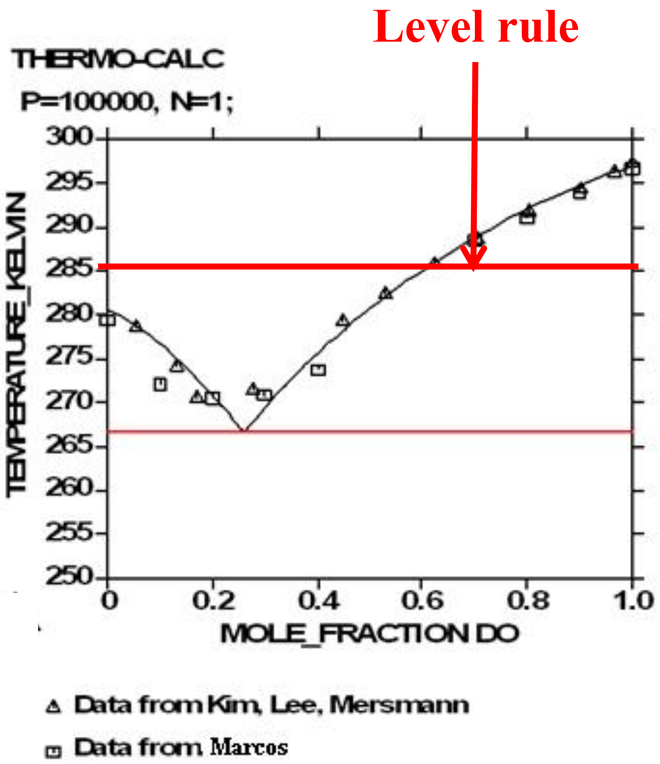
罗婕

4. Subregular Model

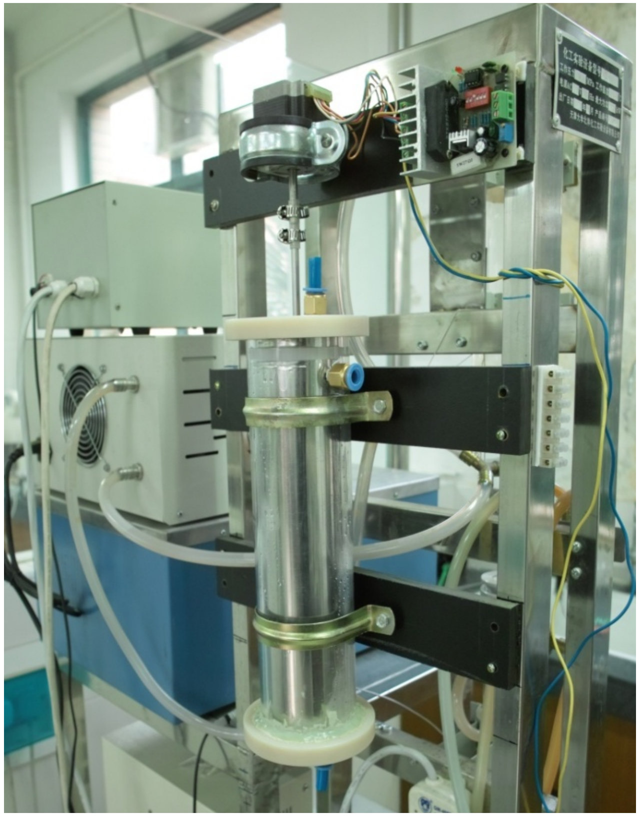
$$\lambda_{ij} = A_{ij} + B_{ij}(x_i - x_j)$$

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

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


Level rule

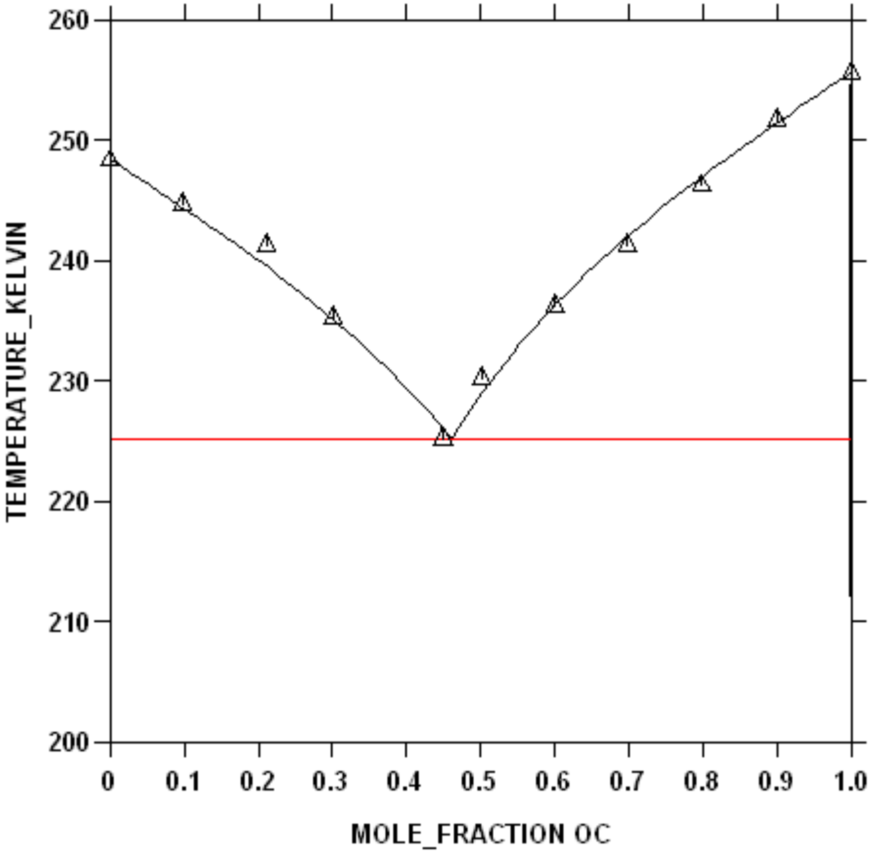
Continue Suspension Crystallization



Continue Suspension Crystallization

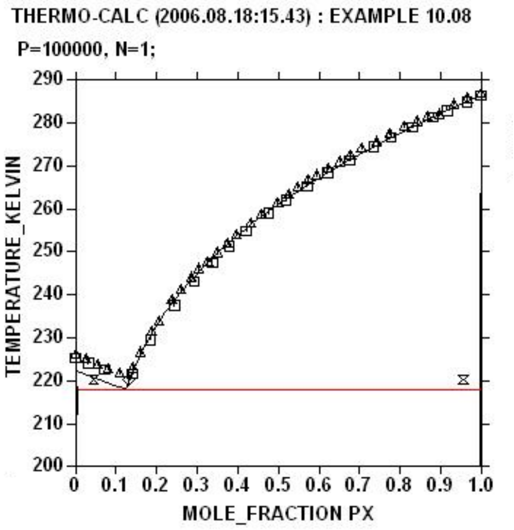
王文静

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

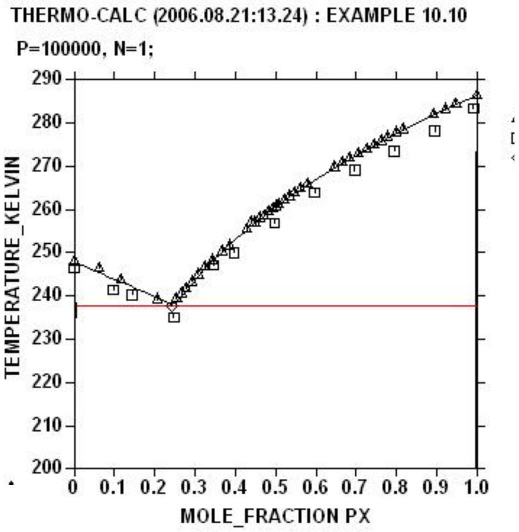


Continue Suspension Crystallization

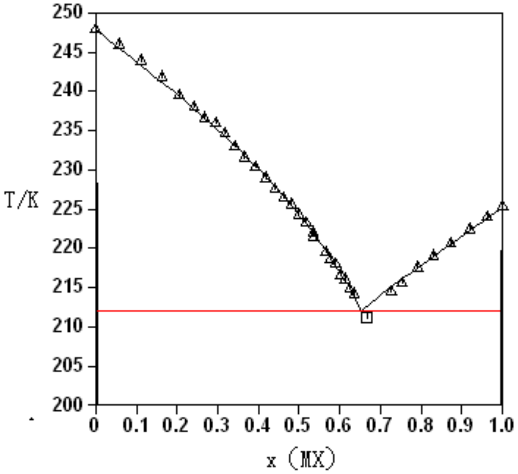
郭艳姿、郭思斯



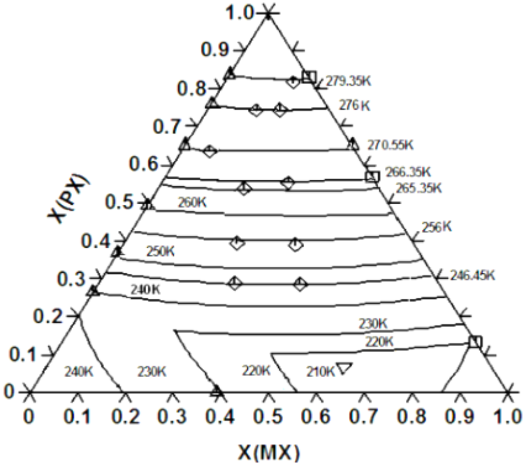
mX-pX



oX-pX



oX-mX



pX-mX-oX Ternary