Border-lines

26-02-28

$\mathrm{Tmo} := 100 \quad \mathrm{Kr} := 10 \quad \mathrm{Krs} := 5 \quad \mathrm{gamL} := 2 \quad p := 0.01 \,..\, 300 \quad v := .5, .501 \,..\, 1 \quad x := .5, .501 \,..\, 1$

1. Melting: **Lindemann -Form [Li1910]**

$\mathrm{TmLv}(v) := \mathrm{Tmo}\cdot v^{\mathrm{gamL}}$

[Li1910] F. A. Lindemann, Physik. Z.11, 609 (1910)

with the Murnaghan-EOS
[Li1910] gives
with the parametres

$$\mathrm{pM}(v) := \frac{\mathrm{Kr}}{\mathrm{Krs}}\cdot\left(v^{-\mathrm{Krs}} - 1\right) \qquad \mathrm{vM}(p) := \left(1 + p\cdot\frac{\mathrm{Krs}}{\mathrm{Kr}}\right)^{-\mathrm{Krs}^{-1}}$$

$\mathrm{LSG} := \mathrm{gamL}\cdot\mathrm{Krs}^{-1}$ and $\mathrm{rpM} := \mathrm{Krs}\cdot\mathrm{Kr}^{-1}$

The modified Lindemann -Form;

$\mathrm{TmLi}(p, \mathrm{gamL}) := \mathrm{Tmo}\cdot(1 + \mathrm{rpM}\cdot p)^{\mathrm{gamL}\cdot\mathrm{Krs}^{-1}}$

The Simon-Glatzel -Form [SG1929]
uses rpM with the free parameter LSG

$\mathrm{TmSG}(p, \mathrm{LSG}) := \mathrm{Tmo}\cdot(1 + \mathrm{rpM}\cdot p)^{\mathrm{LSG}}$

Simon F., Glatzel G.. Z.Anorg. Allg. Chem. 178, 309 (1929)

The less restricted Kechin-form [K19951]
uses two **free parameters: rpK and LK**

$\mathrm{TmKe}(p, \mathrm{Tmo}, \mathrm{rpK}, \mathrm{LK}) := \mathrm{Tmo}\cdot(1 + \mathrm{rpK}\cdot p)^{\mathrm{LK}}$

V. V. Kechin, J. Phys.: Condens. Matter 7, 531 (19951)
V. V. Kechin, Phys. Rev. B 65, 052102 (2001)

One reference point: $(\mathrm{pmr}, \mathrm{Tmr})$ $\mathrm{pmr} := 100$ $\mathrm{Tmr} := 400$ gives for **[SG1929]**

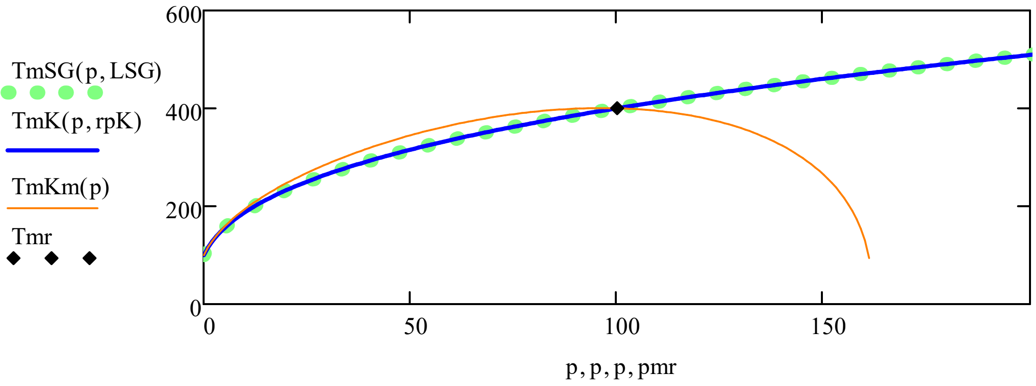
$\mathrm{LSG} := (\log(\mathrm{Tmr}) - \log(\mathrm{Tmo}))\cdot(\log(1 + \mathrm{rpM}\cdot\mathrm{pmr}))^{-1}$ and $\mathrm{gamL} := \mathrm{LSG}\cdot\mathrm{Krs} = 1.763$

and for [K19951]: LrK(rpK) $\quad \mathrm{LrK}(\mathrm{rpK}) := (\log(\mathrm{Tmr}) - \log(\mathrm{Tmo}))\cdot(\log(1 + \mathrm{rpK}\cdot\mathrm{pmr}))^{-1}$

with the free parameter rpK: $\quad \mathrm{rpK} := .5 \quad \mathrm{TmK}(p, \mathrm{rpK}) := \mathrm{Tmo}\cdot(1 + \mathrm{rpK}\cdot p)^{\mathrm{LrK}(\mathrm{rpK})}$

For melting with softening [K19951] **can be modified with parameters ds and qs:**

$\mathrm{ds} := .0001 \quad \mathrm{qs} := .4 \quad \mathrm{TmKm}(p) := \mathrm{TmK}(p, \mathrm{rpK})\cdot[1 + \mathrm{ds}\cdot p\cdot(\mathrm{pmr} - p)]^{\mathrm{qs}}$



Melting close to triple points requires an additional mixing-term !!!! **Example:**

at the tripel-point: $\mathrm{ptri} := 80$ $\mathrm{dpmi} := 15$ $\mathrm{Tmtri} := 200$ $\mathrm{dTmi} := 15$

Two melting-curves without mixing: $\mathrm{Tmo1} := \mathrm{Tmo}$ $\mathrm{rpK1} := .5$ $\mathrm{T12m} := \mathrm{Tmtri} + \mathrm{dTmi}$

$\mathrm{pmo2} := \mathrm{ptri}$ $\mathrm{Tmo2} := \mathrm{T12m}$ $\mathrm{rpK2} := .1$ $\mathrm{Tmr2} := 280$ $\mathrm{pmr2} := 150$

$$\mathrm{Tm1}(p,\mathrm{rpK1},b1) := \mathrm{Tmo1}\cdot(1 + p\cdot\mathrm{rpK1})^{b1}$$

$$\mathrm{LrK}(\mathrm{rpK1}) := (\log(\mathrm{T12m}) - \log(\mathrm{Tmo}))\cdot(\log(1 + \mathrm{rpK1}\cdot\mathrm{ptri}))^{-1} \qquad b1 := \mathrm{LrK}(\mathrm{rpK1}) = 0.206$$

$$\mathrm{Tm2}(p,\mathrm{rpK2},b2) := \mathrm{Tmo2}\cdot[1 + (p - \mathrm{ptri})\cdot\mathrm{rpK2}]^{b2}$$

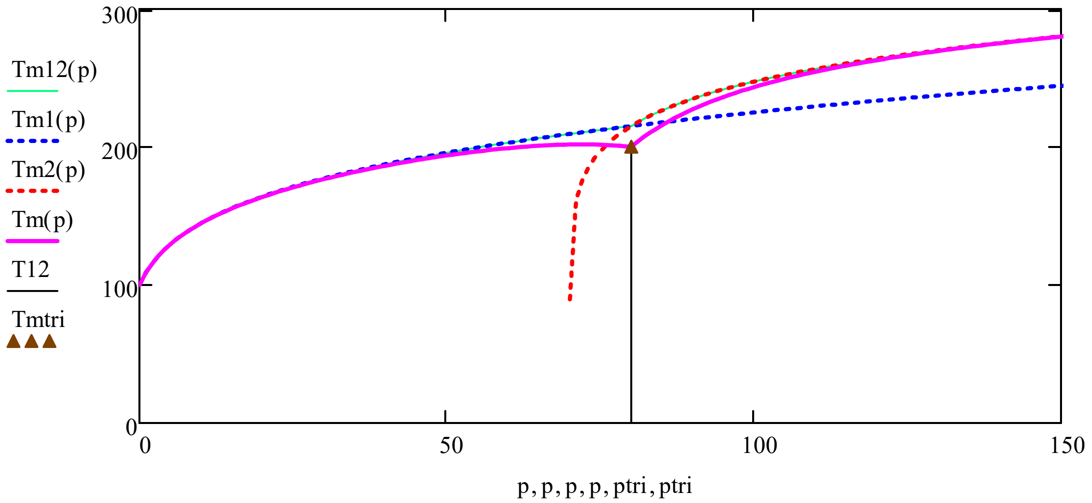
$$\mathrm{LrK2}(\mathrm{rpK2}) := (\log(\mathrm{Tmr2}) - \log(\mathrm{Tmo2}))\cdot[\log[1 + \mathrm{rpK2}\cdot(\mathrm{pmr2} - \mathrm{pmo2})]]^{-1} \qquad b2 := \mathrm{LrK2}(\mathrm{rpK2}) = 0.127$$

$$\mathrm{Tm1}(p) := \mathrm{Tm1}(p,\mathrm{rpK1},b1) \quad \mathrm{Tm2}(p) := \mathrm{Tm2}(p,\mathrm{rpK2},b2) \quad \mathrm{Tm12}(p) := \mathrm{wenn}(p < \mathrm{ptri},\mathrm{Tm1}(p),\mathrm{Tm2}(p))$$

Melting-curves with mixing:

$$\mathrm{pmi}(p) := \mathrm{wenn}(p < \mathrm{ptri},\mathrm{dpmi},-\mathrm{dpmi}) \qquad \mathrm{dTmip}(p) := -\mathrm{dTmi}\,\exp\left(\frac{p - \mathrm{ptri}}{\mathrm{pmi}(p)}\right)$$

$$\mathrm{Tm}(p) := \mathrm{Tm12}(p) + \mathrm{dTmip}(p) \qquad \mathrm{T12} := 0, 1 .. \mathrm{Tmtri}$$



2.Solid-Solid border-lines:

For thermodynamic equilibrium !!

From $\Delta G(p_{tr},T_{tr}) = 0$ we get: $dG(p_{trr}(T),T) / dT = \delta G / \delta T|_p + \delta G / \delta p|_T * dp_{tr}(T) / dT$

$= - S(p_{tr}(T),T) + V(p_{tr}(T),T) * dp_{tr}(T) / dT$

$$\mathbf{dp_{tr}(T) / dT = \Delta S(p_{tr}(T),T) / \Delta V(p_{tr}(T),T)} \quad \textbf{or}$$

$$\mathbf{dT_{tr}(p) / dp = \Delta V(T_{tr}(p),p) / \Delta S(T_{tr}(p),p)}$$

With the EOS for the phases 1 and 2 or i = 1...2
Vi(p,T) = Vi(p,0) x (1 + pthi(Vi(p,T),T) / Ki(p,T))

pth(V,T) = (γ(V)/V) x Uth(V,T) with scaled Debye function uD(T,θ(V))
Uth(V,T) = 3R x θ(V) x uD(T,θ(V)) and
Vi(p,T) = Vi(p,0) + dp_{tr}(T) / dT = $\Delta S(p_{tr}(T),T) / \Delta V(p_{tr}(T),T)$
or roughly with Vi

Vi(p,T) = Vi(p,0) + [3R x θ(Vi) x γ(Vi) / Ki(Vi)] x uD(T,θ(Vi))
this gives as good approximation for the Volume-difference with
[...] = ΔVD and an average ΘD:

$\Delta V_{tr}(T) = \Delta V_{tr}(0) + \Delta VD$ x uD(T,θD)
and similarily (with $\Delta S_{tr}(0) = 0$)
$\Delta S_{tr}(T) = \Delta SD$ x sD(T,θD) and finally with the 3 roughly constant parameters
ΘD, ΔSV0 = ΔSD/VoΔ , ΔVD0 = ΔVD/ΔVo and the two functions sD(T,θD) and uD(T,θD):

$$\mathrm{ptr}(T) := \Delta SV0 \cdot \int_0^{\Theta D} \frac{sD(T,\Theta D)}{1 + \Delta VD0 \cdot uD(T,\Theta D)}\, dT$$

Test of best form for ptr(T):

With the Einstein-Forms for $kB := 1 \quad TE := 100 \quad TD := 1.4 \cdot TE \qquad T := 1 .. 100$

$$FE(T,TE) := 3 \cdot kB \cdot T \cdot \ln\left(1 - \exp\left(\frac{-TE}{T}\right)\right) \qquad fE(T,TE) := T \cdot \ln\left(1 - \exp\left(\frac{-TE}{T}\right)\right)$$

$$SE(T,TE) := 3 \cdot kB \cdot \left[\frac{TE}{T} \cdot \exp\left(\frac{-TE}{T}\right) \cdot \left(1 - \exp\left(\frac{-TE}{T}\right)\right)^{-1} - \ln\left(1 - \exp\left(\frac{-TE}{T}\right)\right)\right]$$

$$UE(T,TE) := 3 \cdot kB \cdot TE \cdot \left(\exp\left(\frac{TE}{T}\right) - 1\right)^{-1} \qquad cE(T,TE) := 3 \cdot kB \cdot \left(\frac{TE}{T}\right)^2 \cdot \exp\left(\frac{TE}{T}\right) \cdot \left(\exp\left(\frac{TE}{T}\right) - 1\right)^{-2}$$

one obtaines the Debye-Forms for the border-lines:

$$FDn(T,TD) := 9 \cdot kB \cdot \frac{T}{TD^3} \cdot \int_1^{TD} TE^2 \cdot \ln\left(1 - \exp\left(\frac{-TE}{T}\right)\right) dTE$$

$$FD(T,TD) := 9 \cdot kB \cdot T \cdot \left(\frac{T}{TD}\right)^3 \cdot \int_0^{\frac{TD}{T}} z^2 \cdot \ln(1 - \exp(-z))\, dz$$

$$SD(T,TD) := 9\cdot kB\cdot\left(\frac{T}{TD}\right)^{3}\cdot\int_{0}^{\frac{TD}{T}} z^{2}\cdot\left[\frac{z}{(\exp(z)-1)}-\ln(1-\exp(-z))\right]dz$$

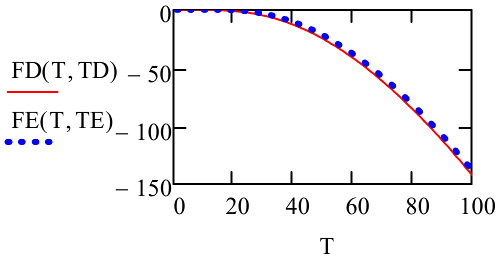
$$UDn(T,TD) := 9\cdot kB\cdot TD\cdot\frac{1}{TD^{4}}\cdot\int_{1}^{TD} TE^{3}\cdot\left(\exp\left(\frac{TE}{T}\right)-1\right)^{-1}dTE$$

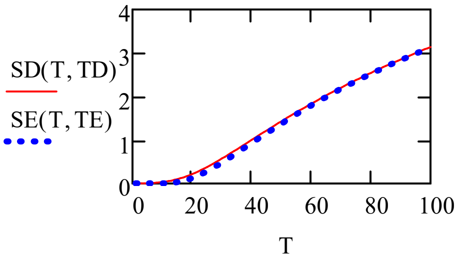
$$UD(T,TD) := 9\cdot kB\cdot T\cdot\left(\frac{T}{TD}\right)^{3}\cdot\int_{0}^{\frac{TD}{T}} z^{3}\cdot(\exp(z)-1)^{-1}dz$$

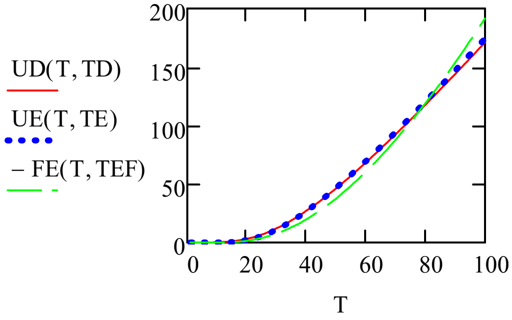
$$cDn(T,TD) := 9\cdot kB\cdot TD\cdot\frac{1}{T^{2}\cdot TD^{4}}\cdot\int_{1}^{TD} TE^{4}\cdot\exp\left(\frac{TE}{T}\right)\cdot\left(\exp\left(\frac{TE}{T}\right)-1\right)^{-2}dTE$$

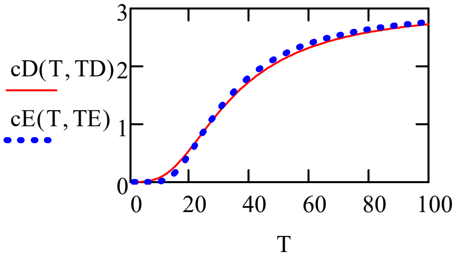
$$cD(T,TD) := 9\cdot kB\cdot\left(\frac{T}{TD}\right)^{3}\cdot\int_{0}^{\frac{TD}{T}} z^{4}\cdot\exp(z)\cdot(\exp(z)-1)^{-2}dz$$

$fe := .75$ $\qquad TEF := TE\cdot fe$









Test of best form for ptr(T) of page 4 indicates that UD(T,TD) can be replaced by -FE(TEF) and SD(T,TD) by SE(T,TEF) to give the following forms:

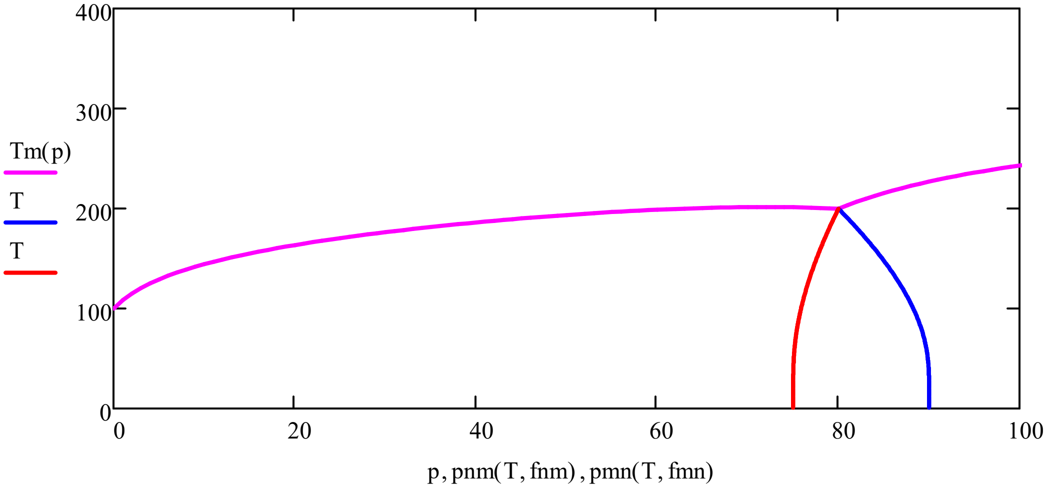
Limiting cases with almost constant : $\Delta V(p,T)$ $\qquad T := 1,2..Tmtri$ $\qquad pmtr := ptri = 80$

2a: ptr(T) for two cases (fmn<0 ,fnm >0) meeting the triple point with pnmo, Tnmo at the melting curve Tm(p) based on the following data:

$\mathrm{pnmo} := 90$ $\mathrm{fnm} := .01$ $\mathrm{Tnm} := 180$ $\mathrm{pmno} := 75$ $\mathrm{fmn} := -.01$ $\mathrm{Tmtri} = 200$

$\mathrm{pnm}(T,\mathrm{fnm}) := \mathrm{pnmo} + \mathrm{fnm}\cdot \mathrm{FE}(T,\mathrm{Tnm})$ $\mathrm{fnm} := \mathrm{wurzel}(\mathrm{pnm}(\mathrm{Tmtri},\mathrm{fnm}) - \mathrm{ptri},\mathrm{fnm}) = 0.032$

$\mathrm{pmn}(T,\mathrm{fmn}) := \mathrm{pmno} + \mathrm{fmn}\cdot \mathrm{FE}(T,\mathrm{Tnm})$ $\mathrm{fmn} := \mathrm{wurzel}(\mathrm{pmn}(\mathrm{Tmtri},\mathrm{fmn}) - \mathrm{ptri},\mathrm{fmn}) = -0.016$



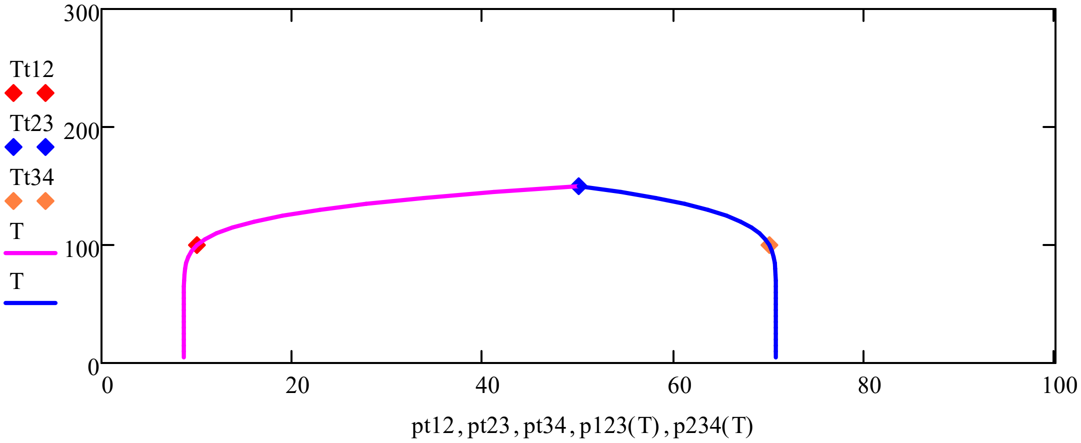
2b: ptr(T) reentrant case based on the following data:

$\mathrm{Tt12} := 100$ $\mathrm{Tt23} := 150$ $\mathrm{pt12} := 10$ $\mathrm{pt23} := 50$ $\mathrm{Tt34} := 100$ $\mathrm{pt34} := 70$ $\mathrm{Tnm} := 900$

$$\mathrm{p123}(T) := \mathrm{pt12} + (\mathrm{pt23} - \mathrm{pt12})\cdot\frac{\mathrm{FE}(T,\mathrm{Tnm}) - \mathrm{FE}(\mathrm{Tt12},\mathrm{Tnm})}{\mathrm{FE}(\mathrm{Tt23},\mathrm{Tnm}) - \mathrm{FE}(\mathrm{Tt12},\mathrm{Tnm})}$$

$T := 0, 5 .. \mathrm{Tt23}$

$$\mathrm{p234}(T) := \mathrm{pt34} + (\mathrm{pt23} - \mathrm{pt34})\cdot\frac{\mathrm{FE}(T,\mathrm{Tnm}) - \mathrm{FE}(\mathrm{Tt34},\mathrm{Tnm})}{\mathrm{FE}(\mathrm{Tt23},\mathrm{Tnm}) - \mathrm{FE}(\mathrm{Tt34},\mathrm{Tnm})}$$



2c: △V almost constant, △F(T) based on 1 average (like case 2a) or

$\mathrm{ptr} := \mathrm{ptri}$ $\mathrm{Ttr} := \mathrm{Tmtri}$ $\mathrm{DT} := 100$

$\mathrm{fnm} = 0.032$ $\mathrm{Tnm} := 180$ $\mathrm{pnmo} = 90$

2 individual Einstein functions(2c) with DT as difference to the single Tnm give no large difference in the fitted borderline

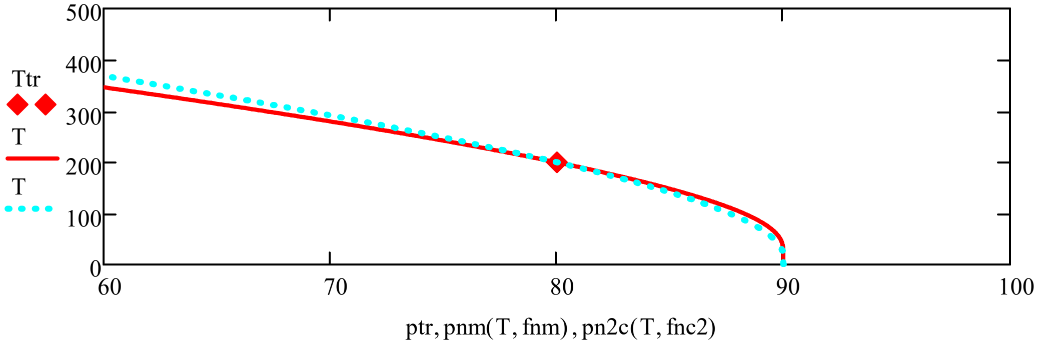
$\mathrm{Tnc1} := \mathrm{Tnm} + \mathrm{DT}$ $\mathrm{Tnc2} := \mathrm{Tnm} - \mathrm{DT}$

$\mathrm{fnc2} := .5 \cdot \mathrm{fnm}$

$T := 1, 2 .. 400$

$\mathrm{pn2c}(T, \mathrm{fnc2}) := \mathrm{pnmo} + \mathrm{fnc2} \cdot (\mathrm{FE}(T, \mathrm{Tnc1}) + \mathrm{FE}(T, \mathrm{Tnc2}))$

$\mathrm{fnc2} := \mathrm{wurzel}(\mathrm{pn2c}(\mathrm{Ttr}, \mathrm{fnc2}) - \mathrm{ptr}, \mathrm{fnc2}) = 0.012$



3: △V(T) variable by fv for reentrant phases and adjusted FET for ptr(T):

$\mathrm{Tt12} := 100$ $\mathrm{Tt23} := 142$ $\mathrm{pt12} := 10$ $\mathrm{pt23} := 40$ $\mathrm{Tnm} := 10$ $\mathrm{TnmV} := 200$ $\mathrm{fv} := .00051$

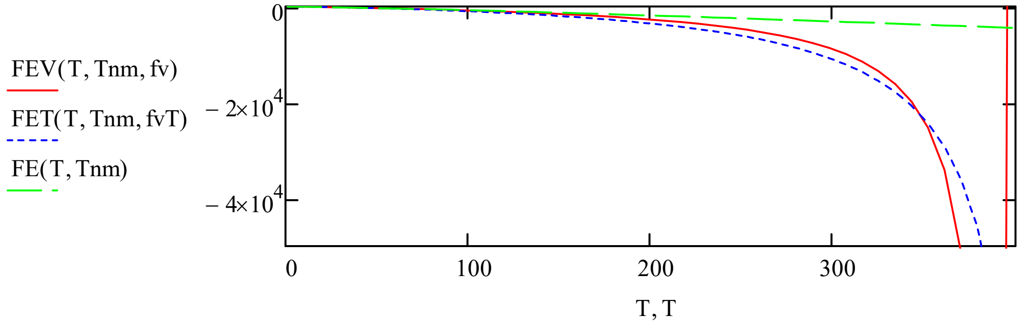
$\mathrm{Tt34} := 100$ $\mathrm{pt34} := 70$ $\mathrm{fv12} := .0026$ $\mathrm{fv34} := .0026$ $\mathrm{fvT} := .0024$

$T := 1, 10 .. 500$

$\mathrm{FEV}(T, \mathrm{Tnm}, \mathrm{fv}) := \mathrm{FE}(T, \mathrm{Tnm}) \cdot (1 - \mathrm{fv} \cdot T \cdot \mathrm{SE}(T, \mathrm{TnmV}))^{-1}$

$\mathrm{FET}(T, \mathrm{Tnm}, \mathrm{fv}) := \mathrm{FE}(T, \mathrm{Tnm}) \cdot (1 - \mathrm{fv} \cdot T)^{-1}$

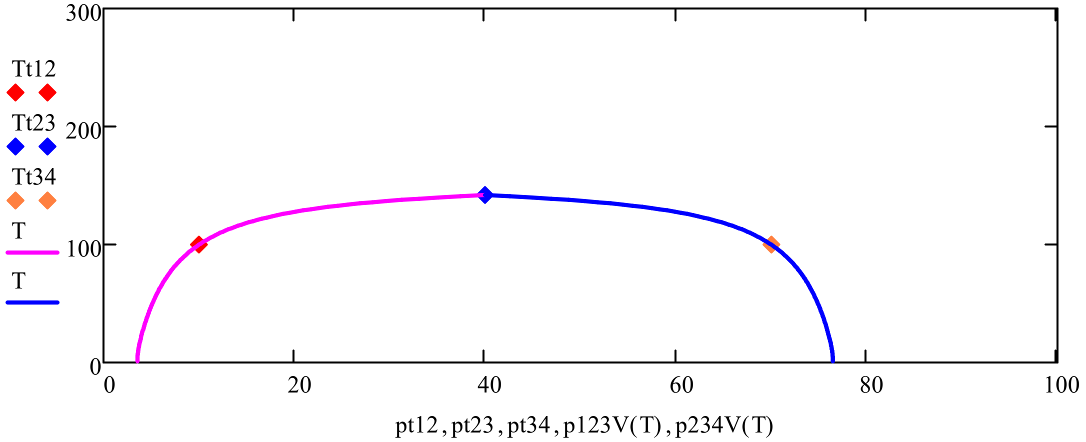
Constant SE (= 1) works well with adjusted fvT in FET(T,Tnm,fvT*)* !!!!!!



$T := 1, 2 .. \mathrm{Tt23}$

$$\mathrm{p123V}(T) := \mathrm{pt12} + (\mathrm{pt23} - \mathrm{pt12}) \cdot \frac{\mathrm{FEV}(T, \mathrm{Tnm}, \mathrm{fv12}) - \mathrm{FEV}(\mathrm{Tt12}, \mathrm{Tnm}, \mathrm{fv12})}{\mathrm{FEV}(\mathrm{Tt23}, \mathrm{Tnm}, \mathrm{fv12}) - \mathrm{FEV}(\mathrm{Tt12}, \mathrm{Tnm}, \mathrm{fv12})}$$

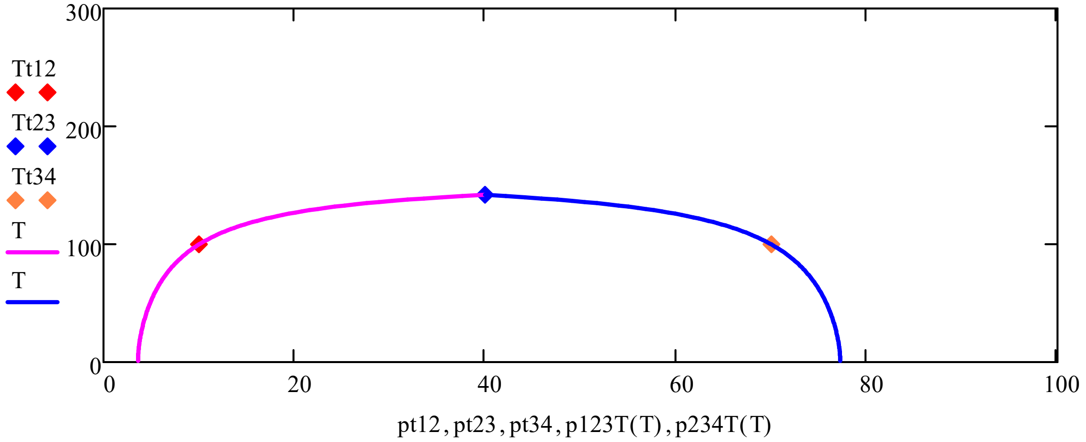
$$\mathrm{p234V}(T) := \mathrm{pt34} + (\mathrm{pt23} - \mathrm{pt34}) \cdot \frac{\mathrm{FEV}(T, \mathrm{Tnm}, \mathrm{fv34}) - \mathrm{FEV}(\mathrm{Tt34}, \mathrm{Tnm}, \mathrm{fv34})}{\mathrm{FEV}(\mathrm{Tt23}, \mathrm{Tnm}, \mathrm{fv34}) - \mathrm{FEV}(\mathrm{Tt34}, \mathrm{Tnm}, \mathrm{fv34})}$$



$fv12 := .0063$ $fv34 := .0062$

$$p123T(T) := pt12 + (pt23 - pt12)\cdot\frac{FET(T, Tnm, fv12) - FET(Tt12, Tnm, fv12)}{FET(Tt23, Tnm, fv12) - FET(Tt12, Tnm, fv12)}$$

$$p234T(T) := pt34 + (pt23 - pt34)\cdot\frac{FET(T, Tnm, fv34) - FET(Tt34, Tnm, fv34)}{FET(Tt23, Tnm, fv34) - FET(Tt34, Tnm, fv34)}$$

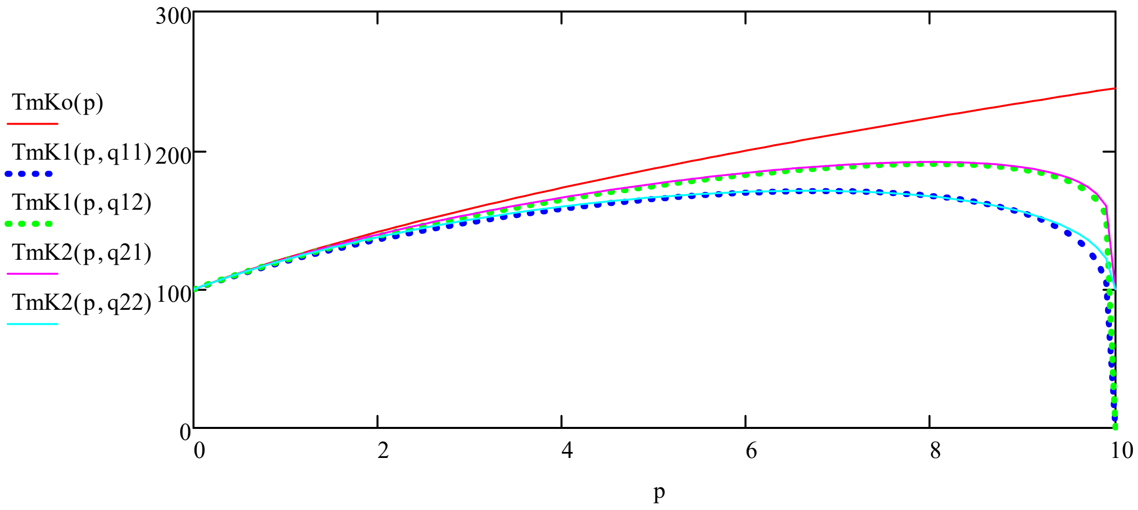


Kechin-form: $TmKo(p) := Tmo\cdot(1 + qa\cdot p)^{qb}$ $Tmo := 100$ $qa := .5$ $qb := .5$ $qt := .1$

$p := 0, .1 .. 10$

Modified for phase transitions: $TmK1(p, q1) := Tmo\cdot(1 + qa\cdot p)^{qb}\cdot(1 - p\cdot qt)^{q1}$

$q11 := .18$ $q12 := .1$ $q21 := .25$ $q22 := .5$ $TmK2(p, q2) := Tmo\cdot\left[1 + qa\cdot p\cdot(1 - p\cdot qt)^{q2}\right]^{qb}$


300
200
100
0
TmKo(p)
TmK1(p, q11)
TmK1(p, q12)
TmK2(p, q21)
TmK2(p, q22)
0
2
4
6
8
10
p