XII CBTERMO

VIII ESCOLA DE TERMODINÂMICA

CURITIBA 2024

COORDENAÇÃO

Prof. Dr. Lúcio Cardozo Filho – DEQ/UEM
Prof. Dr. Marcos L. Corazza – DEQ/UFPR
Prof. Dr. Marcos R. Mafra – DEQ/UFPR

COMITÊ LOCAL

Profa. Dra. Fabiane O. Farias (UFPR)
Profa. Dra. Grazielle de Oliveira (UFPR)
Profa. Dra. Luciana Igarashi-Mafra (UFPR)
Prof. Dr. Marcos R. Mafra (UFPR)
Profa. Dra. Tirzhá Lins Porto Dantas (UFPR)

COMISSÃO ORGANIZADORA

Profa. Dra. Danniele Miranda Bacila – DEQ/UFPR
Profa. Dra. Fabiane O. Farias – DEQ/UFPR
Prof. Dr. Fernando Augusto Pedersen Voll – DEQ/UFPR
Profa. Dra. Grazielle de Oliveira – DEQ/UFPR
Profa. Dra. Luciana Igarashi-Mafra – DEQ/UFPR
Prof. Dr. Luís Ricardo Kanda – DEQ/UFPR
Prof. Dr. Luiz Fernando de Lima Luz Júnior – DEQ/UFPR
Profa. Dra. Regina Weinschutz – DEQ/UFPR
Profa. Dra. Tirzhá Lins Porto Dantas – DEQ/UFPR
Prof. Dr. Vladimir Cabral – DEQ/UEM

COMITÊ CIENTÍFICO

Prof. Dr. Alessandro Galvão (UDESC)
Prof. Dr. Alexander Junges (URI)
Prof. Dr. Amaro Gomes Barreto Junior (UFRJ)
Prof. Dr. André Muniz (UFRGS)
Profa. Dra. Christianne Elisabete da Costa Rodrigues (USP)
Prof. Dr. Elton Franceschi (UNIT)
Prof. Dr. Frederico Wanderley Tavares (UFRJ)
Profa. Dra. Geormenny Rocha Dos Santos (UFPA)
Prof. Dr. Hosiberto Batista de Santana (UFC)
Prof. Dr. José Vladimir de Oliveira (UFSC)
Profa. Dra. Lucienne Lobato Romanielo (UFU)
Prof. Dr. Luís Fernando Mercier Franco (UNICAMP)
Prof. Dr. Luiz Stragevitch (UFPE)
Prof. Dr. Marcelo Castier (Texas A&M University at Qatar)
Profa. Dra. Mariana Conceição da Costa (UNICAMP)
Profa. Dra. Marisa Fernandes Mendes (UFRRJ)
Prof. Dr. Marlus Pinheiro Rolemberg (UNIFAL)
Prof. Dr. Osvaldo Chiavone-Filho (UFRN)
Profa. Dra. Paula Bettio Staudt (UFRGS)
Prof. Dr. Pedro de Alcântara Pessôa Filho (POLI/USP)
Prof. Dr. Pedro Felipe Arce (LORENA/USP)
Prof. Dr. Rafael de Pelegrini Soares (UFRGS)
Prof. Dr. Ricardo Belchior Torres (FEI)
Profa. Dra. Rílvia Saraiva de Santiago Aguiar (UFC)
Profa. Dra. Roberta Ceriani (UNICAMP)
Prof. Dr. Rodrigo Corrêa Basso (UNIFAL)
Profa. Dra. Sandra Regina Salvador Ferreira (UFSC)
Profa. Dra. Silvana Mattedi (UFBA)
Profa. Dra. Simone Monteiro e Silva (UNB)
Prof. Dr. Vladimir Ferreira Cabral (UEM)

ELABORAÇÃO DO LIVRO

Marcelle Guth F. Batista - PPGEQ/UFPR
Nadia Maria do Valle Ramos - PPGEQ/UFPR
Victor Brisk - PPGEQ/UFPR
Ana Maura Novak - EQ/UFPR
Julia Maria Marques Caetano - EQ/UFPR
Stéphany Ribeiro Andrade - EQ/UFPR

REALIZAÇÃO

UFPR
UNIVERSIDADE FEDERAL DO PARANÁ

UEM
Universidade Estadual de Maringá

APOIO

7 ANOS
ENGENHARIA QUÍMICA
UFPR

PPGEAL

PPGEQ
UFPR

PRPPG
Pró-reitoria de
Pesquisa e Pós-graduação

PATROCÍNIO

CAPES
PrInt | UFPR
Programa Institucional de Internacionalização

CNPq

FUNDAÇÃO
ARAUCÁRIA
Apoio ao Desenvolvimento Científico
e Tecnológico do Paraná

Swagelok
Tecflux

XII Congresso Brasileiro de Termodinâmica Aplicada

UFPR - Centro Politécnico
Prédio de Administração:
Auditório da Administração

TERÇA - 07/05/2024

08:00	Palestra 05: Phase equilibrium diagrams construction for understanding of complex systems
09:00	Palestra 06: Comportamento de Fases de Sistemas Complexos na Presença de Dióxido de Carbono
10:00	Coffee-break
10:30	Sessão Pôster III ⬅
11:15	Sessão Oral III
12:00	Almoço
13:30	Sessão Pôster IV
14:30	Mesa redonda: Fluidos pressurizados: modelagem e aparatos experimentais
15:30	Coffee-break
16:00	Premiação / Encerramento

Profa. Dra. Belén Rodriguez

URV - Palestra 05

Prof. Dr. Marcelo Zabaloy

UNS - Mesa Redonda

Prof. Dr. Cláudio Dariva

UNIT - Palestra 06

Prof. Dr. Pablo Hegel

UNS - Mesa Redonda

Prof. Dr. Lúcio Cardozo Filho

UEM - Mesa Redonda

SESSÃO ORAL III

TORREFACTION OF URBAN FOREST WASTE: A THERMODYNAMIC STUDY OF PROCESS SIMULATION USING ASPEN PLUS

Thiago S. Gonzales, Giulia C. Lamas, Pedro P. O. Rodrigues, Simone Monteiro, Edgar A. Silveira*

PROPOSTA DE SIMULADOR DE EQUILÍBRIO TERMODINÂMICO POR MINIMIZAÇÃO DE ENERGIA DE GIBBS

Julles Mitoura dos Santos Junior*, Antônio Carlos Daltro de Freitas, Adriano Pinto Mariano

SOLUBILITY SCREENING OF COUMARINS FROM PTEROCAULON POLYSTACHYUM IN DEEP EUTECTIC SOLVENTS USING COSMO-RS

Victor H. S. Rodrigues*, Arthur F. Cavassa, Rubem M. F. Vargas, Ana Rita C. Duarte, Eduardo Cassel

SESSÃO PÔSTER III

ÁREA 2 - EQUILÍBRIO DE FASES

ÁREA 5 - COLOIDES E INTERFACES

ÁREA 6 - TERMOQUÍMICA

ÁREA 7 - CICLOS TERMODINÂMICOS E ANÁLISE EXERGÉTICA

SESSÃO PÔSTER IV

ÁREA 9 - FÍSICA DA MATÉRIA CONDENSADA

ÁREA 12 - MEIO AMBIENTE

ÁREA 13 - BIOMOLÉCULAS E BIOTECNOLOGIA

ÁREA 14 - PROCESSOS DE SEPARAÇÃO

SUMÁRIO

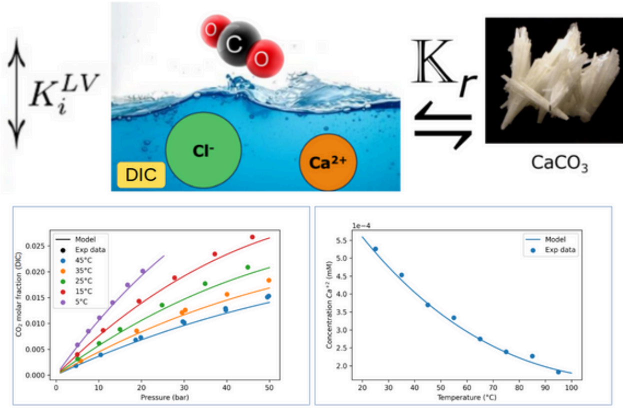
Para acessar os resumos e trabalhos completos, escaneie ou clique no QR Code

TRABALHOS
SUBMETIDOS

ÁREA 2
EQUILÍBRIO DE FASES

R225-2: CALCULATIONS OF CO2 SOLUBILITY IN AQUEOUS PHASE USING CPE ALGORITHMS

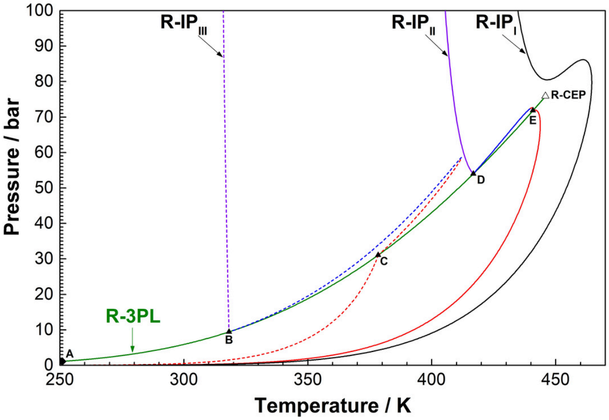
Arthur S. Campagnolo*, Iuri Segtovich, Amaro G. Barreto Jr., Frederico W Tavares



Resumo

R234-2: IDENTIFICATION OF SEGMENTS OF COMPUTED REACTIVE THREE-PHASE LINES TO BE INCLUDED IN THE HETEROGENEOUS REGION OF PHASE DIAGRAMS OF REACTIVE SYSTEMS

Matías J. Molina, S. Belén Rodriguez-Reartes, Marcelo S. Zabaloy*



Resumo

XII CONGRESSO BRASILEIRO DE TERMODINÂMICA APLICADA

5-7 de maio de 2024 | Curitiba - Paraná - Brasil

Certificamos que o trabalho intitulado

IDENTIFICATION OF SEGMENTS OF COMPUTED REACTIVE THREE-PHASE LINES TO BE INCLUDED IN THE HETEROGENEOUS REGION OF PHASE DIAGRAMS OF REACTIVE SYSTEMS

De autoria de

Matías J. Molina, S. Belén Rodriguez-Reartes, Marcelo S. Zabaloy

Foi apresentado, na modalidade pôster, no XII Congresso Brasileiro de Termodinâmica Aplicada, evento realizado no período de 05/05/2024 a 07/05/2024 em Curitiba, Pr, Brasil.

Marcos L. Corazza
UFPR | Organizador

Marcos R. Mafra
UFPR | Organizador

Lucio Cardozo Filho
UEM | Organizador

UFPR

UEM

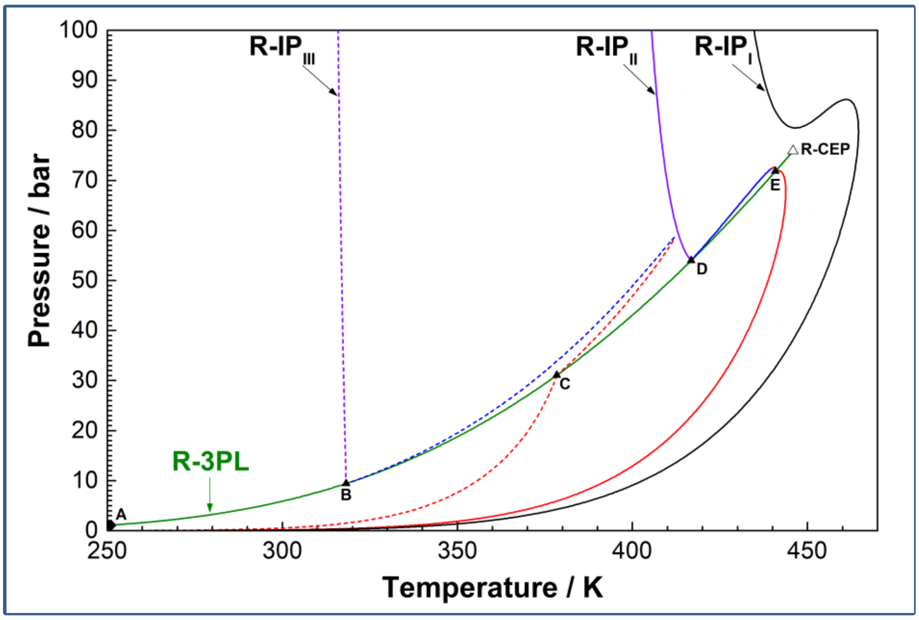
Identification of segments of computed reactive three-phase lines to be included in the heterogeneous region of phase diagrams of reactive systems

Matías J. Molina[1,2], S. Belén Rodriguez-Reartes[1,2,3], Marcelo S. Zabaloy[1,2*]

[1]Departamento de Ingeniería Química, Universidad Nacional del Sur (UNS), Bahía Blanca, Argentina.
[2]Planta Piloto de Ingeniería Química – PLAPIQUI (UNS-CONICET), Bahía Blanca, Argentina.
[3]Department of Chemical Engineering, ETSEQ, Universitat Rovira i Virgili, Tarragona, Spain.

* mzabaloy@plapiqui.edu.ar

GRAPHICAL ABSTRACT



ABSTRACT

For reactive systems, equations of state (EoS) may predict the existence of (reactive) three-phase lines (R-3PLs). In general, only a part of a specific R-3PL contributes to the heterogeneous region (HR) of a reactive phase diagram of specified initial global composition $\mathbf{z^0}$ (also named “reactive isopleth” (R-IP)). In this work, we propose a method for detecting the segments, of an already computed R-3PL, that should contribute to the HR of a yet to be computed R-IP (of already specified $\mathbf{z^0}$). The method consists of solving, for each point of the R-3PL (R-3PP), a system of equations related to reactive two-phase constant phase fraction lines that originate at the R-3PP. The R-3PP contributes to the R-IP if the solution of such system satisfies a number of restrictions. The graphical abstract (GA) shows three R-IPs for the methanol(M) + dimethyl ether(DME) + water(W) reactive system (DME + W ↔ 2M),

calculated using the Peng-Robinson EoS, at varying initial DME/W ratio ($R_{DME\text{-}W}$, mole basis), i.e., at varying initial global component-mole-fraction vector $\mathbf{z^0}$. In all three cases M is initially absent. The GA also includes a complete computed R-3PL (green line) which starts, for the T range of the GA, at point A and ends at a reactive critical end point (R-CEP). The R-IP$_{\mathrm{I}}$ at $R_{DME\text{-}W}$=2.33 ($z_M^0 = 0.0$, $z_{DME}^0 = 0.7$, $z_W^0 = 0.3$) is made of a single reactive saturation segment and the entire R-3PL is compatible with the global initial composition of this R-IP ($\mathbf{z^0}_{\mathrm{I}}$). The R-IP$_{\mathrm{II}}$ at $R_{DME\text{-}W}$=3.5 ($z_M^0 = 0.0$, $z_{DME}^0 = 0.7778$, $z_W^0 = 0.2222$) is made of a reactive phase envelope (R-PE) made of two dew points (red) segments, a bubble points (blue) segment and a cloud (liquid-liquid) points (violet) segment, all of them reactive, and of a segment of a R-3PL compatible with $\mathbf{z^0}_{\mathrm{II}}$ which extends from point A to point E. Finally, the R-IP$_{\mathrm{III}}$ at $R_{DME\text{-}W}$=15 ($z_M^0 = 0.0$, $z_{DME}^0 = 0.9375$, $z_W^0 = 0.0625$) is qualitatively similar to the R-IP$_{\mathrm{II}}$, but now the R-3PL segment compatible with $\mathbf{z^0}_{\mathrm{III}}$ extends from point A to point C.

Keywords: simultaneous chemical and phase equilibria, reactive isopleth, reactive three-phase lines

XII Congresso Brasileiro de Termodinâmica
VIII Escola de Termodinâmica
De 5 a 9 de Maio de 2024
Curitiba - Paraná - Brasil

Identification of segments of computed reactive three-phase lines to be included in the heterogeneous region of phase diagrams of reactive systems

Matías J. Molina[1,2], S. Belén Rodriguez-Reartes[1,2,3], Marcelo S. Zabaloy[1,2]*
[1]Departmento de Ingeniería Química, Universidad Nacional del Sur, Bahía Blanca, Argentina
[2]Planta Piloto de Ingeniería Química-PLAPIQUI (UNS-CONICET), Bahía Blanca, Argentina
[3]Deparment of Chemical Engineering, ETSEQ, Universitat Rovira I Virgili, Tarragona, Spain
*Corresponding author: mzabaloy@plapiqui.edu.ar

Cód: R234-2

INTRODUCTION AND GOAL

- In this work, a method for detecting the segments, of an already computed reactive three-phase line (**R-3PL**), that should contribute to the heterogeneous region (**HR**) of a yet to be computed reactive isopleth (**R-IP**) (of already specified initial global composition **z**^{0}) is proposed.
- The method consists of solving, for each point of the **R-3PL** (**R-3PP**), a system of equations (**SoEs**) related to reactive two-phase constant phase fraction lines that originate at the R-3PP.
- The **R-3PP** contributes to the R-IP if the solution of the **SoEs** satisfies a number of restrictions.

METHODS

Method for detecting the segments of the R-3PL which contribute to the HR of the R-IP to be computed

1. **Compute** the complete R-3PL according to the methodology proposed in ref [1]. This is done without reference to any **z**^{0} .
2. **Specify** an initial global component-mole-fraction vector **z**^{0}.
3. For every already available calculated reactive three-phase point (R-3PP), there are three possible combinations of pair of the existing phases ($j = V, L_\alpha, L_\beta$). **Impose** the mass conservation principle, and the stoichiometric restrictions to each possible pair of phases. For each pair of phases x and y, the **mass conservation principle** and the **stoichiometric restrictions** correspond to the following SoEs:

$$\begin{cases} z_i - x_i \cdot \Phi_x - y_i \cdot \Phi_y = 0 & 1 \le i \le NC \\ z_i - \dfrac{z_i^0 + \sum_{k=1}^{NR} \nu_{i,k} \cdot \xi_k^*}{1 + \sum_{k=1}^{NR} \nu_{T,k} \cdot \xi_k^*} = 0 & 1 \le k \le NR \end{cases}$$

Φ_x is the mole fraction of phase 'x'
Φ_y is the mole fraction of phase 'y'.

4. **Solve** the **SoEs** for all Φ_j , z_i and ξ_k^* variables.
   - When two (out of three) pairs of Φ_j values and their corresponding z_i values are such that every Φ_j and z_i is within the range [0,1], then, the tested R-3PP is compatible with the R-IP initial global composition $\boldsymbol{z}^0$.
   - When there are Φ_j or z_i values outside the range [0,1], then, the tested R-3PP is not compatible with the R-IP global initial composition $\boldsymbol{z}^0$.
5. **Compute** the reactive phase envelope (R-PE) of initial global composition $\boldsymbol{z}^0$ according to the procedure of reference [2].

CONCLUSIONS

- A methodology for detecting all segments, of a specific calculated R-3PL, that contribute to the HR of a reactive diagram of specified initial global composition $\boldsymbol{z}^0$ (also named reactive isopleth) was proposed.
- Through the application of the proposed methodology, it is possible to automatically detect R-3PPs that will be located on the R-PE of the R-IP, i.e., to detect reactive double saturation points.
- The proposed methodology is illustrated in this work for the methanol(M) + dimethyl ether(DME) + water(W) reactive system at varying initial DME/W ratio, i.e., at varying initial global component-mole-fraction vector $\boldsymbol{z}^0$.

REFERENCES

[1] Molina, M.J.; Rodriguez-Reartes, S.B.; Zabaloy, M.S. (2021). XXII Congreso Argentino de Fisicoquímica y Química Inorgánica, 437. **[2]** Molina, M.J.; Rodriguez-Reartes, S.
B.; Zabaloy, M. S. Fluid Phase Equilib. 574 (2023) 113889. **[3]** D.-Y. Peng, D.B. Robinson, *Ind. Eng. Chem. Fundam.* 15 (1976) 59–64. **[4]** DIPPR 801 Database. AIChE, , 2003.

ACKNOWLEDGEMENTS

We acknowledge the financial support provided by the following institutions: Consejo Nacional de Investigaciones Científicas y Técnicas (PIP-11220200101325CO) and Universidad Nacional del Sur (PGI 24/M169). S.B. Rodriguez Reartes acknowledges the financial support of the "María Zambrano" grant awarded by Universitat Rovira i Virgili for the requalification of the Spanish university system for 2021-2023.

RESULTS AND DISCUSSION

Computation results are shown for the **methanol(M)** + **dimethyl ether(DME)** + **water(W)** reactive system (**DME+W ↔ 2M**), at varying DME/W ratio (R_{DME-W}, mole basis), i.e., at varying initial global component-mole-fraction vector **z**^{0}. In all cases M is initially absent. Model: PR-EoS [3] with quadratic mixing rules (QMRs) and null interaction parameters. Standard properties at 298 K and heat capacities in the ideal gas state taken from ref [4].

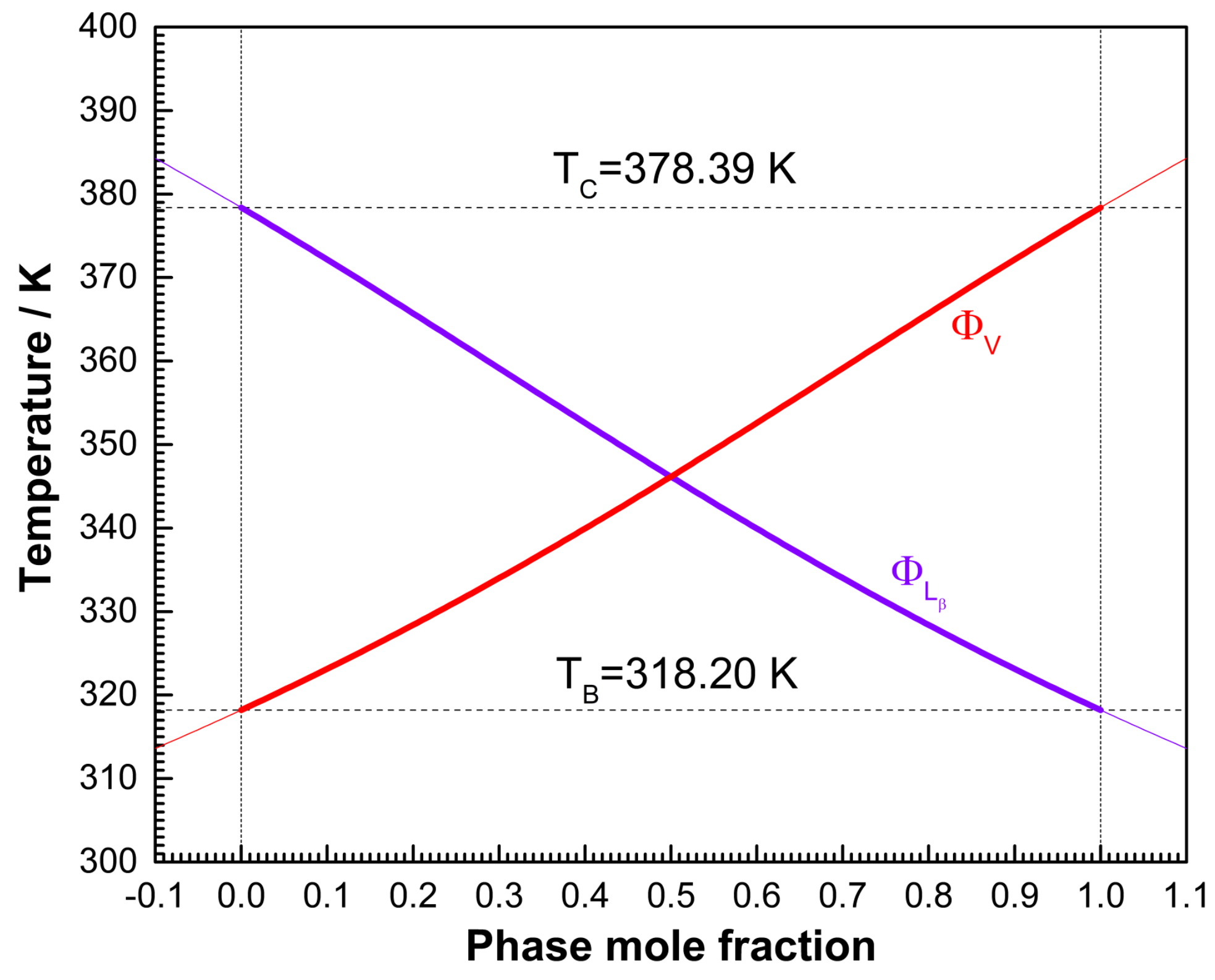


Fig. 1. Temperature vs. calculated phase mole fractions Φ_V and Φ_{L_β} at R-LLV equilibrium for Φ_{L_α}=0 at R_{DME-W} = 15 (global initial composition: $z_M^0 = 0.0$, $z_{DME}^0 = 0.9375$, $z_W^0 = 0.0625$). Red line: phase mole fraction of vapor phase. Violet line: phase mole fraction of liquid β.

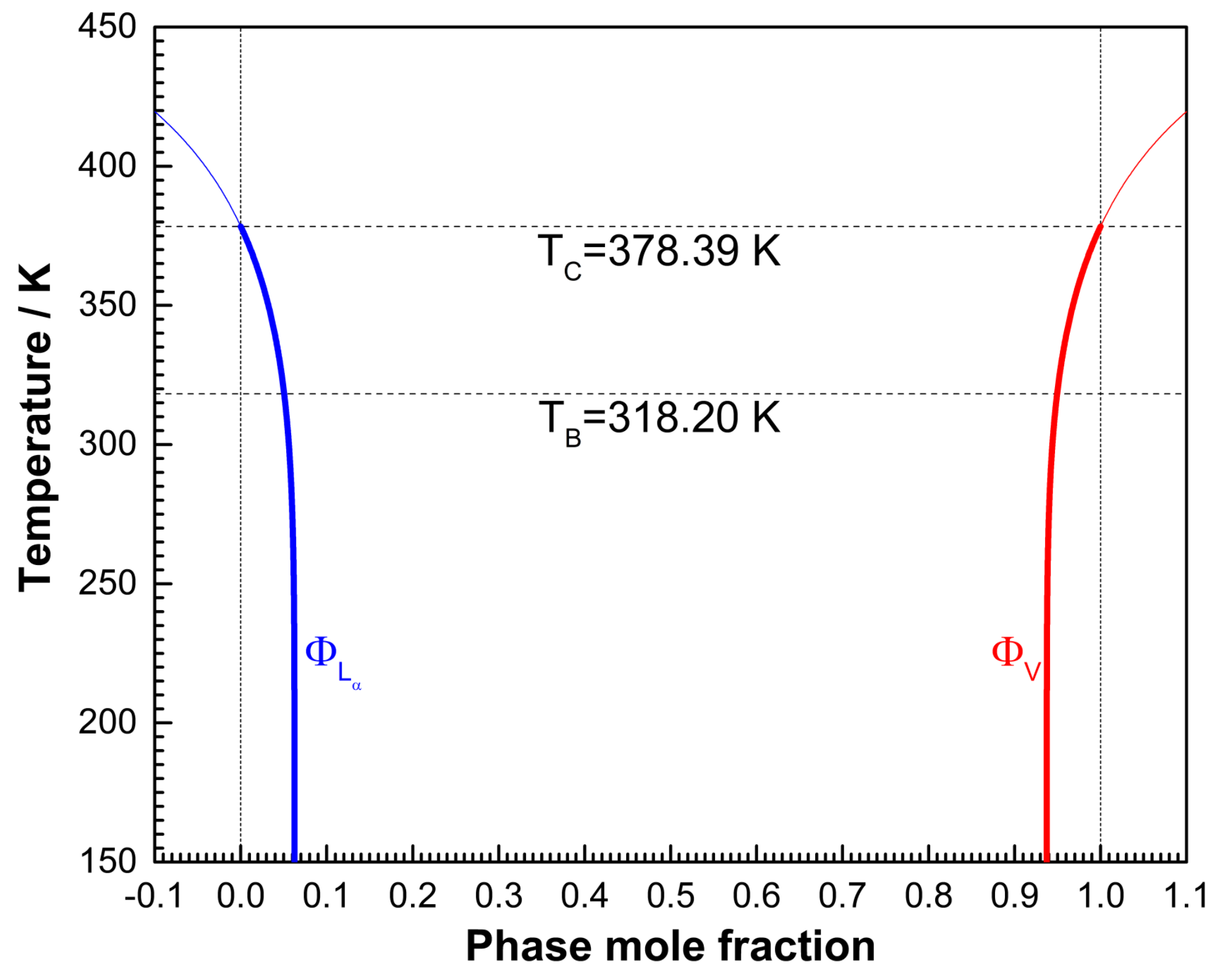


Fig. 2. Temperature vs. calculated phase mole fractions Φ_V and Φ_{L_α} at R-LLV equilibrium for Φ_{L_β}=0 at R_{DME-W} = 15 (global initial composition: $z_M^0 = 0.0$, $z_{DME}^0 = 0.9375$, $z_W^0 = 0.0625$). Red line: phase mole fraction of vapor phase. Blue line: phase mole fraction of liquid α.

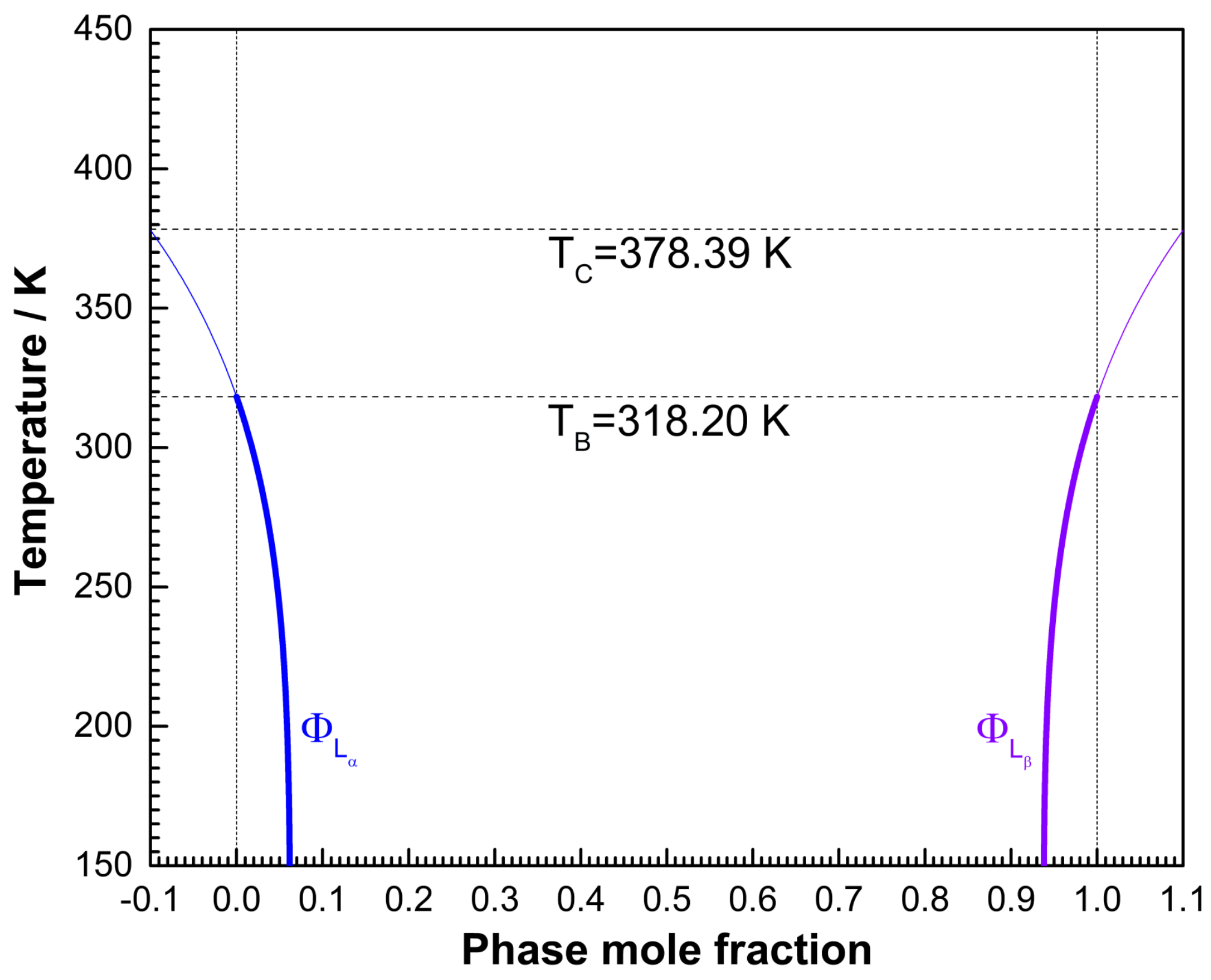


Fig. 3. Temperature vs. calculated phase mole fractions Φ_{L_α} and Φ_{L_β} at R-LLV equilibrium for Φ_V=0 at R_{DME-W} = 15 (global initial composition: $z_M^0 = 0.0$, $z_{DME}^0 = 0.9375$, $z_W^0 = 0.0625$). Blue line: phase mole fraction of liquid α. Violet line: phase mole fraction of liquid β.

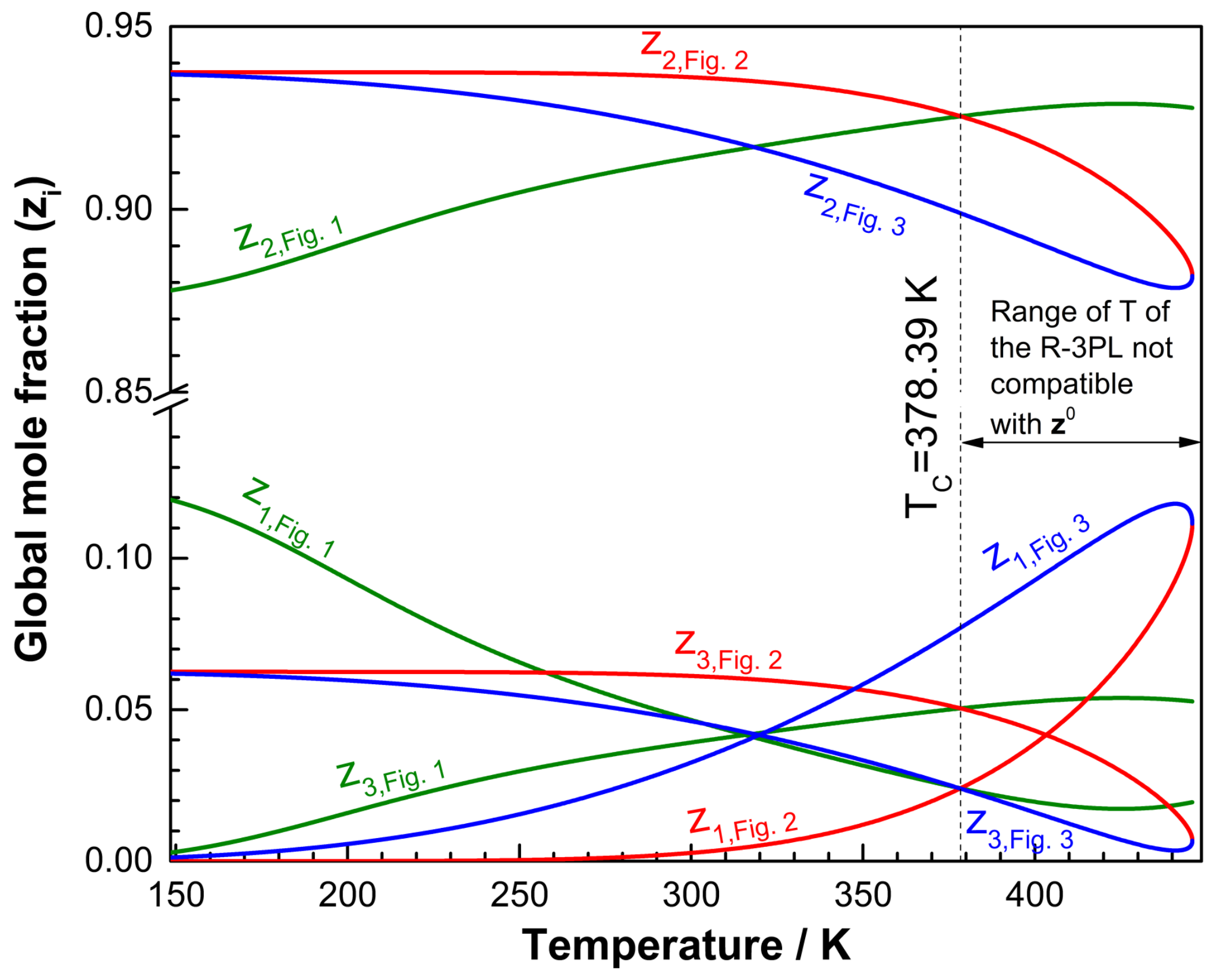


Fig. 4. Global component mole fractions at three-phase reactive equilibrium vs. temperature when a phase is incipient. Green lines: z_i corresponding to the pair of phases $L_\beta V$ with Φ_{L_α}=0 (Fig. 1). Red lines: z_i corresponding to the pair of phases $L_\alpha V$ with Φ_{L_β}=0 (Fig. 2). Blue lines: z_i corresponding to the pair of phases $L_\alpha L_\beta$ with Φ_V=0 (Fig. 3). Global initial composition $z_M^0 = 0.0$, $z_{DME}^0 = 0.9375$, $z_W^0 = 0.0625$

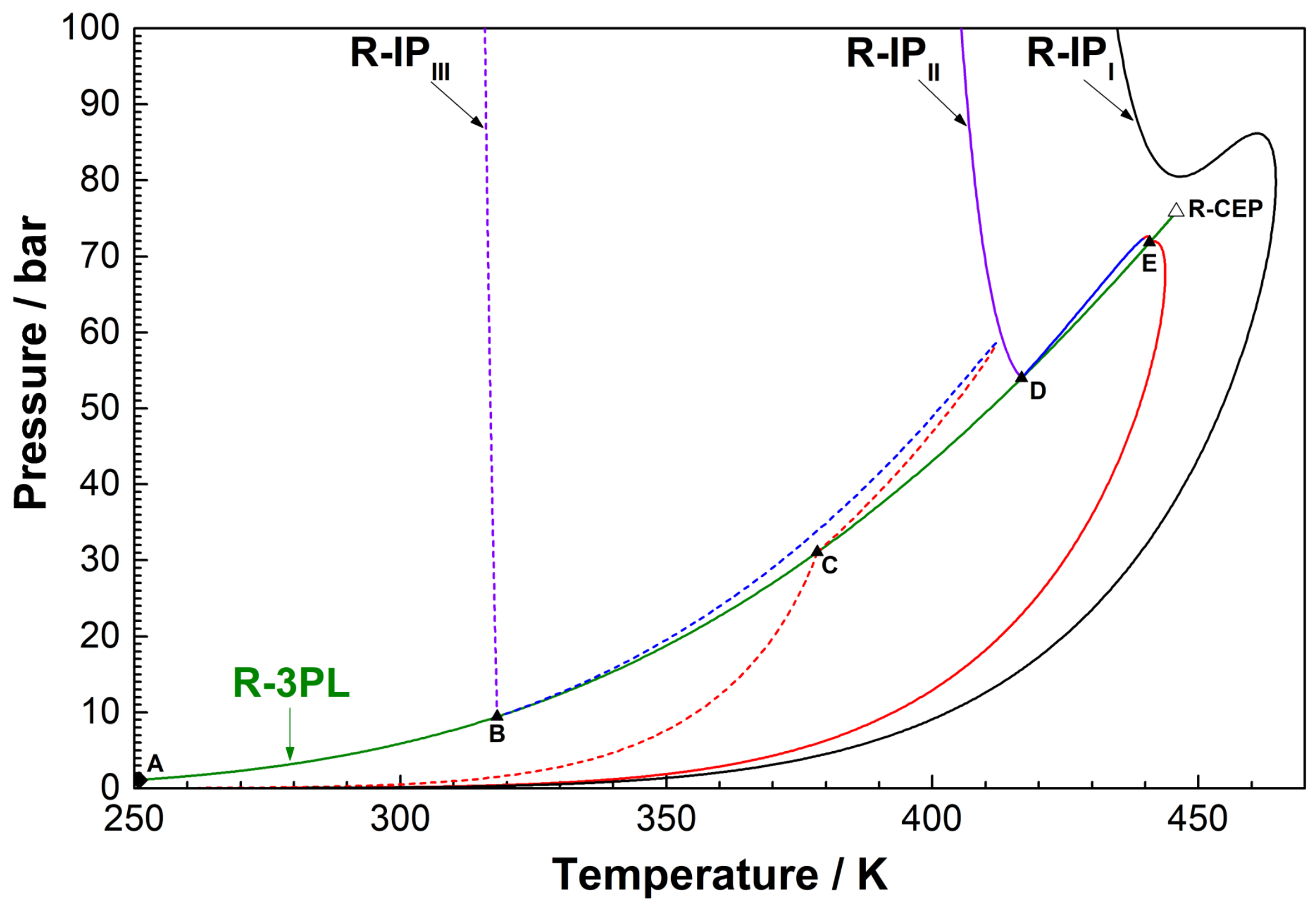


Fig. 5. Pressure – temperature projection of calculated R-IPs at varying initial DME/W ratio ($R_{DME/W}$ molar basis). R-IP I: $R_{DME/W}$=2.33 ($z_M^0 = 0.0$, $z_{DME}^0 = 0.70$, $z_W^0 = 0.30$). R-IP II: $R_{DME/W}$=3.5 ($z_M^0 = 0.0$, $z_{DME}^0 = 0.7778$, $z_W^0 = 0.2222$). R-IP III: $R_{DME/W}$=15 ($z_M^0 = 0.0$, $z_{DME}^0 = 0.9375$, $z_W^0 = 0.062$). Δ: Reactive critical end point (R-CEP). ▲: Double saturation points (points B, C, D, E). ♦ (Point A): R-3PP considered as initial point of the R-3PL in the temperature range shown in this Fig. (250 K – 470 K).

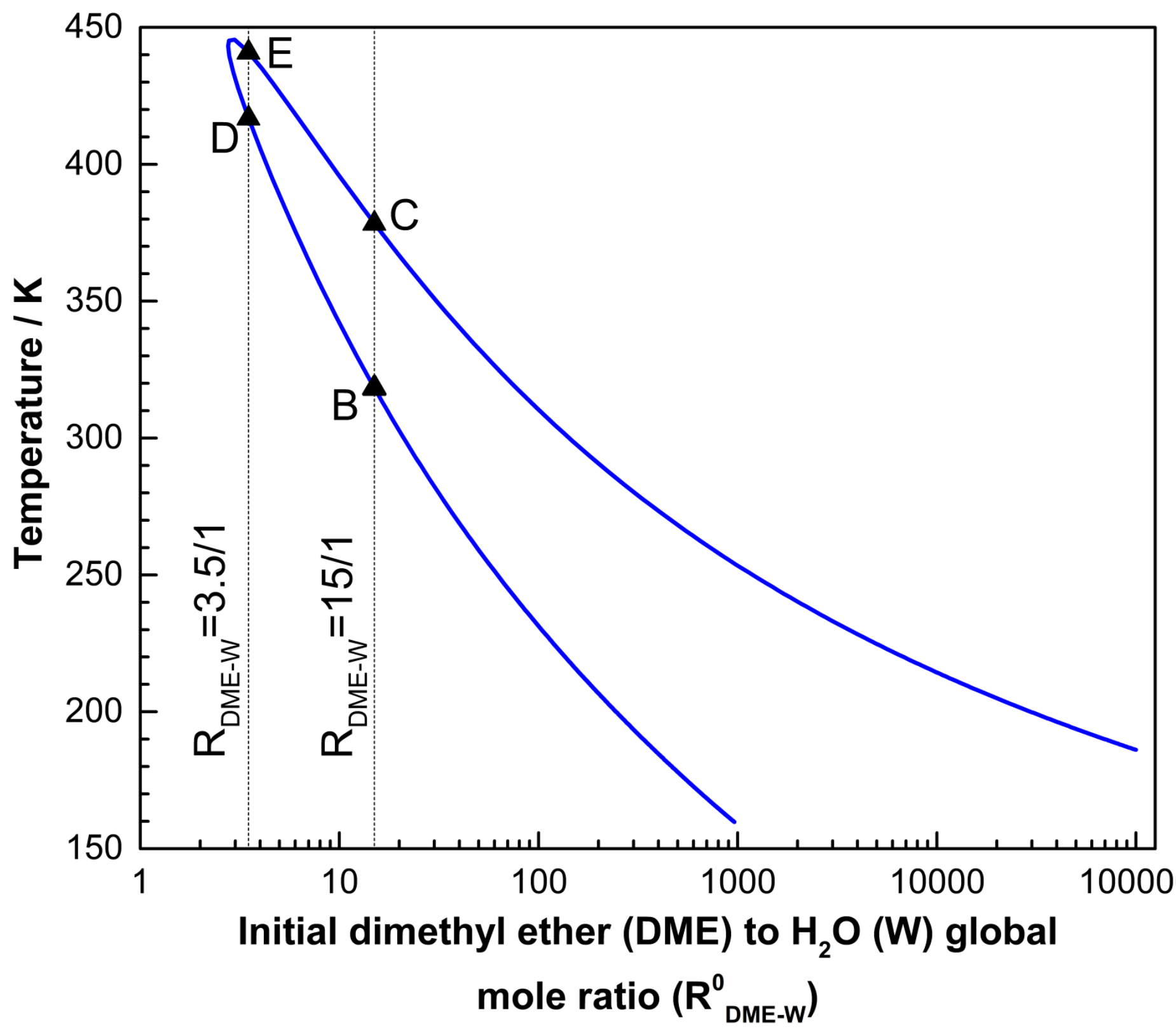


Fig. 6. Temperature of reactive double saturation points versus initial DME/W ratio (in mole basis) at $z_M^0 = 0.0$ for the M + DME + W reactive system. Points B and C: double saturation points of the R-IP III (see Fig. 5). Points D and E: double saturation points of the R-IP II (see Fig. 5).