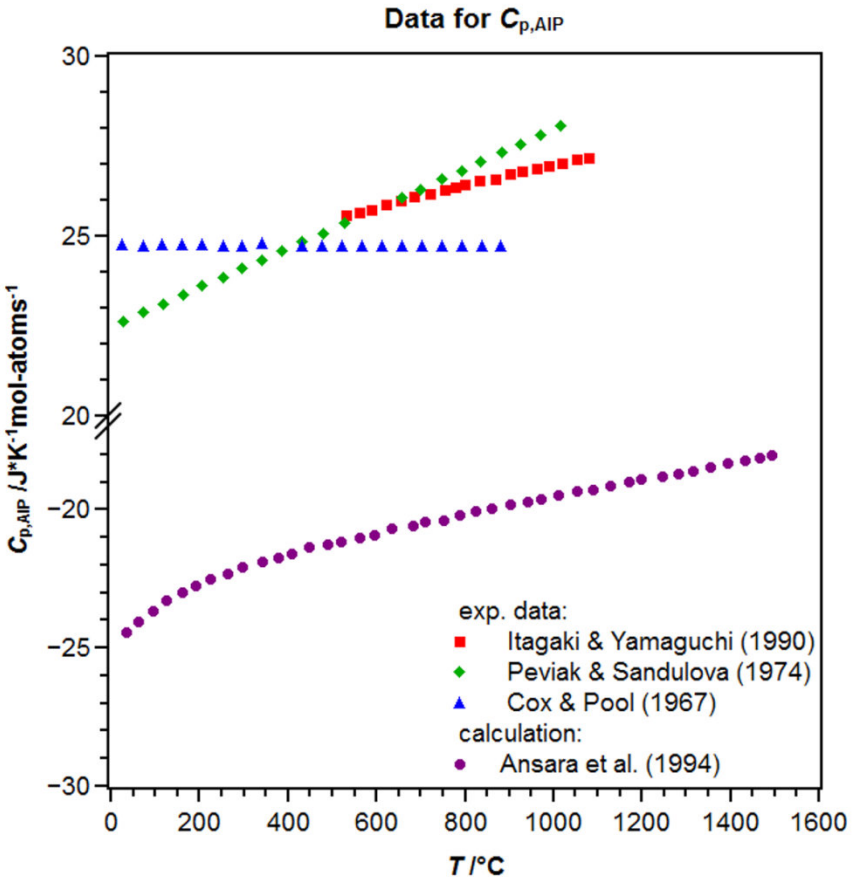
Reassessing the reassessment of the Al-P System

Klaus Hack & Michael Schick, GTT-Technologies, Herzogenrath, Germany

System Al-P: Ansara et al.

description of Ansara et al. [94Ans] produces *negative* values of c_p(AlP) over the whole T-range.



exp. data:

Cox & Pool ⇒ constant, data for low T

Peviak & Sandulova ⇒ linear, positive slope, data for low T

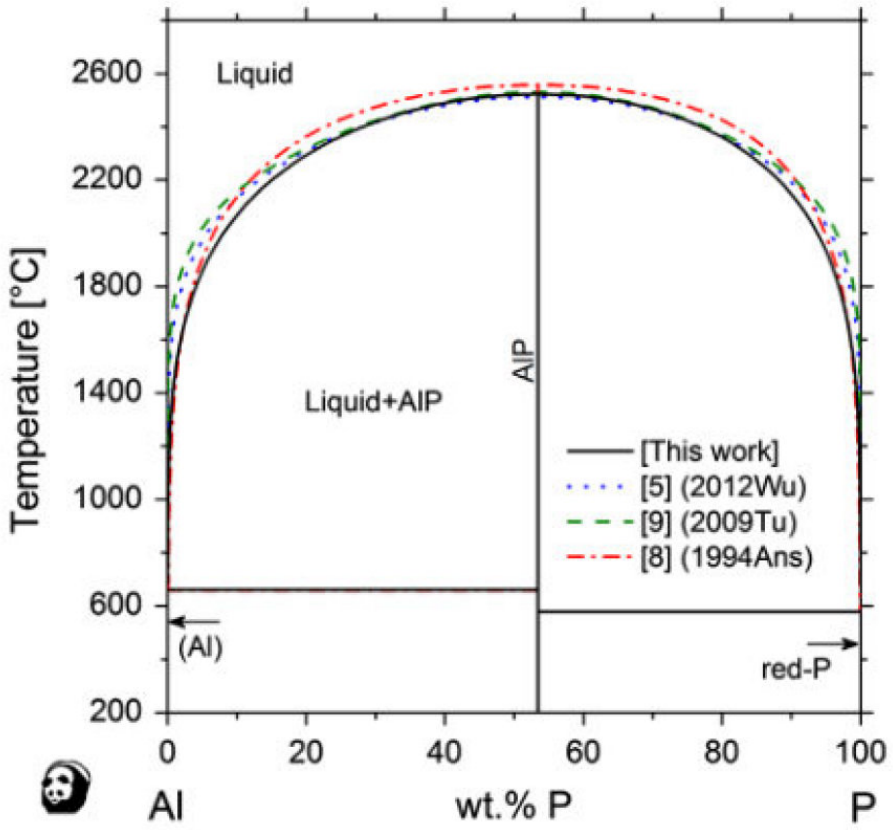
Itagaki & Yamaguchi ⇒ linear, positive slope, limited T-range

[94Ans]:
L. Ansara, C. Chatillon, H.L. Lukas, T. Nishizawa, H. Ohtani, K. Ishida, M. Hillert, B. Sundman, B.B. Argent, A. Watson, T.G. Chart, T. Anderson, Calphad 18 (1994) 177

System Al-P: Liang & Schmid-Fetzer

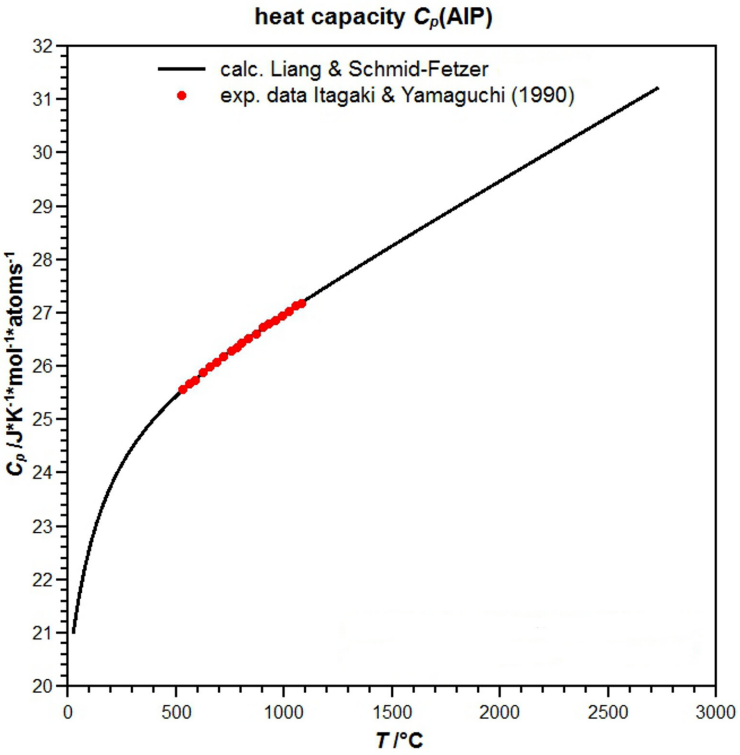
new thermodynamic assessment in:
S.-M. Liang, R. Schmid-Fetzer, Calphad **42** (2013) 76-85

authors go back to original experimental data. Only external data used are from SGTE Unary. However, there are no gas data in SGTE Unary !



System Al-P: Liang & Schmid-Fetzer

new thermodynamic description of AlP:

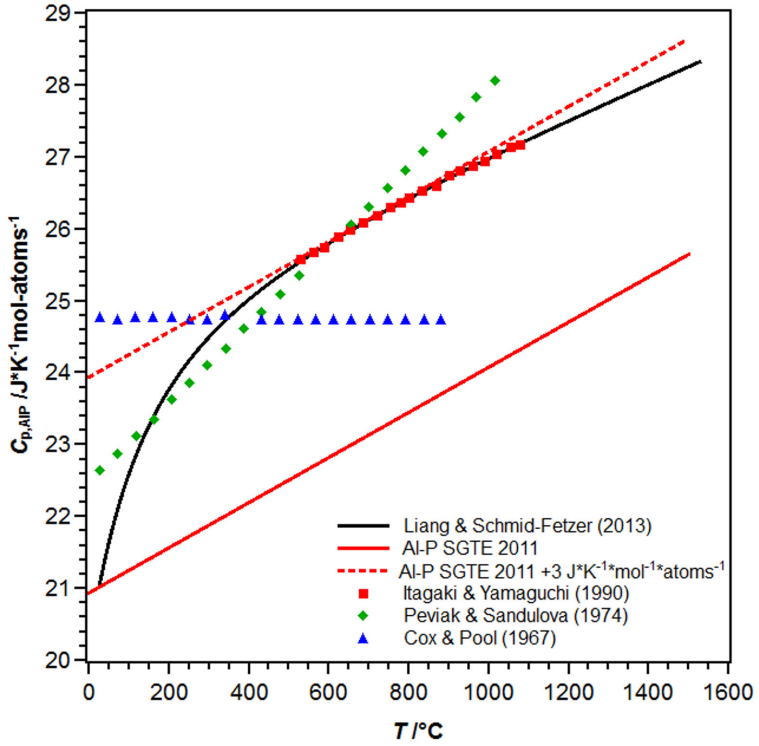


exp. data from Itagaki & Yamaguchi considered best by Liang & Schmid-Fetzer, curve fits data excellently

$$c_P^{AlP} = 48.4 + 4.7 \cdot 10^{-3} T - 690000 \cdot T^{-2}$$

System Al-P: Liang & Schmid-Fetzer

comparison of c_p(AlP)



c_p - curves of Ansara & Schmid-Fetzer show similar shape

c_p(AlP),Ansara + const.,
c_p(AlP),SGTE 2011 + const'.
fit well exp. data from Itagaki & Yamaguchi

System Al-P: Liang & Schmid-Fetzer

thermodynamic modeling of **liquid phase**:
LIQUID $(Al,P)_1$:

$$G_i^{0,liq}(T) = G_i^{liq}(T) - H_i^{SER}$$
$$= a + b\cdot T + c\cdot T\ln T + d\cdot T^2 + e\cdot T^3 + f\cdot T^{-1} + g\cdot T^7 + h\cdot T^{-9}$$

i = Al,P; *G*-functions according to SGTE [91Din].

Regular liquid interaction using exp-function as proposed by Kaptay to prevent inverse miscibility-gap:

$${}^0L_{Al,P}^{liq} = -133862\cdot e^{-\frac{T}{1000K}}$$

This *T* dependence is not used in any of the SGTE databases and is not permitted in FactSage
⇨ ***L*-parameter needs to be refitted !**

[91Din]: A.T. Dinsdale, Calphad 15 (1991) 317

System Al-P: Liang & Schmid-Fetzer

thermodynamic modeling of **gas phase**:
GAS (Al, Al_2, P, P_2, P_4)$_1$ ideal mixing

$$G_i^{0,liq}(T) = G_i^{liq}(T) - H_i^{SER}$$
$$= a + b\cdot T + c\cdot T\ln T + d\cdot T^2 + e\cdot T^3 + f\cdot T^{-1} + RT\ln(10^{-5}\cdot p)$$

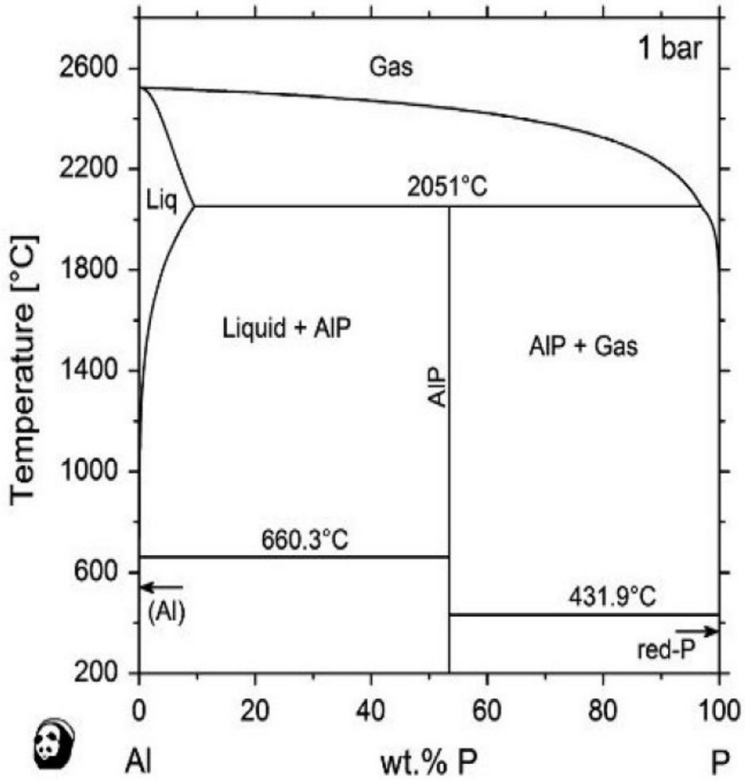
i = Al, Al_2, P, P_2, P_4;

G-functions not from SGTE Pure Substance database!

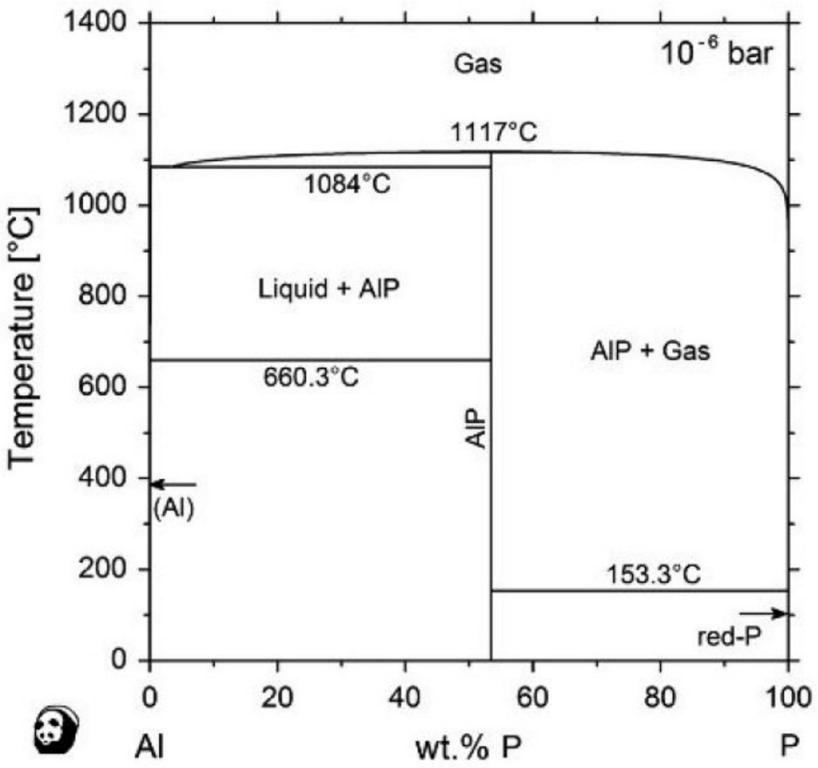
Instead, data were taken from literature:
M. Bennewies, E. Milke, *Thermochemical data of elements and compounds, 2nd Ed.,* Wiley-VCH, Weinheim 2002

System Al-P: Liang & Schmid-Fetzer

original phase diagram from publ. Liang & Schmid-Fetzer incl. gas phase for variable total pressure of gas phase (p_{tot})



no congruent subl. of AlP for p_{tot} = 1 bar

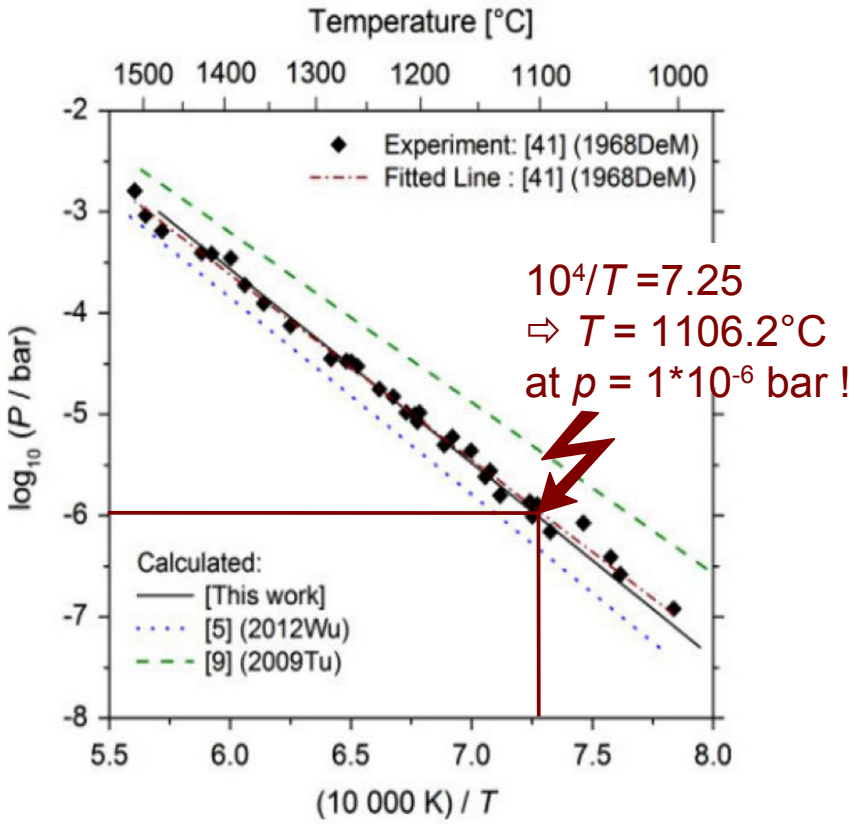


congruent subl. of AlP for $p_{tot} = 10^{-6}$ bar at T = 1117°C

System Al-P: Liang & Schmid-Fetzer

GTT-Technologies

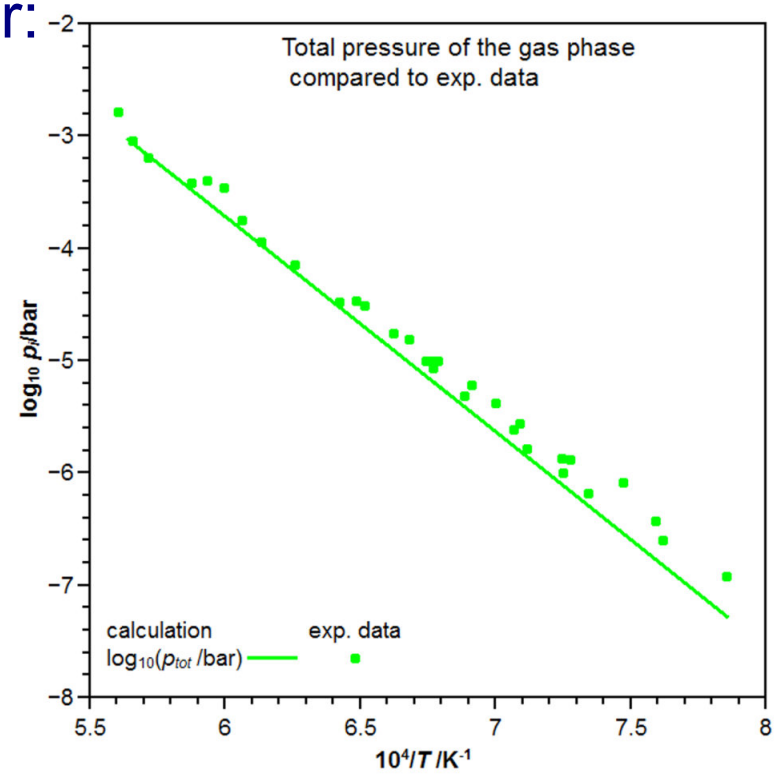
congruent sublimation of AlP for $p_{tot}=10^{-6}$ bar:



$10^4/T = 7.25$
⇨ T = 1106.2°C
at $p = 1*10^{-6}$ bar !

issue: T_{sub} = 1117°C
is not reproduced !

vapour pressure curve calculated with data from Liang & Schmid-Fetzer:



issue: mismatch of curve and exp. data !

Corrigendum: Liang & Schmid-Fetzer

corrigendum has been published by the authors:

S.-M. Liang, R. Schmid-Fetzer, Calphad **45** (2014) 251-253

reason for the shifted vapour pressure curve:
wrong entropy related parameter in G^0(AlP)

$$G^0_{AlP} = -180154 + \mathbf{293.45 \cdot T} - 48.40 \cdot T \ln T - 2.35 \cdot 10^{-3} \cdot T^2 + 3.45 \cdot 10^5 \cdot T^{-1}$$

⇒ entropy S^{298}_{AlP} has to be corrected, too:

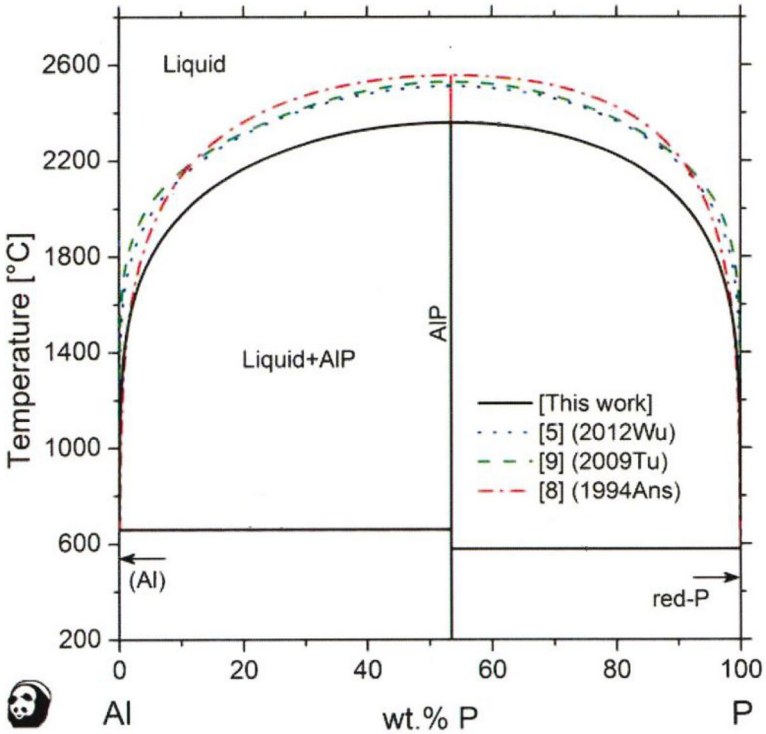
$$S^{298}_{AlP} = \mathbf{18}\ J \cdot K^{-1} \cdot mol^{-1}$$

this value is significantly lower than all experimental and calculated data from other groups

Corrigendum: Liang & Schmid-Fetzer

Adjustment of the phases LIQUID and FCC_A1 as well:

$${}^{0}L^{liq}_{Al,P} = -151900 \cdot e^{-\frac{T}{800K}} \qquad {}^{0}L^{fcc}_{Al,P} = \mathbf{-25500} \text{ to } -51500$$



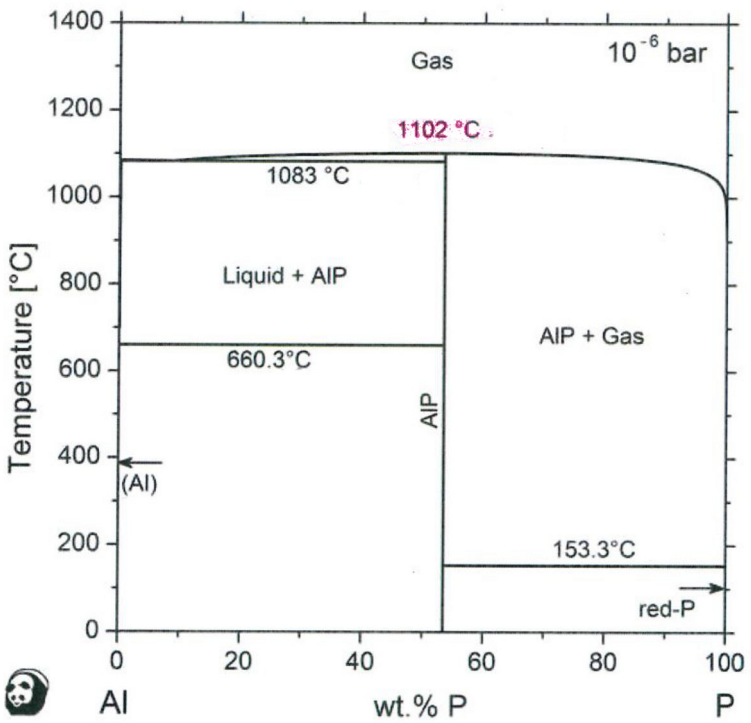
Al-P phase diagram, calculated by Liang & Schmid-Fetzer after correction, gas phase suppressed

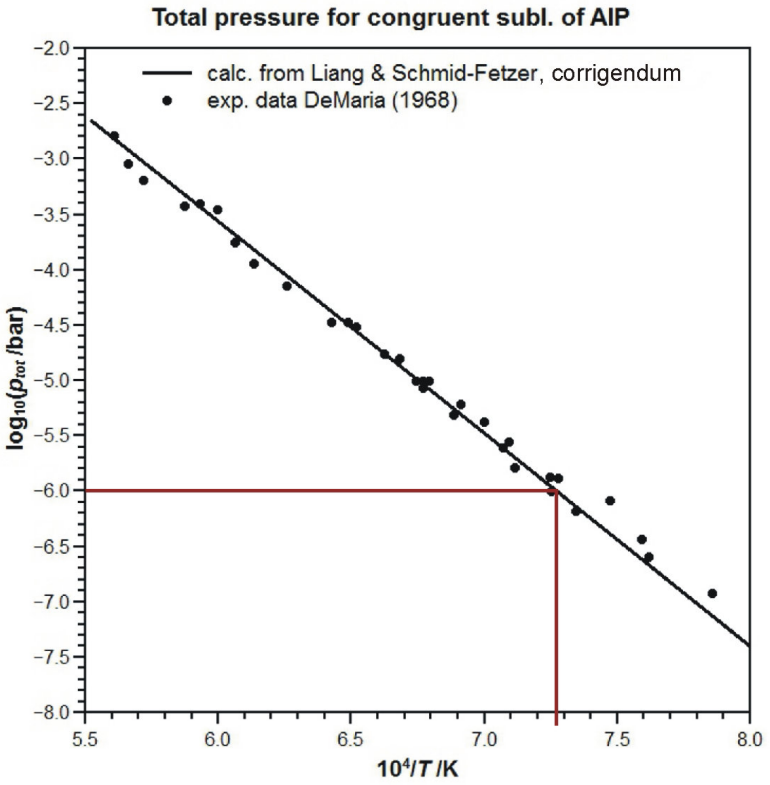
congruent melting temperature T_L(AlP)=2359°C now considerably lower than before

Corrigendum: Liang & Schmid-Fetzer

GTT-Technologies

Al-P phase diagram with gas phase for $p_{tot}=10^{-6}$ bar:





$p_{tot}=10^{-6}$ bar; $10^4/T=7.2714*10^{-4}$ K^{-1} ⇒ T=1102°C,

now in accordance with vapour pressure curve

Adaptation for FactSage

1. Refit of the ${}^0L$-Parameter:

interaction parameter Al,P for LIQUID: ${}^0L^{liq}_{Al,P} = -151900 \cdot e^{-\frac{T}{800K}}$
needs to be refitted

first test was made with series expansion of *exp*-function
⇨ at least 7 parameters needed for appropriate precision

therefore:
fitting ${}^0L^{liq}_{Al,P}$ with standard Gibbs-Energy function

$${}^0L^{liq}_{Al,P} = a + b \cdot T + c \cdot T \ln T + d \cdot T^2 + e \cdot T^3 + f \cdot T^{-1}$$

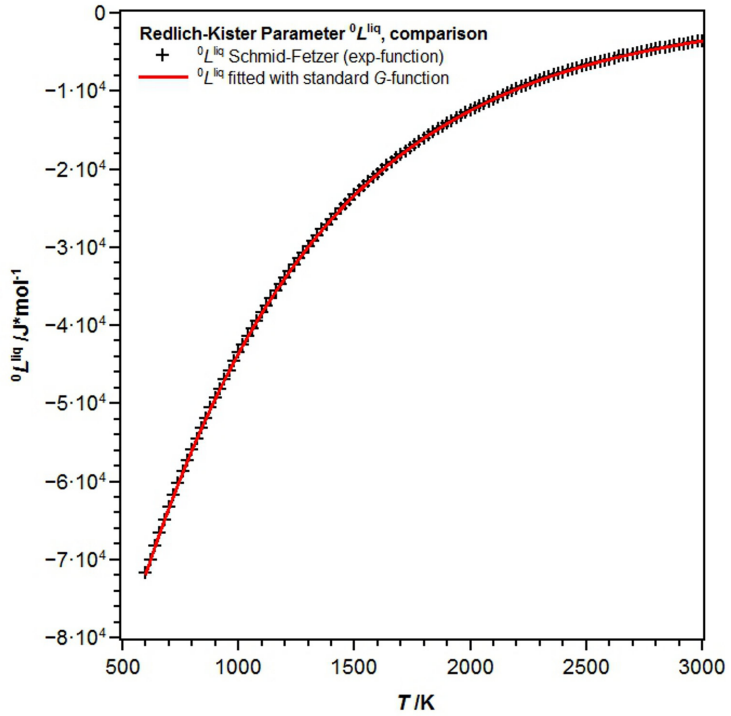
All 6 parameters used for high precision
of (weighted!) least square fit.

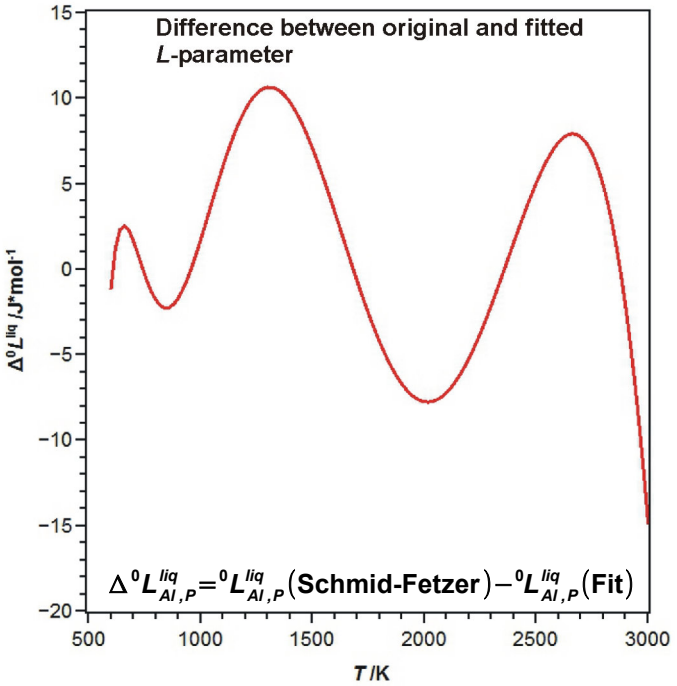
Adaptation for FactSage

GTT-Technologies

1. Refit of the ^0L-Parameter:

Difference between the original *L*-parameter and the fitted one:





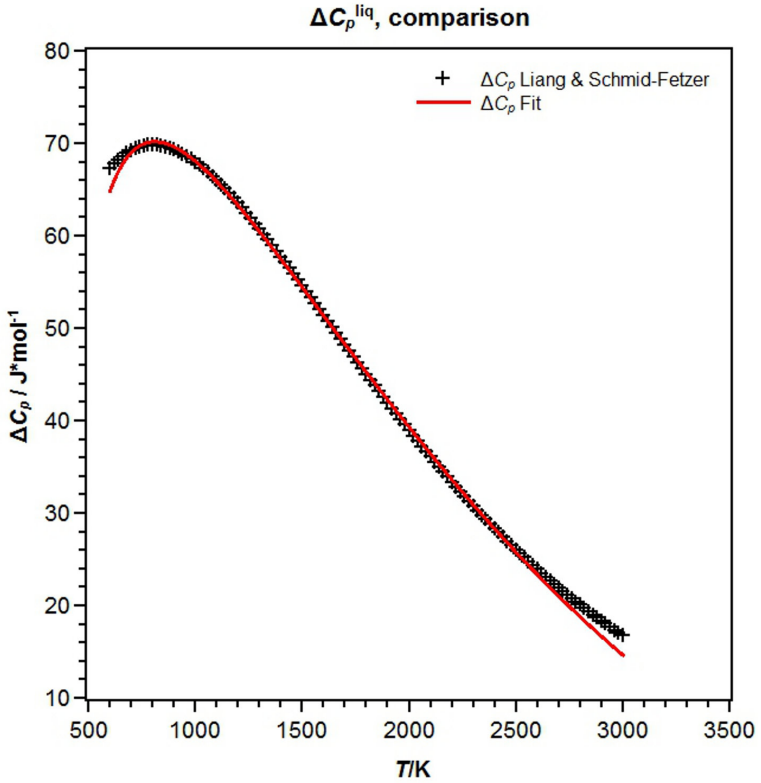
no difference visible on this scale !

max. difference +11 J*mol^{-1}*atoms^{-1} (1000 K<*T*< 1700 K)

Adaptation for FactSage

1. Refit of the ^0L-Parameter:

L-parameter ⇒ additional heat capacity (Δc_p^{liq}) for LIQUID:



Difference increasing for $T<600$ K and $T>2800$K

L-parameter from fit:

$$^0L^{liq}_{Al,P} = -213970.46 + 1033.2727 \cdot T - 129.64175 \cdot T \ln T + 2.7606318 \cdot 10^{-2} \cdot T^2 - 9.6312894 \cdot 10^{-7} \cdot T^3 + 6065980 \cdot T^{-1}$$

Adaptation for FactSage

2. Exchange of the gas phase

if the system Al-P is incorporated into SGTE solution database

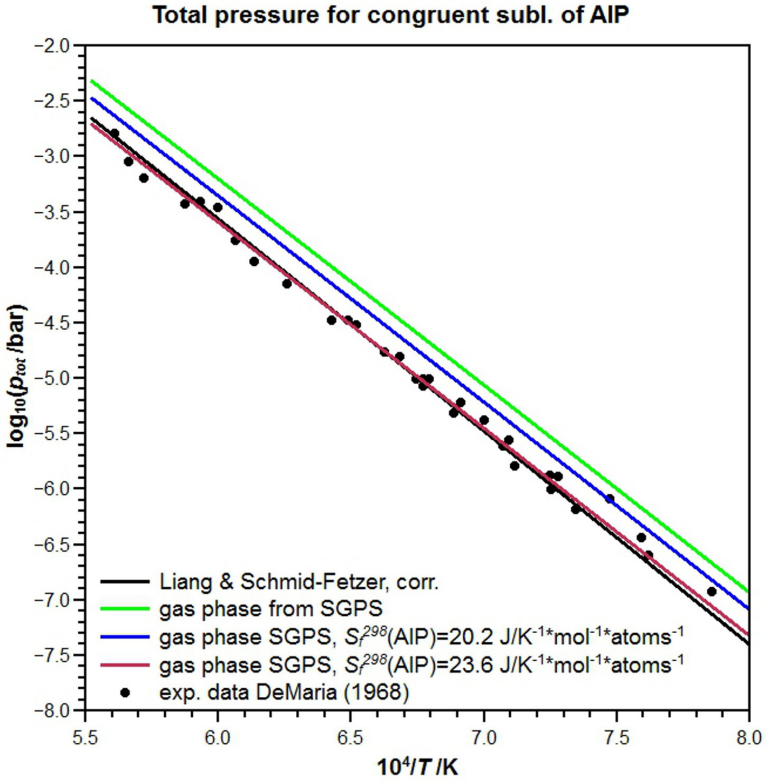
⇒ gas phase based on data from Bennewies and Milke cannot be used !

⇒ gas phase must be exchanged against description in SGTE Pure Substance Database (SGPS) ,
vapour pressure curves for sublimation of AlP have to be recalculated to fit the experimental data

Adaptation for FactSage

2. Exchange of the gas phase

recalculation of vapour pressure curves for sublimation of AlP:



standard entropy of AlP:

$S^{298}_{AlP} = 18.0\ \mathrm{J \cdot K^{-1} \cdot mol^{-1} \cdot atoms^{-1}}$

⇒ green line

$S^{298}_{AlP} = 20.2\ \mathrm{J \cdot K^{-1} \cdot mol^{-1} \cdot atoms^{-1}}$

⇒ blue line

$S^{298}_{AlP} = \mathbf{23.6}\ \mathrm{J \cdot K^{-1} \cdot mol^{-1} \cdot atoms^{-1}}$

⇒ red line

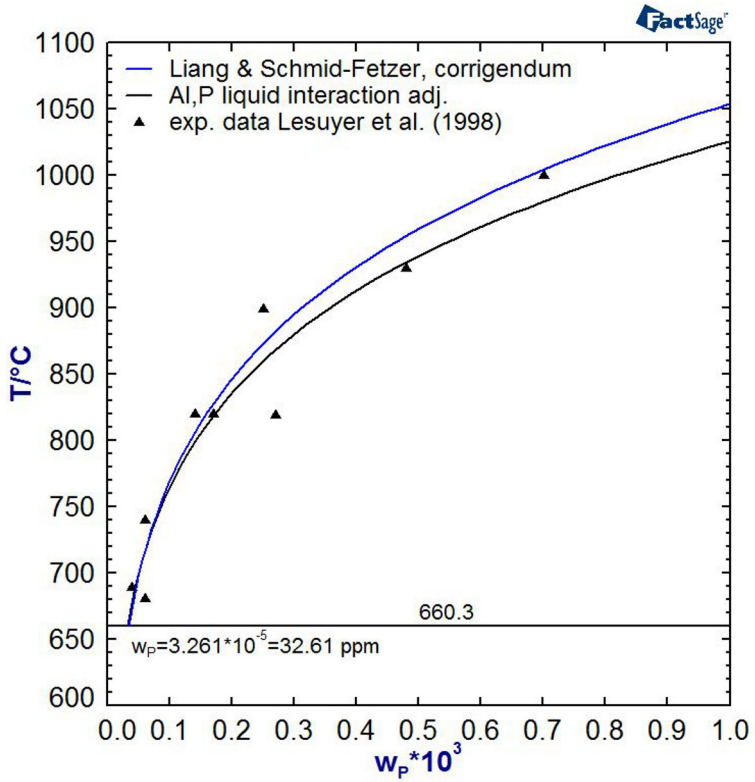
good correspondence with exp. and calc. data from other authors

Adaptation for FactSage

3. Adjustment of Al,P interaction in liquid

changed entropy value ⇒ adjustment of Al,P interaction in liquid phase to fit solubility of P in Al_{liq}

$S^{298}_{AlP} = \mathbf{23.6}\ J \cdot K^{-1} \cdot mol^{-1} \cdot atoms^{-1}$



Solubility of P in Al_{liq}:

$w_P = 3.42 * 10^{-5}$ (34.2 ppm) (Liang & Schmid-Fetzer)

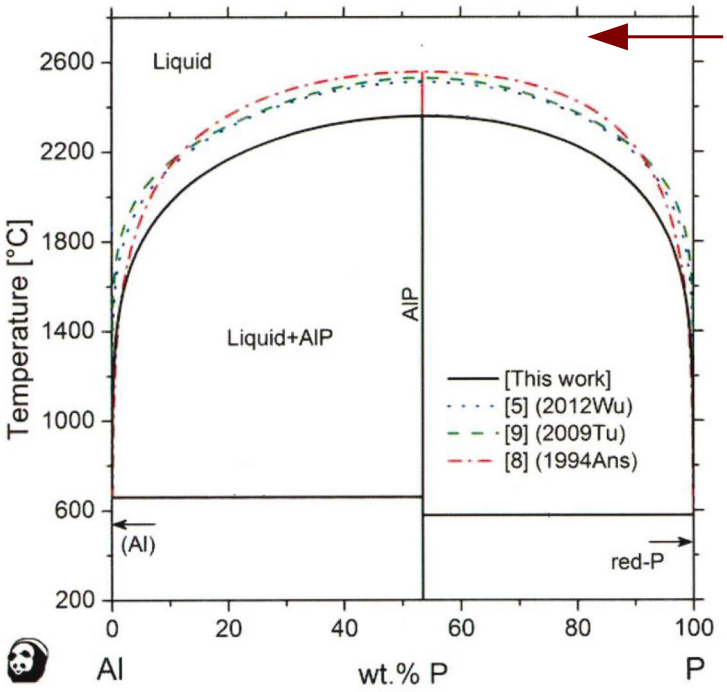
$w_P = 3.26 * 10^{-5}$ (32.6 ppm) (present work)

Adaptation for FactSage

4. Final comparison

binary phase diagram, gas phase deactivated

original image in Liang & Schmid-Fetzer's corrigendum

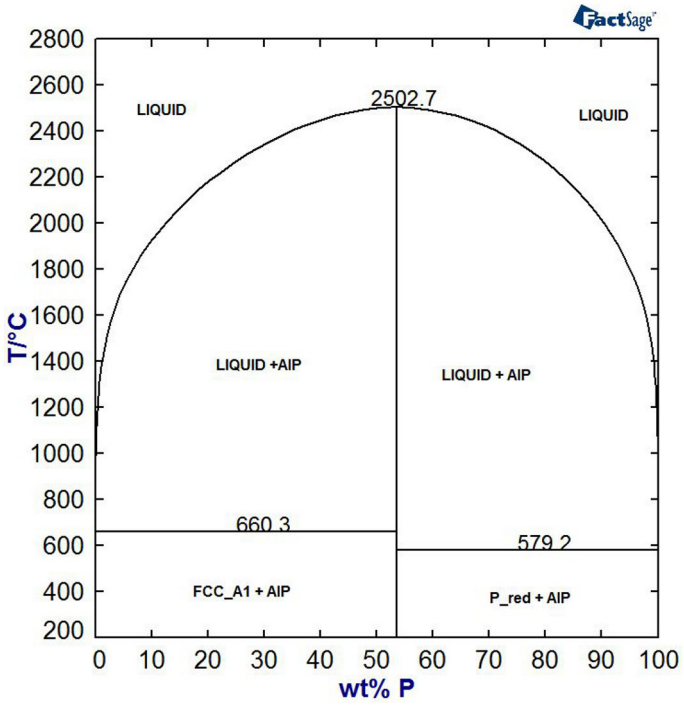


Congruent melting temperature AlP (T_L=2359°C)

much lower than before (2522°C)

reason: low S^{298}_{AlP}

calculated with data after adaptation

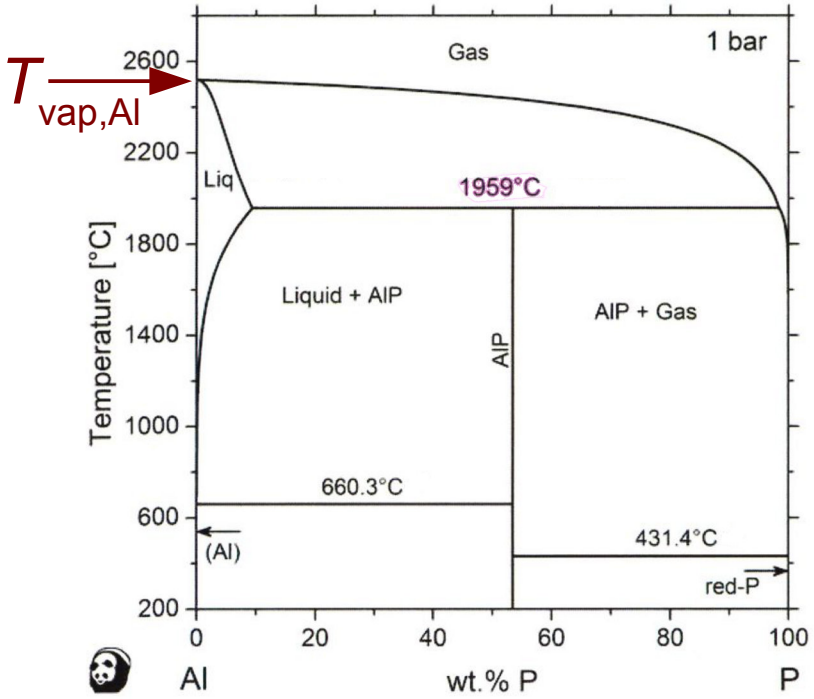


Adaptation for FactSage

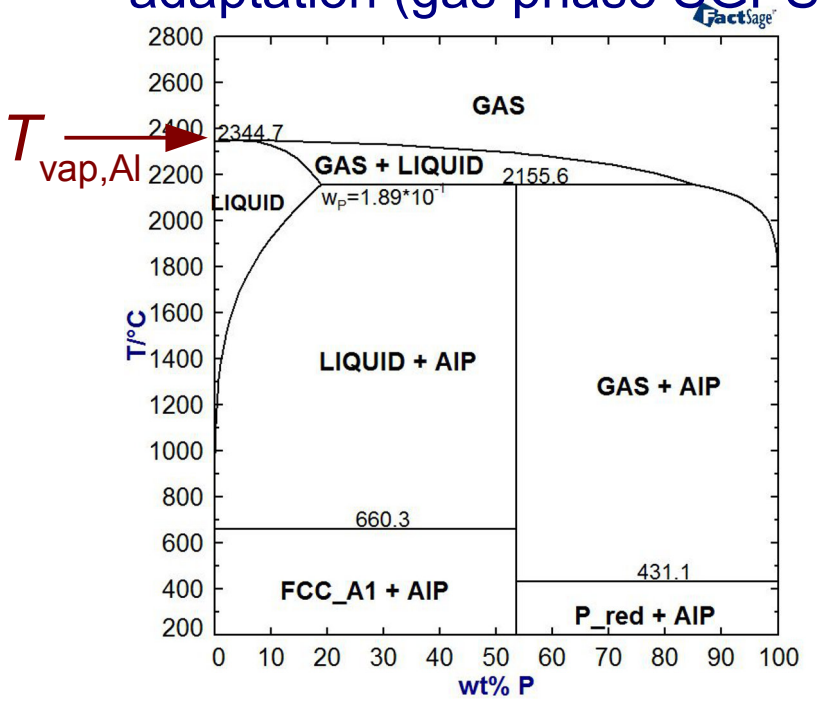
4. Final comparison

binary phase diagram including gas phase, p_{tot}=1 bar

original image in Liang & Schmid-Fetzer's corrigendum



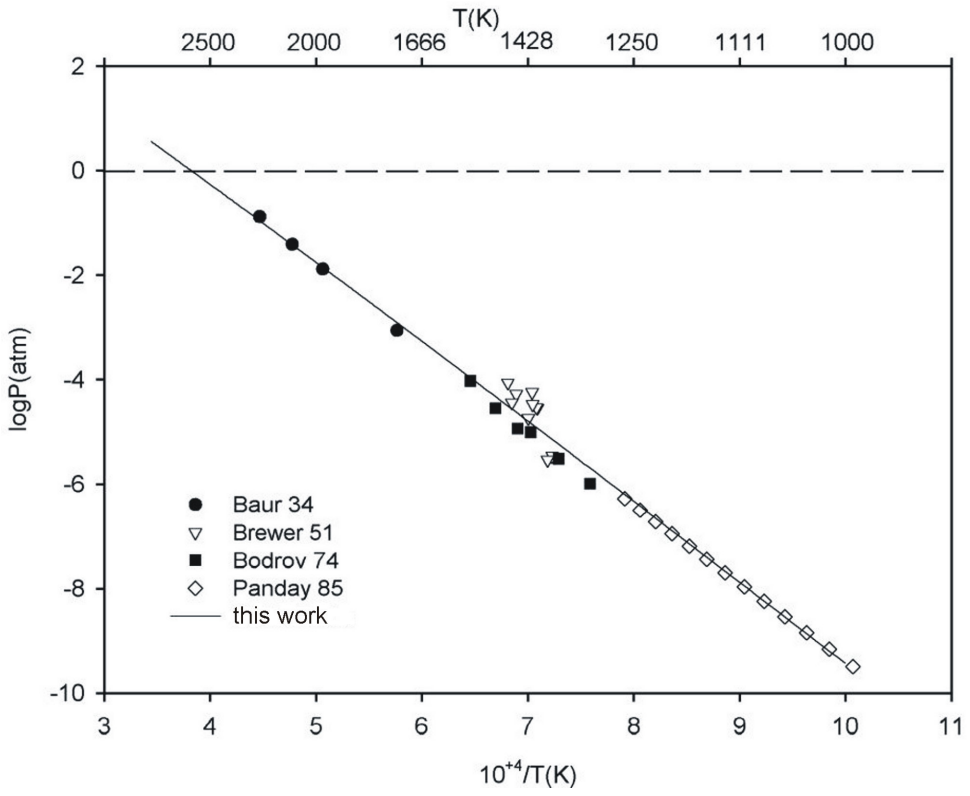
calculated with data after adaptation (gas phase SGPS)



next issue: boiling temp. for pure Al very high (T_{vap}=2520°C) in Liang & Schmid-Fetzer comp. to literature !

Adaptation for FactSage

4. Final comparison



Source of data for SGPS:

Fit of experimental data from various authors and extrapolation to standard pressure log*p*=0 by **Cheynet & Chaud**

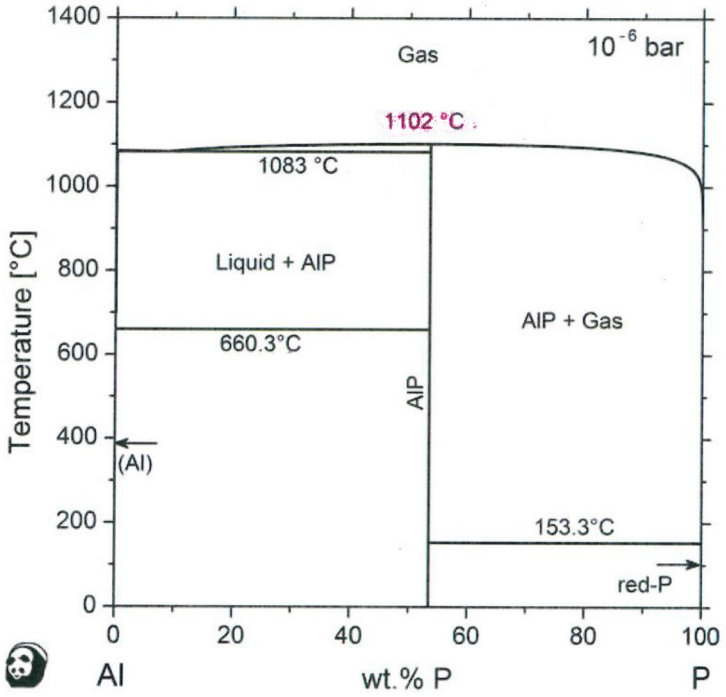
⇒ $T^{Al}_{vap} = 2345\,°C$

Adaptation for FactSage

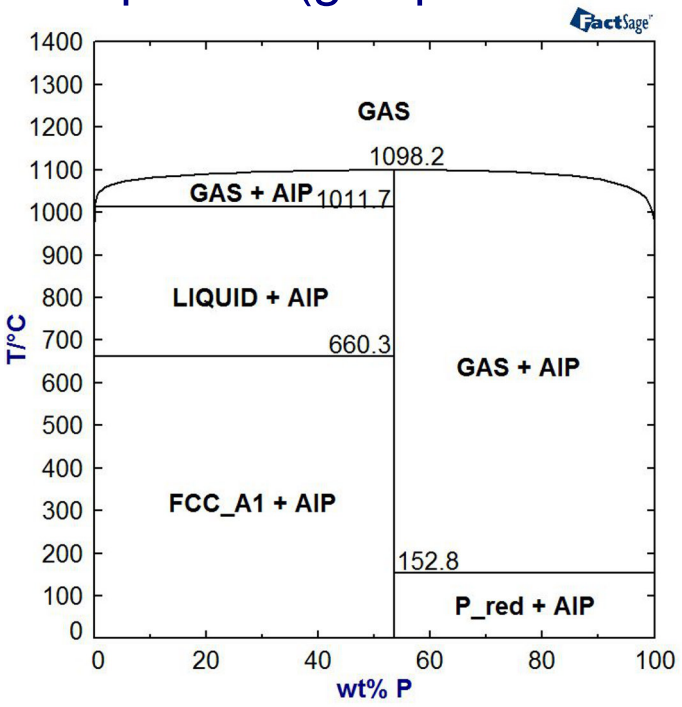
4. Final comparison

binary phase diagram including gas phase, $p_{tot}=10^{-6}$ bar

original image in Liang & Schmid-Fetzer's corrigendum



calculated with data after adaptation (gas phase SGPS)



Conclusion

⇒ fit of the interaction parameter Al,P for the liquid phase ${}^{0}L^{liq}_{Al,P}$ by standard Gibbs polynomial function is sufficiently precise

⇒ gas phase in SGTE Pure Substance database (SGPS) based on data from Cheynet & Chaud is consistent with data from Liang & Schmid-Fetzer, allows use of $S^{298}_{AlP} = 23.6\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}\cdot atoms^{-1}}$, which is in better agreement with exp. data

Thank you for your attention !